Mimicking Noncanonical Oxidations with Redox-Neutral Photocatalysis

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ABSTRACT

Noncanonical oxygenases are a family of Fe-containing enzymes that catalyze oxidative radical cyclizations. Despite creating key structural features that often define a natural product's complexity, the mechanisms of these oxidations remain poorly understood and difficult to mimic. In this work, we show that noncanonical cyclizations from lignan biosynthesis can be recreated when presumed biosynthetic radicals are generated using photocatalysis. These conditions afford the ensuing electron rich radicals sufficient time to undergo challenging 5- or 11-membered ring formation that create the defining structural features of the highly oxidized lignans taiwankadsurins A, B and kadsuphilin N. By showing that these cyclizations can occur without enzymatic assistance, we provide a more general strategy for mimicking noncanonical transformations that should broaden their use in organic synthesis.

INTRODUCTION

Many of the unique shapes and functional properties of natural products emerge in the late stages of biosynthesis following C-H oxidation.¹ Cytochrome P450s and non-heme iron oxygenases that carry out these transformations have been the focus of many studies aiming to emulate their mechanisms of C-H oxidation, as well as their timing in synthetic strategy.²⁻³ While the majority of examples studied thus far involve C-H hydroxylation by an established mechanism of rebound,³ there is growing awareness of noncanonical oxygenases that divert this pathway to create more pronounced structural changes (Scheme 1A).⁴⁻⁵ Examples include the ansa-bridge of streptorubin B,⁶ the aryltetralin of (–)-deoxypodophyllotoxin⁷ and the fused macrocycles of vancomycin⁸ (Scheme 1B), in which oxidative cyclizations rigidify relatively flexible substrates to create the unique three dimensional architectures of the natural products. Because they create the defining structural features that lead to complexity,⁹ these transformations can be strategic targets for retrosynthetic simplification. However, unlike canonical hydroxylation, for which there is a deep mechanistic understanding and many synthetic alternatives,^{1,3} the mechanisms of noncanonical oxidations remain poorly understood¹⁰ and the transformations themselves are difficult to replicate in the absence of the associated enzymes.¹¹ This creates a significant hurdle for their incorporation into a synthetic plan, particularly when the associated enzyme is either unknown or difficult to express in a synthetically useful form.¹¹ In these cases, a synthetic equivalent that could reconstitute the structural changes under practical conditions would be a welcome alternative, which might also provide insights into the mechanisms of these poorly understood transformations.

Scheme 1. (A) Canonical and non-canonical oxidation mediated by iron-containing oxygenases. **(B)** Examples of noncanonical oxidations in the biosynthesis of streptorubin B, (–)-deoxypodophyllotoxin and vancomycin.

Our interest in developing such a tool stems from a striking example of noncanonical biosynthesis that occurs in medicinal plants of *Kadsura* (Scheme 2A). In a remarkable display of divergent biosynthesis,¹² the dibenzocyclooctadienes (DBCODs)¹³ schizanrin F (**1**) and kadsurarin (**2**) are oxidized on their phenyl-methyl ethers to create the defining 5- and 11-membered rings of heteroclitin J (**3**)¹⁴ and kadsuphilin N (**4**),¹⁵ respectively. The intricate framework of the taiwankadsurins (**5a/5b**)¹⁶ is then further developed by oxidative cleavage of the dienone in **3**, to complete the deconstructive functionalization that diversifies the biphenyl into the bridging pyran.^{17–18} While the oxidation of phenyl-methyl ethers to phenoxy methyl radicals is a relatively common metabolic step, it typically affords phenols by a canonical mechanism of hydroxylation and fragmentation.⁵ Therefore, the cyclizations leading to **3** and **4** raise questions about how the associated oxygenases delay or divert rebound to create these more pronounced structural changes. Rebound ($10^8 - 10^{11} \text{ s}^{-1}$)³ is typically faster than radical cyclization ($10^3 - 10^6 \text{ s}^{-1}$)¹⁹ by several orders of magnitude, suggesting that these enzymes either segregate the phenoxy-methyl radical from the Fe(III)-OH to delay rebound, or accelerate cyclization by creating a conformational bias. This mechanistic difference has important implications for biomimicry, since recreating the secondary interactions of a protein's active site in order to change a molecule's conformational preferences remains quite challenging.²⁰ Instead, a chemical synthesis could more readily attempt to mimic these noncanonical steps by relying on the innate reactivity of the proposed biosynthetic radicals, under the assumption that they undergo these relatively challenging cyclizations in the absence of an external conformational bias.

Scheme 2. (A) Biosynthetic hypothesis for **1-3** via noncanonical oxidation. **(B)** Previous studies of the 5-membered spirocyclization. **(C)** This work: mimicking biosynthetic noncanonical oxidations using photoredox catalysis.

While there has not been a total synthesis of an oxidized DBCOD family member, there have been three studies examining the 5-membered spirocyclization (Scheme 2B). A radical mechanism consists of a stereoelectronically allowed 5-*exo-trig* cyclization, but requires a nucleophilic carbon centered radical to add to an electron rich aromatic ring. This is an uncommon, polarity mismatched radical addition^{19,21} that was investigated by Whiting and co-workers in 1998.²² Using Barton's conditions for the generation of the phenoxy-methyl radical and a 2,4-dinitro

arene as a radical trap, they reported only a 3% yield for the spirocyclization of **8** to spirodienone **9**. Coleman and co-workers subsequently investigated a polarity aligned, cationic alternative, recognizing that the biosynthetic cyclization might involve oxidation of the phenoxy-methyl radical to the oxocarbenium ion prior to cyclization. Similar mechanistic proposals have been made for other noncanonical oxygenases, reflecting persistent questions about the Fe-(III)-OH that is formed following C-H abstraction, and whether it can oxidize radicals to cations as a means of avoiding rebound.^{5-6,10} There is also the possibility that these enzymes do not avoid rebound, and that cationic mechanisms of cyclization initiate from alcohols by more classical Lewis acid activation. Coleman's attempts to cyclize biphenyl ethers **10** representative of this pathway uncovered a competitive 7-membered ring formation that led selectively to dibenzodioxepin **12**. The stereoelectronically disfavored 5-*endo-trig* cyclization onto the oxocarbenium ion could only be effected in a second step by treating **12** with a strong Lewis acid.²³ While successful in a symmetrical model system, subsequent efforts by Baran and co-workers to use these conditions on a nonsymmetrical substrate **13**, more appropriate for a synthesis of **3**, led to a complex mixture of products that reflected poor regioselectivity in the ionization of the dibenzodioxepin.²⁴

In light of these studies, we sought to mimic the noncanonical steps leading to **3-5** by generating the presumed biosynthetic radicals under conditions that could better tolerate relatively slow carbocyclizations. We noted that Barton's conditions are susceptible to a competitive radical addition to the thiocarbonyl of the starting material, which occurs with a second order rate constant of $\sim 10^6 \text{ m}^{-1}\text{s}^{-1}$ (Scheme 2B).²⁵ Therefore, we considered more recently developed photoredox mediated conditions,²⁶ in which carbon centered radicals are formed by one electron reduction of an (*N*-acyloxy)-phthalimide (NHPI) redox-active ester (Scheme 2C).²⁷ By generating the phenoxy methyl radical catalytically under redox neutral conditions, we hoped to approximate the biosynthetic environment of the oxygenase's active site, under the assumption that it prolongs radical lifetime without necessarily influencing its innate reactivity. This led us to identify radical progenitors **16** and **17** as strategic molecules from which to explore this hypothesis.

Before being able to evaluate these radical cyclizations, we needed to address a longstanding challenge of atroposelective biaryl bond formation, which has been a defining feature of the DBCOD literature (Scheme 3).^{13,28} The particular challenge, as it relates to **16** and **17**, is the relative (*P*)-configuration of the biaryl axis and the configurations of the benzylic esters at C6 and C9. Both reside in pseudo axial positions of the twist-boat-chair conformation, and, as configured, create a conformational bias that would favor the opposite atropisomer (*M,6S,9R*)-**16b** or **17b** in the cyclization of a linear precursor **19**.²⁹ This challenge in medium-sized ring formation has not been solved by previous DBCOD syntheses, and helps to explain why there is only a single previous synthesis of a "fully-substituted" DBCOD, containing the complete stereotetrad in the 8-membered ring.³⁰ Therefore, to address this challenge, we chose to invert the stereochemistry at C6 and tether the benzylic alcohol at C9, in anticipation that these changes would allow a stereoselective intramolecular cyclization (Scheme 3).

Scheme 3. Retrosynthetic analysis for the atroposelective biaryl bond formation.

Our syntheses of **16** and **17** began by a 4-step preparation of (*E*)-Cy₂B-enolate **25**, in which the benzylic stereocenter at C6 (DBCOD numbering) was set in 93% *ee* using North's catalytic asymmetric hydrocyanation (Scheme 4A).³¹ This stereocenter was then used to control the ensuing *anti*-aldol (**TS-I**) with good 1, 3-*syn*-induction (20:1 *dr*) to provide **27** in 66% yield and high enantiopurity (>99% *ee*) following recrystallization on 13 g scale. Tertiary alcohol **28** was then prepared under Bartoli's conditions in a 70% yield with 3:1 diastereoselectivity on 14 g scale by pseudo-axial addition of a methyl nucleophile to the 6-membered titanium chelate (**TS-II**).³² In preparation for the ensuing biaryl bond formation, we installed a cyclic borinic ester to tether the C9-alcohol over a two-step sequence, and then selectively deprotected the phenol to direct halogenation at C16.³³ The ensuing intramolecular Suzuki coupling was then catalyzed by Buchwald's SPhos Pd G2 pre-catalyst³⁴ in conjunction with additional ligand and potassium phosphate (K₃PO₄) to afford **30** in 87% yield on 6 g scale. Given the well-documented challenges of forming tetrasubstituted biaryl bonds stereoselectively,²⁸ the efficiency of these conditions is noteworthy. We believe that the (*P*)-configuration of the chiral axis results from a conformational bias to minimize A_{1,3}-strain at C6, and the confinement of the C9-O bond within the borinic ester (Scheme 4B). This conformation should be maintained in a stereodetermining transmetalation (**TS-III**),³⁵ which ensures a *syn* co-planar orientation of the C9-O bond and the forming biaryl axis, as well as a conformation that eclipses the aryl-Pd(II) and the benzylic hydrogen at C6 to minimize steric interactions with the silyl ether. From **30**, we then used a series of functional group manipulations to install the acetate at C9, invert the stereochemistry at C6, and retain differentiation of the phenyl ethers, providing a point of divergence in the form of **31**. Carboxylic acids **33** and **36** were then prepared over 5-step sequences that incorporated benzoate or angelate esters at C6, and either *O*-silyl or *O*-Me substitution at C1. These stable radical progenitors could be prepared on gram scale over a longest linear sequence of 20 steps.

Scheme 4. (A) Forward synthesis of radical precursors. (B) Conformational analysis of the atroposelective biaryl coupling.

Reagents and conditions: a) **23** (0.1 mol%), TMSCN (1.2 equiv), CH₂Cl₂, O₂, –20 °C, 24 hours, then H₃PO₄/FeSO₄, MeOH, rt, 15 min, 99% yield, 93% ee; b) TIPSCl (1.2 equiv), imidazole (1.5 equiv), DMF, rt, 18 hours, 96%; c) EtMgBr (1.5 equiv), CH₂Cl₂, 0 °C – rt, 4 hours, then HCl, 0 °C – rt, 1 hour, 94%; d) 2,2,6,6-tetramethylpiperidine (1.68 equiv), EtMgBr (1.5 equiv), reflux, 12 hours, then **24** (1.0 equiv), –78 °C, 1 hour, then Cy₂BCl (1.2 equiv), –78 °C – rt, 1 hour, then **26** (1.0 equiv), –78 °C, 3 hours then –30 °C, 2 hours, 79% of a 20:1 *dr* mixture, then 2 recrystallizations from hexanes, 66%, > 99% ee; e) LiH (1.5 equiv), TiCl₄ (2.0 equiv), THF, –30 °C, 30 min, then MeMgCl (4.0 equiv), –78 °C, 1 hour, then –40 °C, 2 hours, 70% yield, 3:1 *dr*; f) MeB(OH)₂ (1.2 equiv), 4 Å Mol. Sieve, CH₂Cl₂, rt, 12 hours, 97%; g) ^tBuLi (2.0 equiv), THF, –78 °C, 1 hour, then rt, 3 hours; h) KHF₂ (2.0 equiv), MeOH/THF, rt, 1 hour, 81% over 2 steps; i) DBDMH (0.5 equiv), CHCl₃, 0 °C, 30 min, 97%; j) SPhos Pd G2 (20 mol%), SPhos (20 mol%), K₃PO₄ (5 equiv), PhMe, 60 °C, 16 hours, 87%; k) allyl bromide (1.5 equiv), Cs₂CO₃ (2.0 equiv), DMSO, rt, 12 hours, then H₂O₂ (1.5 equiv), NaOH/MeOH, 0 °C, 2 hours, 95%; l) DMAP (20 mol%), Ac₂O

(10 equiv), pyridine (10 equiv), CH₂Cl₂, rt, 18 hours; m) TBAF·3 H₂O (3 equiv), HOAc (1.2 equiv), THF, rt, 24 hours, 73% over 2 steps; n) IBX (1.2 equiv), DMSO, rt, 3 hours, then NaBH₄ (3.0 equiv), MeOH, 0 °C, 15 min, 81%; o) DMAP (1.0 equiv), BzCl (6.0 equiv), DIPEA (2.0 equiv), pyridine, 60 °C, 18 hours, 89%; p) NaHSO₄·SiO₂, CH₂Cl₂, rt, 6 hours; q) **32** (1.5 equiv), Cs₂CO₃ (2.0 equiv), DMSO, rt, 2 hours, 71% over 2 steps; r) Pd(dppf)Cl₂ (10 mol%), H₂O (50 mol%), NaBH₄ (4.0 equiv), THF, rt, 4 hours; s) TESCI (10 equiv), imidazole (12 equiv), DMF/CH₂Cl₂, rt, 12 hours, then *aq.* citric acid, rt, 10 min, 80% over 2 steps; t) Pd(dppf)Cl₂ (2 mol%), H₂O (50 mol%), NaBH₄ (3.0 equiv), THF, rt, 1 hour; u) MeI (2.0 equiv), Cs₂CO₃ (2.0 equiv), DMSO, rt, 2 hours, 96% over 2 steps; v) **34** (1.5 equiv), LiHMDS (1.2 equiv), THF, 0 °C, 1 hour, 78%; w) NaHSO₄·SiO₂, CH₂Cl₂, rt, 3 hours; x) **35** (1.5 equiv), Cs₂CO₃ (2.0 equiv), DMSO, rt, 2 hours, then TBAF·3 H₂O (3.0 equiv), THF, rt, 2 hours, 73% over 2 steps.

To investigate the key radical cyclization that would afford spirodienone **3** (Scheme 5A), we esterified acid **33** with NHPI using diisopropylcarbodiimide (DIC) in dichloromethane (CH₂Cl₂) before adding 1 mol% of tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate [Ru(bpy)₃(PF₆)₂] and 2 equivalents of triethylamine (Et₃N) as a solution in dimethylformamide (DMF). Subsequent irradiation with blue LEDs resulted in a successful spirocyclization that returned heteroclitin J (**3**)¹⁴ in an isolated yield of 88% on 250 mg scale. Based on previous studies of similar photocatalytic reactions,²⁷ we believe that Et₃N reduces photo-excited Ru-(II) to Ru-(I), which in turn reduces the *N*-phthalimidoyl ester of **16** to trigger fragmentation. This would release phthalimide anion, carbon dioxide (CO₂) and the phenoxy-methyl radical **18**, before installation of the quaternary stereocenter by 5-*exo-trig* spirocyclization. Oxidation of the subsequent radical **37** by the triethylaminyl radical cation would then close the electron transfer loop, before transfer of the triethylsilyl group to the phthalimide anion. We do not observe dibenzodioxepin or regioisomeric products that we would expect from cationic intermediates, providing support for a radical mechanism of spirocyclization.

Since the addition of radicals to electron rich aromatic rings is uncommon, we were intrigued by the high efficiency for spirocyclization, and whether a conformational bias imposed by the DBCOD core could be overcome in order to form the 11-membered ring required for **4**. We explored this question by subjecting angelate ester **17** to similar photoredox conditions, and gratifyingly obtained a 1:1 mixture of alkane **38** and alkene **39** in a combined yield of 57% at complete consumption of the starting material (Scheme 5B). We did not detect any amount of spirodienone by-products, suggesting high selectivity for the electronically favored 11-membered ring formation, and we attributed the ~40% loss of mass balance to decomposition of 3° radical **40** following macrocyclization. The formation of **38** and **39** is consistent with the disproportionation of **40**, which creates **38** as a 5:1 mixture of inseparable diastereomers at C2'. The (*S*)-configuration at C3' is installed selectively for both **38** and **39**, which would be expected for a transannular cyclization involving the thermodynamically preferred *s-cis* conformation of the angelate ester (Scheme 5B, inset). While the biosynthesis of **4** terminates macrocyclization by rebound *exo* to the macrocycle, we were unable to conduct a similar termination by C-X bond formation (X = O or Se), which instead returned products of premature termination without macrocyclization. Therefore, we developed a macrocyclization that could afford olefin **39** more cleanly, under the assumption that we could install the 3° hydroxyl group of the natural product in a subsequent step. To this end, we explored Fu's recently developed metallaphotoredox conditions,^{26,36-37} with the goal of terminating macrocyclization via a more programmable³⁸ process. Once again, irradiation of **17**, but this time in the presence of bis(triphenylphosphine)palladium(II) dichloride [Pd(PPh₃)₂Cl₂] (10 mol%), XantPhos (12 mol%), water (H₂O) and potassium carbonate (K₂CO₃) in dimethylacetamide (DMA) afforded **39** in an improved yield of 53% (72% based on recovered starting material), and only trace amounts of **38**. We attribute this change in selectivity to the coordination of Pd, which provides a better-behaved closure to the catalytic cycle by β-hydride elimination (Scheme 5B, inset).

Scheme 5. (A) Synthesis of heteroclitin J (**3**), and proposed mechanism of photoredox catalyzed radical cyclization. **(B)** Stereoselective 11-*endo-trig* radical cyclization controlled by metallaphotoredox catalysis. ^(a)Yield and diastereomeric ratio (*dr*) determined by ^1H -NMR analysis of the crude reaction mixture using ethylene carbonate as an internal standard. ^(b)Isolated yield.

To complete the synthesis of taiwankadsurins A and B (**5a/b**), we cleaved the most electron rich double bond of the spirodienone by ozonolysis using a reductive work-up (Scheme 6). The resulting keto-ester **41** was then susceptible to hemi-ketalization with the 3° alcohol, creating the bridging pyran of the final polycyclic framework. Taiwankadsurins **5a/b** were formed as a mixture of separable diastereomers in a combined yield of 70% and a 9:1 ratio that is similar to the ratio isolated by Shen and co-workers from *Kadsura philippinensis*.¹⁶ To complete the

synthesis of kadsuphilin N (**4**) from **39**, we employed a Mukaiyama hydration,³⁹ which installed the 3° alcohol at C2' as a 5:1 mixture of separable diastereomers in favor of the natural (*R*)-configuration. The stereoselectivity of hydration was consistent with the addition of a Mn-H to the *pro*-(*R*)-face of the olefin, followed by stereoretentive oxygenation.⁴⁰ We wish to highlight the combination of metallaphotoredox and Mukaiyama hydration as a redox neutral and stereoselective equivalent to the biosynthetic cyclization that could find more general use for the carbohydroxylation of olefins. Overall, our syntheses of **5a/b** and **4** require longest linear sequences of 22 steps, and proceed in 5.0 % and 3.4 % overall yields, respectively. The routes have sustained late-stage optimization studies and provided tens of milligrams of the natural products in high purity, completing the first total syntheses of such highly oxidized DBCOD family members.

Scheme 6. Synthesis of taiwankadsurin A (**5a**) and B (**5b**), and kadsuphilin N (**4**). Reagents and conditions: a) NHPI (1.1 equiv), DIC (1.2 equiv), CH₂Cl₂, rt, 12 hours, then Ru(bpy)₃(PF₆)₂ (1 mol%), NEt₃ (2.0 equiv), DMF, rt, 3 hours, Blue LEDs, 88%; b) O₃/O₂, CH₂Cl₂, -78 °C, ~ 5 seconds, then Me₂S, -78 °C – rt, 1 hour, 63% **5a** + 7% **5b**; c) NHPI (1.1 equiv), DIC (1.2 equiv), CH₂Cl₂, rt, 12 hours, then Pd(PPh₃)₂Cl₂ (10 mol%), Xantphos (12 mol%), K₂CO₃ (1.2 equiv), H₂O (1.0 equiv), DMA, rt, 8 hours, 53% **39**, 72% brsm; d) O₂ (1 atm), Mn(dpm)₃ (5 mol%), PhSiH₃ (5 equiv), ⁱPrOH/1,2-DCE (1:1), 0 °C, 4 h, then PPh₃ (1.5 equiv), rt, 30 min, 65% **4** + 13% C2' epimer, 5:1 *dr*.

The successful mimicry of noncanonical cyclizations using photoredox catalysis suggests that related biosynthetic transformations, including those shown in Scheme 1B, might similarly be mimicked under conditions that tolerate long-lived radicals. In this regard, the modern photoredox toolbox will be enabling, as it provides many opportunities for reaction exploration in the late-stages of a synthesis. In turn, this should provide confidence in the early planning stages of design when considering a noncanonical disconnection. Beyond synthetic applications, we believe that a better mechanistic picture of noncanonical oxygenases will emerge from bio-mimicry, including the extent to which these enzymes exert a conformational bias that cannot be accessed by the substrate alone. These secondary

enzyme-substrate interactions remain difficult to replicate, which helps to explain why radical rearrangement is so uncommon for existing C-H oxidation reactions that use an Fe=O.⁴¹ In this regard, we note that it is possible to generate carbon-centered radicals from alcohols under similar conditions to those used here.²⁷ Therefore, we see a future opportunity to interface canonical C-H hydroxylation reactions with subsequent photoredox catalysis as a means of exploring noncanonical transformations with increasing efficiency and scope.

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Mimicking Noncanonical Oxidations with Redox-Neutral Photocatalysis

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Supporting Information

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1. General Experimental

Purchasing and purification of reagents:

Chemicals and solvents were purchased from Sigma Aldrich, Alfa Aesar, Strem Chemicals, TCI or Oakwood, and used as received without further purification unless otherwise noted. Solvents were dried and purified using a PureSolv MD 7 (from Innovative Technology) or MB SPS 800 (from MBraun). We have not observed differences in the reaction outcome using either of these solvent purifiers. Unless otherwise noted, solvent was degassed by sparging N₂ for 10 min at rt prior to use.

Acquisition and analysis of NMR data:

Proton nuclear magnetic resonance (¹H NMR) spectra were acquired using Bruker Ascend 500 MHz or 400 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak. Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; quint = quintet; dd = doublet of doublets; dt = doublet of triplets; dq = doublet of quartets; tt = triplet of triplets; qd = quartet of doublets; qq = quartet of quartets; ddd = doublet of doublet of doublets; ddt = doublet of doublet of triplets; dddd = doublet of doublet of doublet of doublets; br = broad; m = multiplet (range of multiplet is given). Carbon nuclear magnetic resonance (¹³C NMR) spectra were acquired using Bruker Ascend 126 MHz or 101 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak (7.26 for CHCl₃ residue in ¹H NMR and 77.16 for CDCl₃ in ¹³C NMR).

Additional information:

High resolution mass spectra (HRMS) were recorded using a Bruker maXis Impact TOF mass spectrometer by electrospray ionization time of flight reflectron experiments. Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker Alpha FT-IR spectrometer. Optical rotations were recorded on a Jasco DIP-140 polarimeter (using the sodium D line; 589 nm). High performance liquid chromatography (HPLC) was measured on an Agilent 1200 Infinity Series HPLC system using a Chiralpak® IC analytical column (250 × 4.6 mm, 5 μm). Analytical thin-layer chromatography was performed on pre-coated 250 mm layer thickness silica gel 60 F254 plates (EMD Chemicals Inc). Visualization was performed by ultraviolet light and/or by staining with potassium permanganate or cerium molybdate. Purifications by column chromatography were performed using standard column chromatography using silica gel (40-63 μm, 230-400 mesh). The blue LED light strip (*Product Code: CL-FRS5050WPDD-5M-12V-BL*) and the 12V, 25W power supply (*Product Code: CL-PS94670-25W*) for photoredox chemistry was purchased from Creative Lighting Solutions. The LED strip was cut into 2 meters pieces and coiled inside of a 125 × 65 crystallization dish wrapped with aluminum foil.

2. Comparison of NMR Data

Table S1. NMR Comparison of heteroclitin J (**3**).

	¹ H-NMR			¹³ C-NMR	
	Natural ¹	Synthetic		Natural ¹	Synthetic
4	6.52 (s, 1H)	6.51 (d, <i>J</i> = 1.2 Hz, 1H)	1	196.04	196.05
11	6.51 (s, 1H)	6.50 (s, 1H)	2	131.88	131.92
6	5.90 (s, 1H)	5.89 (d, <i>J</i> = 1.1 Hz, 1H)	3	155.61	155.71
9	5.89 (s, 1H)	5.88 (s, 1H)	4	123.05	123.09
8	2.25 (q, <i>J</i> = 7.2 Hz, 1H)	2.24 (q, <i>J</i> = 7.2 Hz, 1H)	5	141.79	141.85
17	1.27 (s, 3H)	1.25 (s, 3H)	6	81.46	81.46
18	1.33 (d, <i>J</i> = 7.2 Hz, 3H)	1.31 (d, <i>J</i> = 7.2 Hz, 3H)	7	75.18	75.21
19	4.79, 4.06 (ABq, <i>J</i> = 8.8 Hz, 1H each)	4.68 (d, <i>J</i> = 9.0 Hz, 1H) 4.05 (d, <i>J</i> = 9.0 Hz, 1H)	8	44.13	44.20
7-OH	2.54 (br s, 1H)	2.54 (s, 1H)	9	82.37	82.41
2-OCH ₃	3.77 (s, 3H)	3.75 (s, 3H)	10	129.24	129.30
3-OCH ₃	4.09 (s, 3H)	4.06 (s, 3H)	11	101.21	101.23
20	5.95, 5.91 (brs-like, 1H each)	5.93 (d, <i>J</i> = 1.4 Hz, 1H) 5.88 (d, <i>J</i> = 1.5 Hz, 1H)	12	150.16	150.19
Ac	1.88 (s, 3H)	1.86 (s, 3H)	13	130.42	130.44
Bz	7.34 (d, <i>J</i> = 7.2 Hz, 2H)	7.32 (d, <i>J</i> = 7.5 Hz, 2H)	14	143.43	143.47
	7.30 (t, <i>J</i> = 8 Hz, 2H)	7.29 (t, <i>J</i> = 7.7 Hz, 2H)	15	120.29	120.35
	7.53 (t, <i>J</i> = 7.2 Hz, 1H)	7.51 (tt, <i>J</i> = 7.1, 1.6 Hz, 1H)	16	63.25	63.28
			17	28.41	28.47
			18	17.75	17.77
<p>heteroclitin J</p>			19	77.35	78.87
			20	101.98	102.02
			2-OCH ₃	58.94	58.97
			3-OCH ₃	58.89	58.92
			Ac	168.62	168.68
				20.35	20.39
			Bz	165.09	165.12
				128.31	128.35
				129.74	129.75
				128.17	128.21
				133.88	133.91

Table S2. NMR Comparison of kadsuphilin N (**4**).

	¹ H-NMR			¹³ C-NMR	
	Natural ²	Synthetic		Natural ²	Synthetic
4	6.84 (s, 1H)	6.84 (s, 1H)	1	151.5	151.6
11	6.47 (s, 1H)	6.48 (s, 1H)	2	141.8	141.9
6	5.76 (s, 1H)	5.76 (s, 1H)	3	152.3	152.4
9	5.48 (s, 1H)	5.48 (s, 1H)	4	111.0	111.0
8	1.97 (m, 1H)	1.97 (q, <i>J</i> = 7.2 Hz, 1H)	5	130.8	130.9
17	1.37 (s, 3H)	1.34 (s, 3H)	6	86.6	86.7
18	1.30 (d, <i>J</i> = 6.9 Hz, 3H)	1.30 (d, <i>J</i> = 7.2 Hz, 3H)	7	73.8	73.9
19	4.16 (dd, <i>J</i> = 8.0, 5.0 Hz, 1H)	4.17 (dd, <i>J</i> = 12.4, 4.3 Hz, 1H)	8	44.1	44.2
	3.63 (dd, <i>J</i> = 8.0, 5.0 Hz, 1H)	3.63 (dd, <i>J</i> = 12.4, 4.5 Hz, 1H)	9	83.9	84.0
7-OH	--	2.59 (s, 1H)	10	132.8	132.9
1-OCH ₃	3.46 (s, 3H)	3.46 (s, 3H)	11	102.5	102.6
2-OCH ₃	3.84 (s, 3H)	3.84 (s, 3H)	12	148.6	148.7
3-OCH ₃	3.92 (s, 3H)	3.92 (s, 3H)	13	137.5	137.6
20	6.03 (s, 1H)	6.03 (d, <i>J</i> = 1.1 Hz, 1H)	14	139.0	139.1
	5.94 (s, 1H)	5.94 (d, <i>J</i> = 1.0 Hz, 1H)	15	121.2	121.3
3'	1.92 (m, 1H)	1.96 – 1.88 (m, 1H)	16	121.7	121.8
4'	1.23 (s, 3H)	1.24 (s, 3H)	17	28.4	28.5
5'	0.96 (d, <i>J</i> = 7.2 Hz, 3H)	0.97 (d, <i>J</i> = 7.2 Hz, 3H)	18	17.8	18.0
2'-OH	--	1.80 (s, 1H)	19	72.4	72.5
Ac	1.49 (s, 3H)	1.49 (s, 3H)	20	101.5	101.7
<p>kadsuphilin N</p>			1-OCH ₃	60.5	60.6
			2-OCH ₃	60.7	60.8
			3-OCH ₃	56.2	56.3
			1'	172.4	172.5
			2'	76.6	76.8
			3'	42.4	42.6
			4'	21.4	21.5
			5'	12.8	12.9
			Ac	168.7	168.8
				20.3	20.4

Table S3. NMR Comparison of taiwankadsurin A (**4a**).

	¹ H-NMR			¹³ C-NMR	
	Natural ³	Synthetic		Natural ³	Synthetic
4	6.08 (d, <i>J</i> = 2.7 Hz, 1H)	6.08 (d, <i>J</i> = 2.7 Hz, 1H)	1	97.6 s	97.7
11	6.60 (s, 1H)	6.60 (s, 1H)	2	171.1 s	171.1
6	6.49 (d, <i>J</i> = 2.7 Hz, 1H)	6.49 (d, <i>J</i> = 2.7 Hz, 1H)	3	165.5 s	165.5
9	6.69 (d, <i>J</i> = 3.0 Hz, 1H)	6.69 (d, <i>J</i> = 3.0 Hz, 1H)	4	117.3 d	117.4
8	2.36 (m, 1H)	2.37 (qd, <i>J</i> = 6.8, 3.3 Hz, 1H)	5	150.4 s	150.5
17	1.34 (s, 3H)	1.34 (s, 3H)	6	73.3 d	73.4
18	1.05 (d, <i>J</i> = 6.9 Hz, 3H)	1.05 (d, <i>J</i> = 6.8 Hz, 3H)	7	79.3 s	79.4
19	5.00 (d, <i>J</i> = 10.5 Hz, 1H)	5.00 (d, <i>J</i> = 10.2 Hz, 1H)	8	45.3 d	45.3
	4.54 (d, <i>J</i> = 10.5 Hz, 1H)	4.54 (d, <i>J</i> = 10.2 Hz, 1H)	9	70.5 d	70.6
1-OH	--	3.51 (s, 1H)	10	127.8 s	127.9
2-OCH ₃	3.96 (s, 3H)	3.96 (s, 3H)	11	99.1 d	99.1
3-OCH ₃	3.57 (s, 3H)	3.57 (s, 3H)	12	150.3 s	150.4
20	6.02 (s, 1H)	6.02 (d, <i>J</i> = 1.4 Hz, 1H)	13	129.0 s	129.5
	5.99 (s, 1H)	5.99 (d, <i>J</i> = 1.4 Hz, 1H)	14	144.6 s	144.3
Ac	2.21 (s, 3H)	2.21 (s, 3H)	15	118.2 s	118.2
Bz	8.31 (d, <i>J</i> = 7.5 Hz, 2H)	8.31 (d, <i>J</i> = 7.2 Hz, 2H)	16	57.1 s	57.1
	7.53 (t, <i>J</i> = 7.5 Hz, 2H)	7.53 (t, <i>J</i> = 7.8 Hz, 2H)	17	28.3 q	28.4
	7.65 (t, <i>J</i> = 7.5 Hz, 1H)	7.65 (t, <i>J</i> = 7.4 Hz, 1H)	18	8.8 q	8.9
<p>Taiwankadsurin A</p>			19	80.5 t	80.6
			20	101.9 t	102.0
			2-OCH ₃	53.7 q	53.8
			3-OCH ₃	51.8 q	51.9
			Ac	169.1 s	169.2
				21.3 q	21.4
			Bz	165.5 s	165.7
				128.4 s	128.5
				128.9 d	129.0
				130.6 d	130.7
				134.1 d	134.2

Table S4. NMR Comparison of taiwankadsurin B (**4b**).

	¹ H-NMR			¹³ C-NMR	
	Natural ³	Synthetic		Natural ³	Synthetic
4	6.17 (d, <i>J</i> = 2.7 Hz, 1H)	6.17 (d, <i>J</i> = 2.7 Hz, 1H)	1	97.8 s	97.9
11	6.60 (s, 1H)	6.60 (s, 1H)	2	170.2 s	170.3
6	6.91 (d, <i>J</i> = 2.7 Hz, 1H)	6.90 (d, <i>J</i> = 2.7 Hz, 1H)	3	165.7 s	165.8
9	6.80 (d, <i>J</i> = 3.0 Hz, 1H)	6.79 (d, <i>J</i> = 3.0 Hz, 1H)	4	118.5 d	118.6
8	2.38 (m, 1H)	2.39 (qd, <i>J</i> = 6.8, 3.3 Hz, 1H)	5	149.6 s	149.7
17	1.37 (s, 3H)	1.38 (s, 3H)	6	73.4 d	73.5
18	1.04 (d, <i>J</i> = 6.6 Hz, 3H)	1.04 (d, <i>J</i> = 6.8 Hz, 3H)	7	78.6 s	78.71
19	4.98 (d, <i>J</i> = 9.9 Hz, 1H)	4.98 (d, <i>J</i> = 10.0 Hz, 1H)	8	45.4 d	45.5
	4.63 (d, <i>J</i> = 9.9 Hz, 1H)	4.63 (d, <i>J</i> = 10.0 Hz, 1H)	9	70.5 d	70.5
1-OH	--	4.86 (s, 1H)	10	127.8 s	127.9
2-OCH ₃	3.61 (s, 3H)	3.61 (s, 3H)	11	99.4 d	99.5
3-OCH ₃	3.56 (s, 3H)	3.56 (s, 3H)	12	149.9 s	150.0
20	5.96 (s, 1H)	5.96 (d, <i>J</i> = 1.3 Hz, 1H)	13	128.8 s	129.2
	5.95 (s, 1H)	5.95 (d, <i>J</i> = 1.4 Hz, 1H)	14	142.5 s	142.8
Ac	2.21 (s, 3H)	2.21 (s, 3H)	15	120.7 s	120.8
Bz	8.32 (d, <i>J</i> = 7.2 Hz, 2H)	8.32 (d, <i>J</i> = 7.2 Hz, 2H)	16	58.8 s	58.9
	7.52 (t, <i>J</i> = 7.2 Hz, 2H)	7.53 (t, <i>J</i> = 7.7 Hz, 2H)	17	28.6 q	28.8
	7.64 (t, <i>J</i> = 7.2 Hz, 1H)	7.64 (t, <i>J</i> = 7.4 Hz, 1H)	18	8.5 q	8.6
<p>Taiwankadsurin B</p>			19	78.6 t	78.69
			20	101.7 t	101.8
			2-OCH ₃	54.1 q	54.3
			3-OCH ₃	51.8 q	51.9
			Ac	169.1 s	169.3
				21.3 q	21.4
			Bz	165.6 s	165.8
				130.0 s	128.8
				128.8 d	128.9
				130.6 d	130.7
				133.9 d	134.0

3. Synthesis and Characterization of Synthetic Intermediates

Compound 22

Procedure: A 250 mL, flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with 3,4-dimethoxy-5-hydroxybenzaldehyde (50 mmol, 9.11 g, 1.0 equiv), imidazole (60 mmol, 4.08 g, 1.2 equiv) and TBSCl (55 mmol, 8.29 g, 1.1 equiv). CH_2Cl_2 (100 mL) was then added, and the resulting mixture was stirred at rt for 12 h. It was then poured on HCl (1 M, 100 mL), and extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified on silica gel (20:1 hexanes/EtOAc) to provide **22** (14.82 g, 50.0 mmol, *quant.*) as a pale-yellow oil.

Characterization:

1H NMR (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.11 (d, $J = 1.8$ Hz, 1H), 7.02 (d, $J = 1.8$ Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 1.02 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 154.4, 150.0, 146.3, 131.9, 117.4, 105.3, 60.7, 56.3, 25.8, 18.5, -4.5. Our characterization data matches the data reported previously.⁴

Compound SI-1

Procedure: The literature procedure was followed with slight modifications.⁵ A 100 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with (*S,S*)-VO(salen)NCS (**23**) (**31**) (0.03 mmol, 20.1 mg, 0.1 mol%) and **22** (30 mmol, 8.89 g, 1.0 equiv). It was then evacuated and refilled with O_2 three times before a balloon of O_2 was left connected to the flask by a needle inserted into the septum. CH_2Cl_2 (30 mL), which had been sparged with O_2 for 10 min was then added to afford a homogeneous solution (dark green). The resulting homogeneous solution was then cooled to -20 °C, at which point TMSCN (36 mmol, 4.50 mL, 1.2 equiv) was added dropwise by syringe. The resulting mixture was then placed in a -20 °C freezer for 24 h. The reaction mixture was then quenched at this temperature by the addition of a solution consisting of $FeSO_4 \cdot 7H_2O$ (3 mmol, 834.2 mg) and H_3PO_4 (12 mmol, 85 wt% aq., 0.82 mL) in MeOH (6 mL), and stirred for 15 min while the reaction mixture gradually warmed to rt. It was then poured on brine (50 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified on silica gel (3:1 hexanes/EtOAc) to provide **SI-1** (9.70 g, 30.0

mmol, *quant.*) as a pale-green oil with an *e.e.* of 92.7% as determined by chiral HPLC.

Characterization:

R_f = (hexanes/EtOAc 3:1): 0.40; IR (neat) ν = 3427, 2931, 2858, 1589, 1500, 1455, 1426, 1344, 1252, 1229, 1114 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.69 (d, J = 2.1 Hz, 1H), 6.64 (d, J = 2.0 Hz, 1H), 5.39 (d, J = 6.7 Hz, 1H), 3.84 (s, 3H), 3.82 (d, J = 6.7 Hz, 1H), 3.77 (s, 3H), 0.99 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.2, 149.8, 141.2, 130.9, 119.0, 112.6, 103.8, 63.3, 60.6, 56.2, 25.7, 18.4, -4.5; HPLC (Chiralpak[®] IC analytical column, eluent 5:95 *i*PrOH:hexanes, 1 mL/min) t_R 9.7 min (major), 8.1 min (minor), 92.7% *e.e.*; $[\alpha]^{23}_D$ +20.1°, (c = 1.0, CHCl_3); HRMS: Calcd. for $\text{C}_{16}\text{H}_{25}\text{NO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$ = 346.1445 m/z , found = 346.1440 m/z .

HPLC trace of the racemic mixture:

Signal 1: DAD1 A, Sig=209,2 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.086	BB	0.1871	1.16411e4	976.22260	49.9088
2	9.735	VB	0.2346	1.16836e4	780.71277	50.0912

HPLC trace of the chiral product:

Signal 1: DAD1 A, Sig=209,2 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.081	BB	0.1882	271.15393	22.56488	3.6460
2	9.715	BB	0.2329	7165.92236	483.49017	96.3540

Compound SI-2

Procedure: A 100 mL, flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-1** (30 mmol, 9.70 g, 1.0 equiv) and DMF (30 mL). TIPSCl (36 mol, 7.70 mL, 1.2 equiv) was then added via syringe, followed by the addition of imidazole (45 mmol, 3.06 g, 1.5 equiv) as a solid. The resulting solution was then stirred at rt for 18 h, and then quenched by the addition of *N,N*-dimethylaminoethanol (1.20 mL), and stirred for another 1 h. It was then diluted with EtOAc (100 mL), and washed with HCl (1 M, 50 mL). The aqueous layer was further extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified on silica gel (20:1 hexanes/EtOAc) to provide **SI-2** (13.75 g, 28.65 mmol, 96%) as a colorless oil.

Characterization:

R_f = (hexanes/EtOAc 10:1): 0.57; **IR** (neat) ν = 2942, 2866, 1589, 1500, 1462, 1426, 1346, 1251, 1224, 1146, 1108 cm^{-1} ; **1H NMR** (500 MHz, $CDCl_3$) δ 6.68 (d, J = 2.0 Hz, 1H), 6.62 (d, J = 1.7 Hz, 1H), 5.47 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 1.25 – 1.17 (m, 3H), 1.11 (d, J = 7.3 Hz, 9H), 1.07 (d, J = 7.3 Hz, 9H), 1.00 (s, 9H), 0.17 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.2, 149.8, 141.1, 132.2, 119.5, 112.0, 103.1, 64.0, 60.5, 56.1, 25.8, 18.4, 17.93, 17.92, 12.1, -4.6; **$[\alpha]_D^{23}$** +3.8°, (c = 1.0, $CHCl_3$); **HRMS**: Calcd. for $C_{25}H_{45}NO_4Si_2$ $[M+Na]^+$ = 502.2779 m/z , found = 502.2788 m/z .

Compound 24

Procedure: A 500 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-2** (33.28 mmol, 16.79 g, 1.0 equiv). The flask was evacuated and refilled with N_2 three times, prior to the addition of CH_2Cl_2 (140 mL). The resulting solution was then cooled to 0 °C in an ice bath, at which point EtMgBr (50.0 mmol, 3 M in Et_2O , 16.67 mL, 1.5 equiv) was added dropwise via syringe. The solution was then warmed to rt and stirred for 4 h, and then cooled to 0 °C again in an ice bath. The reaction mixture was then quenched by the addition of HCl (2M, 140 mL), and stirred for an additional 1 h at rt. The biphasic mixture was then extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified on silica gel (20:1 hexanes/EtOAc) to provide **24** (15.98 g, 31.28 mmol, 94%) as a pale-yellow oil.

Characterization:

R_f = (hexanes/EtOAc 10:1): 0.64; **IR** (neat) ν = 2940, 2866, 1717, 1586, 1498, 1462, 1423, 1389, 1343, 1251, 1235, 1221, 1115 cm^{-1} ; **1H NMR** (500 MHz, $CDCl_3$) δ 6.66 (d, J = 1.9 Hz, 1H), 6.61 (d, J = 1.8 Hz, 1H), 5.05 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.69 (dq, J = 18.6, 7.3 Hz, 1H), 2.45 (dq, J = 18.6, 7.3 Hz, 1H), 1.16 – 1.10 (m, 3H), 1.05 – 1.01 (m, 18H), 1.00 (s, 9H), 0.93 (t, J = 7.3 Hz, 3H), 0.16 (s, 3H), 0.15 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.5, 153.8, 149.5, 140.1, 134.6, 111.6,

103.0, 81.3, 60.5, 56.1, 28.5, 25.8, 18.5, 18.0, 12.2, 7.6, -4.5, -4.6; [α] $^{23}_D$ +33.8°, (c = 1.0, CHCl₃); **HRMS**: Calcd. for C₂₇H₅₀O₅Si₂ [M+Na]⁺ = 533.3089 m/z, found = 533.3081 m/z.

Compound 26

Procedure: A 1 L oven-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with 5-hydroxypiperonal (50 mmol, 8.31 g, 1.0 equiv) and CHCl₃ (500 mL). 1,3-Dibromo-5,5-dimethylhydantoin (DBDMH, 25 mol, 7.15 g, 0.5 equiv) was added in portions (an orange color appeared when the first portion of DBDMH was added, the next portion was added after the orange color faint). The resulting mixture was stirred at rt for 12 h. *N,N*-Diisopropylethylamine (DIPEA, 120 mmol, 20.90 mL, 2.4 equiv) and MOMCl (100 mmol, 7.60 mL, 2.0 equiv) was then added via syringe, and the mixture was stirred for another 12 h at rt. It was then poured on HCl (1M, 200 mL), and extracted with CH₂Cl₂ (3 × 200 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was then purified on silica gel (10:1 to 5:1 hexanes/EtOAc) to provide **26** (10.87 g, 37.60 mmol, 75%) as a white solid.

Characterization:

R_f = (hexanes/EtOAc 5:1): 0.32; **IR** (neat) ν = 2949, 2880, 1666, 1595, 1475, 1464, 1403, 1380, 1343, 1315, 1281, 1222, 1153, 1132 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 10.26 (s, 1H), 7.20 (s, 1H), 6.09 (s, 2H), 5.33 (s, 2H), 3.61 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 190.7, 149.2, 144.0, 137.1, 128.9, 116.7, 104.0, 103.0, 97.4, 57.8; **HRMS**: Calcd. for C₁₀H₉BrO₅ [M+Na]⁺ = 310.9526 m/z, found = 310.9525 m/z.

Compound 27

Procedure: *TMPMgBr* was made following the literature procedure.⁶ A 500 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with 2,2,6,6-tetramethylpiperidine (freshly distilled over CaH₂, 42 mmol, 7.15 mL) and dissolved in THF (37.5 mL). EtMgBr (37.5 mmol, 12.5 mL of 3M solution in Et₂O, 1.5 equiv) was then added via syringe. The resulting solution was then refluxed under N₂ for 12 h, dilute with additional THF (37.5 mL) and cooled to -78 °C in a dry ice / acetone bath. A solution of **24** (25 mmol, 12.77 g, 1.0 equiv) in THF (50 mL) was then added dropwise over 30 min with a syringe pump. The deprotonation was complete within another 1 h at -78 °C, at which point a solution of Cy₂BCl (30 mmol, 1.2 equiv) in hexane (30 mL) was added via syringe, warm to rt and stirred for another 1 h. It was then cooled down again to -78 °C, and a solution of **26** (25 mmol, 7.23 g, 1.0 equiv) in hexanes and CH₂Cl₂ (1:1 mixture, 75 mL) was added dropwise over 30 min with a syringe pump. The resulting mixture was then stirred at -78 °C for 3 h, and additional 2 h at -30 °C. It was quenched by the addition of NaHCO₃ (saturated, 100 mL) and diethanolamine (75 mmol, 7.89 g, 3.0 equiv), and stirred for another 30 min at rt. The mixture was then filtered, and the filtrate was extracted with EtOAc (3 × 200 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was then purified on silica gel (10:1 to 5:1 hexanes/EtOAc) to provide **27** (15.80 g, 19.75 mmol, 79%) as a 20:1 *d.r.* mixture. To further purify the product, it was then dissolved in hexanes (150 mL) with gentle heat, cooled to rt, and left in a -20 °C freezer for 12 h. The resulting white solid was collected by filtration. The process was repeated with 100 mL of hexanes, and gave 13.20 g, 16.50 mmol, 66% of **27** as a white solid with > 99% *e.e.* as determined by chiral HPLC.

Characterization:

R_f = (hexanes/EtOAc 5:1): 0.32; **IR** (neat) ν = 3453, 2937, 2864, 1708, 1585, 1497, 1471, 1425, 1390, 1355, 1334, 1280, 1248, 1222, 1158, 1148, 1109 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 6.66 (s, 1H), 6.54 (d, *J* = 1.7 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 5.95 (d, *J* = 1.5 Hz, 1H), 5.95 (d, *J* = 1.5 Hz, 1H), 5.29 (d, *J* = 6.0 Hz, 1H), 5.15 (d, *J* = 6.0 Hz, 1H), 5.08 (dd, *J* = 7.1, 6.0 Hz, 1H), 5.02 (s, 1H), 3.90 (d, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.53 (s, 3H), 3.49 (qd, *J* = 7.2, 6.0 Hz, 1H), 1.08 – 1.03 (m, 3H), 1.01 – 0.96 (m, 30H), 0.13 (s, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ 214.6, 153.7, 149.4, 148.7, 140.2, 137.5, 136.4, 136.3, 133.6, 112.4, 108.5, 103.6, 103.0, 101.9, 97.1, 80.6, 75.6, 60.5, 57.5, 56.0, 45.6, 25.8, 18.4, 17.98, 17.96, 16.1, 12.2, -4.58, -4.62; **HPLC** (Chiralpak® IC analytical column, eluent 10:90 *i*PrOH:hexanes, 1 mL/min) *t_R* 7.9 min (major), 10.8 min (minor), > 99% *e.e.*; [α]_D²³ -17.2°, (*c* = 1.0, CHCl₃); **HRMS**: Calcd. for C₃₇H₅₉BrO₁₀Si₂ [M+Na]⁺ = 821.2722 m/z, found = 821.2729 m/z.

HPLC trace of the racemic mixture:

Signal 1: DAD1 A, Sig=218,2 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.902	MM	0.2789	2.52526e4	1508.90442	49.9706
2	10.827	MM	0.3902	2.52823e4	1079.85156	50.0294

HPLC trace of the chiral product:

Signal 1: DAD1 A, Sig=218,2 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.902	MM	0.2763	2.56568e4	1547.61865	99.6137
2	10.848	MM	0.3296	99.49126	5.03051	0.3863

Compound 28

Procedure: The literature procedure was followed with slight modifications.⁷ A 100 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **27** (5.0 mmol, 4.00 g, 1.0 equiv) and LiH (7.5 mmol, 59.6 mg, 1.5 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of THF (25 mL). The mixture was then cooled to $-30\text{ }^{\circ}C$ in a dry ice bath, at which point $TiCl_4$ (10.0 mmol, 1 M in CH_2Cl_2 , 10.0 mL, 2.0 equiv) was added dropwise via syringe, and stirred at this temperature for 30 min. The resulting red solution was then

cooled to $-78\text{ }^{\circ}\text{C}$, a solution of MeMgCl (20 mmol, 1 M solution in THF, 20 mL, 4.0 equiv) was added dropwise over 30 min with a syringe pump. The mixture was stirred at this temperature for 1 h, warmed to $-40\text{ }^{\circ}\text{C}$ and stirred for another 2 h. It was then quenched by the addition of a solution containing NH_4Cl (saturated, 20 mL) and NH_4OH (concentrated, 5 mL), and stirred for another 15 min at rt. The resulting mixture was then filtered, and the filtrate was extracted with EtOAc ($3 \times 50\text{ mL}$). The combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was then purified on silica gel (5:1 to 3:1 hexanes/EtOAc) to provide the major diastereomer (**28**) (3.31 g, 4.06 mmol, 81%) as a pale-yellow oil, and the minor diastereomer (453.8 mg, 0.56 mmol, 11%) as a pale-yellow oil. A similar experiment with 25 mmol of **27** gave 14.33 g, 17.6 mmol, 70% of **28** and 3:1 diastereomeric ratio.

Characterization:

Major diastereomer (28): R_f = (hexanes/EtOAc 5:1): 0.21; IR (neat) ν = 3441, 2938, 2865, 1585, 1500, 1470, 1426, 1386, 1350, 1290, 1272, 1225, 1160, 1145, 1115 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.72 (br s, 1H), 6.55 (s, 1H), 6.43 (br s, 1H), 5.91 (d, J = 1.4 Hz, 1H), 5.90 (d, J = 1.4 Hz, 1H), 5.35 (d, J = 9.0 Hz, 1H), 5.27 (d, J = 6.0 Hz, 1H), 5.21 (d, J = 6.0 Hz, 1H), 5.13 (s, 1H), 4.52 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.56 (s, 1H), 3.54 (s, 3H), 1.54 (s, 3H), 1.55 – 1.45 (m, 1H), 1.14 – 0.77 (m, 30H), 0.46 (d, J = 7.1 Hz, 3H), 0.15 (br s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 153.4, 148.9, 140.5, 137.7, 137.1, 135.9, 135.2, 115.0, 109.9, 106.2, 103.7, 101.8, 97.2, 80.5, 79.9, 74.5, 60.6, 57.5, 56.2, 45.1, 25.8, 21.6, 18.5, 18.3, 18.1, 12.7, 12.3, -4.6; $[\alpha]^{23}_{\text{D}}$ +13.9°, (c = 1.0, CHCl_3); HRMS: Calcd. for $\text{C}_{38}\text{H}_{63}\text{BrO}_{10}\text{Si}_2$ $[\text{M}+\text{Na}]^+$ = 837.3035 m/z , found = 837.3028 m/z .

Minor diastereomer: R_f = (hexanes/EtOAc 5:1): 0.32; IR (neat) ν = 3377, 2938, 2864, 1585, 1499, 1469, 1426, 1388, 1354, 1331, 1249, 1223, 1160, 1114 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.82 (s, 1H), 6.75 (d, J = 1.2 Hz, 1H), 6.68 (d, J = 1.7 Hz, 1H), 5.94 (s, 2H), 5.34 (d, J = 9.8 Hz, 1H), 5.26 (d, J = 6.0 Hz, 1H), 5.22 (d, J = 6.0 Hz, 1H), 5.19 (s, 1H), 5.04 (br s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.53 (s, 3H), 3.40 (br s, 1H), 2.11 (dq, J = 9.8, 7.3 Hz, 1H), 1.28 (s, 3H), 1.05 – 0.96 (m, 30H), 0.43 (d, J = 7.4 Hz, 3H), 0.15 (s, 3H), 0.12 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 153.2, 148.9, 148.8, 140.4, 138.6, 137.7, 136.3, 135.9, 115.5, 109.8, 106.4, 103.5, 101.9, 97.2, 79.7, 79.2, 75.7, 60.6, 57.5, 56.1, 47.3, 25.8, 22.0, 18.4, 18.2, 18.1, 12.7, 12.5, -4.6, -4.7; $[\alpha]^{23}_{\text{D}}$ -23.6°, (c = 1.0, CHCl_3); HRMS: Calcd. for $\text{C}_{38}\text{H}_{63}\text{BrO}_{10}\text{Si}_2$ $[\text{M}+\text{Na}]^+$ = 837.3035 m/z , found = 837.3041 m/z .

Compound SI-3

Procedure: A 250 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **28** (20.0 mmol, 16.32 g, 1.0 equiv), $\text{MeB}(\text{OH})_2$ (24 mmol, 1.44 g, 1.2 equiv) and 4 Å Mol. Sieve (10 g). CH_2Cl_2 (100 mL) was then added, and the resulting mixture was stirred at rt for 12 h. It was then filtered and concentrated *in vacuo*. The crude product was purified on silica gel (10:1 hexanes/EtOAc) to provide **SI-3** (16.35 g, 19.46 mmol, 97%) as a pale-yellow oil.

Characterization:

R_f = (hexanes/EtOAc 10:1): 0.37; IR (neat) ν = 2938, 2865, 1585, 1499, 1471, 1425, 1404, 1383, 1364, 1335, 1273, 1239, 1224, 1159 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.83 (br s, 1H), 6.36 (br s, 1H), 6.32 (s, 1H), 5.94 (s, 2H), 5.32 (d, J = 10.6 Hz, 1H), 5.29 (d, J = 6.1 Hz, 1H), 5.23 (d, J = 6.0 Hz, 1H), 4.64 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.55 (s, 3H), 1.62 – 1.53 (m, 1H), 1.48 (s, 3H), 1.04 – 0.95 (m, 30H), 0.70 (d, J = 6.9 Hz, 3H), 0.22 (s, 3H), 0.13 (s, 3H), 0.11 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 153.2, 149.1, 148.2, 140.0, 138.1, 136.4, 136.1, 135.2, 114.7, 110.5, 106.5, 103.0, 102.0, 97.2, 79.6, 73.6, 60.6, 57.5,

55.9, 42.7, 25.8, 20.7, 18.5, 18.3, 18.2, 12.9, 12.1, -0.9, -4.58, -4.63; $[\alpha]^{23}_D +7.2^\circ$, ($c = 1.1$, CHCl_3); **HRMS**: Calcd. for $\text{C}_{39}\text{H}_{64}\text{BBrO}_{10}\text{Si}_2$ $[\text{M}+\text{Na}]^+ = 861.3207$ m/z, found = 861.3212 m/z.

Compound SI-4

Procedure: A 500 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-3** (14.59 mmol, 12.25 g, 1.0 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of THF (150 mL). The mixture was then cooled to -78°C in a dry ice / acetone bath, at which point $t\text{-BuLi}$ (29.18 mmol, 1.7 M pentane, 17.2 mL, 2.0 equiv) was added dropwise over 30 min with a syringe pump. The resulting mixture was stirred at -78°C for 1 h, and another 3 h at rt. It was then quenched by the addition of a solution consisting 20 mL of saturated NH_4Cl and H_2O (100 mL), and extracted with EtOAc (3×100 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was dissolved in MeOH and THF (1:1, 150 mL), and KHF_2 (29.18 mmol, 2.28 g, 2.0 equiv) was added as solid. The resulting solution was stirred at rt for 1h, dilute with PhMe (50 mL), and concentrated *in vacuo* to ~ 50 mL. H_2O (50 mL) and brine (50 mL) was then added, the resulting mixture was extracted with EtOAc (3×100 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified on silica gel (5:1 to 3:1 hexanes/EtOAc) to provide **SI-4** (7.63 g, 11.80 mmol, 81%) as a white foam.

Characterization:

R_f = (hexanes/EtOAc 5:1): 0.14; **IR** (neat) $\nu = 3511, 2942, 2866, 1599, 1508, 1464, 1433, 1324, 1248, 1201, 1159, 1139$ cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.72 (s, 1H), 6.69 (br s, 1H), 6.58 (br s, 1H), 5.96 (br s, 2H), 5.76 (s, 1H), 5.46 (d, $J = 3.4$ Hz, 1H), 5.37 (d, $J = 6.0$ Hz, 1H), 5.29 (d, $J = 6.0$ Hz, 1H), 4.63 (s, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.53 (s, 3H), 2.81 (s, 1H), 2.37 – 2.25 (m, 1H), 1.28 (s, 3H), 1.07 – 0.92 (m, 21H), 0.79 (s, 3H), 0.63 (d, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 153.1, 152.7, 152.0, 148.5, 141.6, 137.1, 135.2, 135.1, 124.7, 108.6, 104.5, 101.4, 99.5, 96.6, 87.9, 81.9, 77.6, 61.2, 57.0, 56.0, 41.1, 22.4, 18.24, 18.16, 13.2, 12.8, 1.1; $[\alpha]^{23}_D -8.5^\circ$, ($c = 1.0$, CHCl_3); **HRMS**: Calcd. for $\text{C}_{33}\text{H}_{51}\text{BO}_{10}\text{Si}$ $[\text{M}+\text{Na}]^+ = 669.3237$ m/z, found = 669.3229 m/z.

Compound 29

Procedure: A 500 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was

charged with **SI-4** (15.48 mmol, 10.01 g, 1.0 equiv) and dissolved in CHCl_3 (150 mL). The mixture was then cooled to 0 °C in an ice bath, at which point 1,3-Dibromo-5,5-dimethylhydantoin (DBDMH, 7.74 mol, 2.21 g, 0.5 equiv) was added as solid in portions (an orange color appeared when the first portion of DBDMH was added, the next portion was added after the orange color faint). The resulting solution was stirred at 0 °C for 30 min and concentrated *in vacuo*. The crude product was purified on silica gel (3:1 hexanes/EtOAc) to provide **29** (10.91 g, 15.04 mmol, 97%) as an off-white solid. Single crystals for X-ray diffraction were crystallized by vapor diffusion from Hexanes and EtOAc.

Characterization:

R_f = (hexanes/EtOAc 3:1): 0.32; IR (neat) ν = 3464, 2942, 2866, 1604, 1575, 1464, 1426, 1334, 1247, 1220, 1194, 1153, 1108 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.00 (s, 1H), 6.65 (s, 1H), 6.14 (s, 1H), 5.95 (s, 2H), 5.48 (d, J = 3.6 Hz, 1H), 5.38 (d, J = 6.0 Hz, 1H), 5.31 (s, 1H), 5.28 (d, J = 6.0 Hz, 1H), 3.93 (s, 3H), 3.84 (s, 3H), 3.53 (s, 3H), 2.73 (s, 1H), 2.23 (qd, J = 7.1, 3.8 Hz, 1H), 1.35 (s, 3H), 1.09 – 1.03 (m, 3H), 1.01 (d, J = 6.3 Hz, 9H), 0.91 (d, J = 6.9 Hz, 9H), 0.80 (d, J = 7.2 Hz, 3H), 0.77 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.0, 152.7, 151.1, 146.0, 141.5, 136.3, 135.7, 135.1, 124.7, 106.4, 103.4, 101.4, 99.6, 96.5, 87.7, 78.8, 78.3, 61.3, 57.0, 56.0, 41.5, 22.8, 18.2, 18.0, 13.7, 12.7, 1.0; $[\alpha]^{23}_D$ +7.0°, (c = 0.8, CHCl_3); HRMS: Calcd. for $\text{C}_{33}\text{H}_{50}\text{BBrO}_{10}\text{Si}$ $[\text{M}+\text{Na}]^+$ = 747.2342 m/z, found = 747.2355 m/z.

Compound 30

Procedure: A 500 mL flame-dried Schlenk flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **29** (10.67 mmol, 7.74 g, 1.0 equiv), SPhos Pd G2 (2.13 mmol, 1.53 g, 20 mol%), SPhos (2.13 mmol, 874.4 mg, 20 mol%) and K_3PO_4 (53.35 mmol, 11.32 g, 5.0 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of PhMe (213 mL). The mixture was then warmed to 60 °C in a pre-heated oil bath for 16 h. It was then poured on a mixture consisting H_3PO_4 (2M, 50 mL) and brine (50 mL), and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified on silica gel (3:1 hexanes/EtOAc) to provide **30** (6.00 g, 9.31 mmol, 87%) as a pale-yellow foam.

Characterization:

R_f = (hexanes/EtOAc 3:1): 0.22; IR (neat) ν = 3398, 2938, 2865, 1614, 1460, 1368, 1334, 1303, 1272, 1248, 1231, 1192, 1140, 1106 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.78 (s, 1H), 6.38 (s, 1H), 5.96 (d, J = 1.3 Hz, 1H), 5.95 (d, J = 1.3 Hz, 1H), 5.74 (s, 1H), 5.20 (d, J = 5.2 Hz, 1H), 5.14 (d, J = 5.2 Hz, 1H), 4.81 (s, 1H), 4.78 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.38 (s, 3H), 1.96 (q, J = 7.2 Hz, 1H), 1.40 (s, 3H), 1.22 (d, J = 7.2 Hz, 3H), 0.89 (s, 21H), -0.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 151.2, 148.9, 146.0, 138.3, 136.7, 135.5, 134.3, 117.6, 114.8, 104.6, 102.1, 101.3, 97.0, 81.7, 78.0, 61.1, 57.0, 55.8, 43.7, 23.4, 18.24, 18.17, 12.6, -1.8; $[\alpha]^{23}_D$ -76.8°, (c = 1.1, CHCl_3); HRMS: Calcd. for $\text{C}_{33}\text{H}_{49}\text{BO}_{10}\text{Si}$ $[\text{M}+\text{Na}]^+$ = 667.3080 m/z, found = 667.3056 m/z.

Compound SI-5

Procedure: A 250 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **30** (9.31 mmol, 6.00 g, 1.0 equiv) and Cs_2CO_3 (18.62 mmol, 6.07 g, 2.0 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of DMSO (20 mL) and allyl bromide (13.97 mmol, 1.21 mL, 1.5 equiv). The resulting mixture was stirred at rt for 12 h. MeOH (100 mL) was then added, and the mixture was cooled to 0 °C. NaOH (1 M in H_2O , 30 mL) and 30% H_2O_2 (13.97 mmol, 1.43 mL, 1.5 equiv) was then added, and the resulting mixture was stirred for 2 h, quenched by the addition of $NaHCO_3$ (saturated, 20 mL) and $Na_2S_2O_3$ (saturated, 20 mL), and concentrated *in vacuo*. It was then extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with H_2O (100 mL), brine (100 mL) and dried over $MgSO_4$. It was then filtered and concentrated *in vacuo*. The crude product was purified on silica gel (3:1 hexanes/EtOAc) to provide **SI-5** (5.88 g, 8.89 mmol, 95%) as a pale-yellow foam.

Characterization:

R_f = (hexanes/EtOAc 3:1): 0.31; IR (neat) ν = 3321, 2942, 2893, 2866, 1618, 1600, 1496, 1460, 1428, 1373, 1329, 1289, 1250, 1229, 1193, 1161, 1146, 1131, 1104 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.30 (s, 1H), 5.99 (d, J = 1.3 Hz, 1H), 5.92 (d, J = 1.3 Hz, 1H), 5.70 (dddd, J = 16.8, 10.4, 6.2, 5.4 Hz, 1H), 5.28 (d, J = 5.3 Hz, 1H), 5.15 (d, J = 5.3 Hz, 1H), 5.07 (ddd, J = 17.3, 3.2, 1.6 Hz, 1H), 5.01 (dd, J = 10.4, 1.5 Hz, 1H), 4.74 (d, J = 5.0 Hz, 1H), 4.64 (s, 1H), 4.42 (ddt, J = 12.7, 5.2, 1.3 Hz, 1H), 4.29 (ddt, J = 12.7, 6.3, 1.2 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.46 (s, 3H), 2.07 (s, 1H), 1.75 (q, J = 7.0 Hz, 1H), 1.61 (d, J = 5.6 Hz, 1H), 1.38 (s, 3H), 1.32 (d, J = 7.1 Hz, 3H), 0.89 – 0.82 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 148.85, 148.83, 141.2, 138.2, 138.1, 136.3, 135.5, 135.1, 121.8, 118.9, 117.1, 109.3, 102.0, 101.2, 97.0, 83.4, 78.2, 76.0, 73.7, 61.1, 57.1, 56.0, 47.9, 25.6, 18.3, 18.1, 17.7, 12.6; $[\alpha]^{23}_D$ -78.4°, (c = 1.0, $CHCl_3$); HRMS: Calcd. for $C_{35}H_{52}O_{10}Si$ $[M+Na]^+$ = 683.3222 m/z, found = 683.3218 m/z.

Compound SI-6

Procedure: A 250 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-5** (9.0 mmol, 5.93 g, 1.0 equiv) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 1.8 mmol, 219.9 mg, 20 mol%).

The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of CH₂Cl₂ (45 mL). Pyridine (90 mmol, 7.25 mL, 10 equiv) and Ac₂O (90 mmol, 8.51 mL, 10 equiv) was then added via syringe, and the resulting mixture was stirred at rt for 18 h. It was then cooled to 0 °C in an ice bath, and quenched by the addition of MeOH (90 mmol, 3.64 mL, 10 equiv) dropwise. The mixture was warmed to rt and stirred for another 30 min, poured on HCl (1M, 150 mL), and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic fractions were washed with NaHCO₃ (saturated, 100 mL) and brine (100 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was then evacuated and refill with N₂ (repeat 3 times), prior to the addition of THF (18 mL). A solution of TBAF·3 H₂O (27 mmol, 8.52 g, 3.0 equiv) and HOAc (10.8 mmol, 617.7 µL, 1.2 equiv) in THF (27 mL) was then added, and the resulting mixture was stirred at rt for 24 h. It was then poured on NaHCO₃ (saturated, 50 mL) and brine (50 mL), and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (1:2 hexanes/EtOAc) to provide **SI-6** (3.58 g, 6.55 mmol, 73%) as a pale-yellow foam.

Characterization:

R_f = (hexanes/EtOAc 1:2): 0.28; IR (neat) ν = 3568, 3456, 2937, 1742, 1623, 1596, 1497, 1478, 1459, 1428, 1414, 1371, 1325, 1225, 1192, 1148, 1107 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.07 (s, 1H), 6.48 (s, 1H), 6.00 (d, *J* = 1.3 Hz, 1H), 5.98 (d, *J* = 1.3 Hz, 1H), 5.89 – 5.77 (m, 1H), 5.62 (s, 1H), 5.16 (d, *J* = 6.2 Hz, 1H), 5.10 (ddd, *J* = 17.2, 3.2, 1.5 Hz, 1H), 5.03 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.82 (d, *J* = 6.2 Hz, 1H), 4.56 (s, 1H), 4.45 (ddt, *J* = 12.1, 5.2, 1.4 Hz, 1H), 4.25 (ddt, *J* = 12.2, 5.5, 1.3 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.08 (s, 3H), 1.99 (br s, 1H), 1.91 (q, *J* = 7.0 Hz, 1H), 1.62 (s, 1H), 1.55 (s, 3H), 1.36 (s, 3H), 1.19 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.1, 153.0, 149.8, 149.0, 140.8, 137.9, 137.5, 135.4, 134.7, 134.1, 122.6, 120.8, 116.4, 106.7, 103.5, 101.7, 97.5, 82.1, 76.5, 75.1, 73.9, 60.8, 56.8, 56.3, 47.2, 24.5, 20.5, 16.8; [α]_D²³ -54.9° (c = 1.1, CHCl₃); HRMS: Calcd. for C₂₈H₃₄O₁₁ [M+Na]⁺ = 569.1993 m/z, found = 569.1996 m/z.

Compound 31

Procedure: A 250 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-6** (6.40 mmol, 3.50 g, 1.0 equiv) and iodoxybenzoic acid (IBX, 7.68 mmol, 2.15 g, 1.2 equiv). The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of DMSO (32 mL). The resulting mixture was stirred at rt for 3 h. It was then cooled to 0 °C in an ice bath, at which point MeOH (32 mL) was added. NaBH₄ (19.2 mmol, 726.3 mg, 3.0 equiv) was then added as solid in one portion. The mixture was stirred at 0 °C for another 15 min, and quenched by the addition of NH₄Cl (saturated, 100 mL). It was then concentrated *in vacuo*, and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with NaHCO₃ (saturated, 100 mL), water (100 mL) and brine (50 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (1:1 hexanes/EtOAc) to provide **31** (2.84 g, 5.20 mmol, 81%) as a white solid.

Characterization:

R_f = (hexanes/EtOAc 1:1): 0.32; IR (neat) ν = 3568, 3442, 2979, 2940, 1743, 1626, 1598, 1505, 1480, 1455, 1432, 1416, 1369, 1331, 1253, 1226, 1196, 1146, 1111 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.69 (s, 1H), 6.52 (s, 1H), 5.96 (br s, 2H), 5.85

– 5.71 (m, 1H), 5.65 (s, 1H), 5.09 – 5.03 (m, 1H), 5.04 (d, $J = 6.9$ Hz, 1H), 5.00 (dd, $J = 10.4, 1.4$ Hz, 1H), 4.75 (s, 1H), 4.74 (d, $J = 7.0$ Hz, 1H), 4.41 (dd, $J = 12.1, 5.3$ Hz, 1H), 4.13 (dd, $J = 12.1, 5.6$ Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.08 (s, 1H), 2.83 (s, 3H), 2.09 (q, $J = 7.2$ Hz, 1H), 1.99 (s, 1H), 1.54 (s, 3H), 1.41 (s, 3H), 1.23 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.8, 152.0, 151.1, 148.8, 141.2, 138.4, 138.0, 134.4, 134.3, 132.9, 123.0, 122.3, 116.6, 110.4, 104.5, 101.9, 98.6, 85.9, 83.5, 75.2, 73.9, 60.9, 56.5, 56.3, 42.0, 29.1, 20.6, 17.3; $[\alpha]^{23}_{\text{D}} -102.5^\circ$, ($c = 1.0$, CHCl_3); **HRMS**: Calcd. for $\text{C}_{28}\text{H}_{34}\text{O}_{11}$ $[\text{M}+\text{Na}]^+ = 569.1993$ m/z, found = 569.1994 m/z.

Compound SI-7

Procedure: A 100 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **31** (5.20 mmol, 2.84 g, 1.0 equiv) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 5.20 mmol, 635.3 mg, 1.0 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of pyridine (25 mL). DIPEA (10.4 mmol, 1.81 mL, 2.0 equiv) and BzCl (31.2 mmol, 3.62 mL, 6.0 equiv) was then added via syringe, and the resulting mixture was stirred in a pre-heated oil bath at 60 °C for 18 h. It was then cooled to rt and quenched by the addition of MeOH (2 mL) dropwise and stirred for another 30 min at rt. The mixture was then diluted with EtOAc (200 mL), washed with HCl (2M, 200 mL), and the aqueous phase was then extracted with EtOAc (2 $\times$ 200 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified on silica gel (2:1 hexanes/EtOAc) to provide **SI-7** (3.02 g, 4.64 mmol, 89%) as an off-white solid.

Characterization:

R_f = (hexanes/EtOAc 2:1): 0.29; **IR** (neat) $\nu = 3552, 2985, 2939, 2909, 1718, 1626, 1596, 1500, 1478, 1451, 1431, 1371, 1324, 1269, 1249, 1231, 1189, 1157, 1109$ cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.48 (t, $J = 7.4$ Hz, 1H), 7.40 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.29 (t, $J = 7.8$ Hz, 2H), 6.86 (s, 1H), 6.60 (s, 1H), 6.02 (s, 1H), 5.83 (d, $J = 1.5$ Hz, 1H), 5.80 (s, 1H), 5.79 – 5.70 (m, 1H), 5.73 (d, $J = 1.5$ Hz, 1H), 5.03 (ddd, $J = 17.2, 3.4, 1.7$ Hz, 1H), 4.98 (ddd, $J = 10.5, 3.1, 1.4$ Hz, 1H), 4.52 (d, $J = 5.8$ Hz, 1H), 4.38 (ddt, $J = 12.3, 5.1, 1.5$ Hz, 1H), 4.30 (d, $J = 5.8$ Hz, 1H), 4.20 (ddt, $J = 12.3, 5.4, 1.5$ Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 2.86 (s, 3H), 2.29 (q, $J = 7.3$ Hz, 1H), 2.14 (s, 1H), 1.60 (s, 3H), 1.36 (s, 3H), 1.30 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.8, 164.8, 152.0, 151.0, 148.7, 141.4, 138.1, 136.4, 134.6, 132.9, 132.8, 130.1, 129.7, 129.5, 127.9, 122.6, 121.9, 116.1, 110.6, 102.8, 101.2, 96.5, 84.5, 83.4, 74.3, 73.8, 60.8, 56.22, 56.16, 43.2, 28.8, 20.7, 17.2; $[\alpha]^{23}_{\text{D}} -137.6^\circ$, ($c = 1.0$, CHCl_3); **HRMS**: Calcd. for $\text{C}_{35}\text{H}_{38}\text{O}_{12}$ $[\text{M}+\text{Na}]^+ = 673.2256$ m/z, found = 673.2256 m/z.

Allyl bromoacetate (**32**)

Procedure: A 500 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with allyl alcohol (100 mmol, 6.80 mL, 1.0 equiv), pyridine (120 mmol, 9.67 mL, 1.2 equiv) and dissolved in CH₂Cl₂ (250 mL). It was cooled to 0 °C in an ice bath, at which point bromoacetyl bromide (100 mmol, 8.71 mL, 1.0 equiv) was added dropwise via syringe. The resulting mixture was stirred at 0 °C for 1 h, and quenched by the addition of HCl (1M, 200 mL). The mixture was then extracted with CH₂Cl₂ (3 × 200 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (20:1 hexanes/EtOAc) to provide **32** (16.09 g, 89.9 mmol, 90%) as a colorless oil.

Characterization:

¹H NMR (500 MHz, CDCl₃) δ 5.89 (ddt, *J* = 17.1, 10.5, 5.8 Hz, 1H), 5.34 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.25 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.63 (dt, *J* = 5.8, 1.3 Hz, 2H), 3.83 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 166.9, 131.3, 119.1, 66.7, 25.8. Our characterization data matches the data reported previously.⁸

Compound SI-8

Procedure: The literature procedure was followed for the first step with slight modifications.⁹ A 100 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-7** (3.60 mmol, 2.34 g, 1.0 equiv) and NaHSO₄·SiO₂ (3.60 g). The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of CH₂Cl₂ (72 mL). The resulting mixture was stirred vigorously at rt for 6 h, filtered through celite, and concentrated *in vacuo*. To the crude product was added Cs₂CO₃ (7.20 mmol, 2.35 g, 2.0 equiv). The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of DMSO (10 mL). Allyl bromoacetate (**32**) (5.40 mmol, 673.6 μL, 1.5 equiv) was then added via syringe, and the resulting mixture was stirred at rt for 2 h. It was then diluted with H₂O (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with H₂O (100 mL) and brine (50 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (2:1 hexanes/EtOAc) to provide **SI-8** (1.81 g, 2.57 mmol, 71%) as an off-white solid. Single crystals for X-ray diffraction were crystallized by vapor diffusion from Hexanes and EtOAc.

Characterization:

R_f = (hexanes/EtOAc 2:1): 0.22; IR (neat) *v* = 3569, 3428, 2980, 2939, 1743, 1626, 1597, 1504, 1480, 1454, 1431, 1416, 1369, 1331, 1252, 1225, 1195, 1146, 1109 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.50 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 6.83 (s, 1H), 6.56 (s, 1H), 5.90 (s, 1H), 5.77 (s, 1H), 5.85 – 5.69 (m, 2H), 5.76 (d, *J* = 1.6 Hz, 1H), 5.60 (d, *J* = 1.5 Hz, 1H), 5.20 – 5.11 (m, 2H), 5.05 (ddd, *J* = 17.2, 3.4, 1.7 Hz, 1H), 4.98 (ddd, *J* = 10.5, 3.1, 1.4 Hz, 1H), 4.52 – 4.43 (m, 3H), 4.22 (ddt, *J* = 12.3, 5.5, 1.5 Hz, 1H), 4.06 (d, *J* = 16.1 Hz, 1H), 3.95 (s, 3H), 3.92 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 2.30 (q, *J* = 7.1 Hz, 1H), 2.13 (s, 1H), 1.59 (s, 3H), 1.38 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.9, 168.4, 164.6, 152.2, 151.0, 148.7, 141.3, 139.3, 135.6, 134.9, 133.1, 133.0, 131.9, 129.9, 129.6, 129.4, 128.0, 121.7, 120.8, 118.2, 116.0, 110.3, 102.7, 101.2, 85.2, 83.3, 74.1, 73.8, 68.2, 65.2, 60.7, 56.1, 43.3, 29.0, 20.6, 17.2; [α]_D²³ -125.8° (c = 1.0, CHCl₃); HRMS: Calcd. for C₃₈H₄₀O₁₃ [M+Na]⁺ = 727.2361 m/z, found = 727.2365 m/z.

Compound 33

Procedure: A 100 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-8** (1.80 mmol, 1.27 g, 1.0 equiv), Pd(dppf)Cl₂ (0.18 mmol, 131.7 mg, 10 mol%) and NaBH₄ (7.20 mmol, 272.4 mg, 4.0 equiv). The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of THF (18 mL) and H₂O (0.9 mmol, 16.2 μ L, 0.5 equiv). The resulting mixture was stirred at rt for 4 h. It was then poured on a mixture of HCl (1 M, 30 mL) and brine (30 mL), and extracted with EtOAc (3 $\times$ 50 mL). The combined organic layers were washed with H₂O (100 mL) and brine (50 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. To the crude product was added imidazole (21.6 mmol, 1.47 g, 12.0 equiv), DMF (18 mL), CH₂Cl₂ (18 mL) and TESCI (18.0 mmol, 3.02 mL, 10.0 equiv). The resulting solution was stirred at rt for 12 h. Citric acid (0.5 M aq., 9 mL) was then added and stirred for another 10 min. It was then diluted with EtOAc (50 mL) and acidified by the addition of HCl (1 M, 50 mL). The mixture was then extracted with EtOAc (3 $\times$ 50 mL). The combined organic layers were washed with H₂O (100 mL) and brine (50 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (2:1 hexanes/EtOAc to 10:1 EtOAc/MeOH) to provide **33** (1.06 g, 1.44 mmol, 80%) as an off-white foam.

Characterization:

R_f = (EtOAc): 0.17; IR (neat) ν = 3569, 2942, 2876, 1747, 1721, 1625, 1596, 1501, 1479, 1456, 1428, 1369, 1337, 1316, 1250, 1220, 1193, 1148, 1109 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.53 (t, J = 7.4 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.8 Hz, 2H), 6.76 (s, 1H), 6.58 (s, 1H), 5.83 (s, 1H), 5.79 (s, 1H), 5.74 (d, J = 1.2 Hz, 1H), 5.61 (d, J = 1.2 Hz, 1H), 4.28 (d, J = 16.1 Hz, 1H), 3.95 (s, 3H), 3.81 (s, 3H), 3.80 (d, J = 16.1 Hz, 1H), 2.26 (q, J = 7.3 Hz, 1H), 2.23 (br s, 1H), 1.61 (s, 3H), 1.39 (s, 3H), 1.30 (d, J = 7.2 Hz, 3H), 0.71 (t, J = 7.9 Hz, 9H), 0.54 (dq, J = 15.6, 7.8 Hz, 3H), 0.43 (dq, J = 16.1, 8.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.1, 168.6, 164.7, 152.0, 148.8, 146.1, 138.7, 137.5, 134.8, 133.4, 130.3, 129.3, 129.2, 128.2, 120.6, 119.5, 108.6, 103.2, 101.5, 85.7, 82.9, 74.0, 67.6, 60.5, 56.1, 43.6, 29.0, 20.8, 17.2, 6.6, 5.4; [α]_D²³ -80.1°, (c = 1.1, CHCl₃); HRMS: Calcd. for C₃₈H₄₆O₁₃Si [M+Na]⁺ = 761.2600 m/z, found = 761.2601 m/z.

Compound SI-9

Procedure: A 50 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **31** (0.80 mmol, 437.3 mg, 1.0 equiv), Pd(dppf)Cl₂ (0.016 mmol, 11.7 mg, 2 mol%) and NaBH₄ (2.40 mmol, 90.8 mg, 3.0 equiv). The vial was evacuated and refill with N₂ (repeat 3 times), prior to the addition of THF (8 mL) and H₂O (0.40 mmol, 7.2 µL, 0.5 equiv). The resulting mixture was stirred at rt for 1 h. It was then poured on saturated NH₄Cl (50 mL) extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. To the crude product was added Cs₂CO₃ (1.60 mmol, 521.3 mg, 2.0 equiv). The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of DMSO (4 mL). Iodomethane (1.60 mmol, 99.6 µL, 2.0 equiv) was then added via syringe, and the resulting mixture was stirred at rt for 2 h. It was then diluted with H₂O (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with H₂O (100 mL) and brine (50 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (1:1 hexanes/EtOAc) to provide **SI-9** (400.0 mg, 0.768 mmol, 96%) as a white foam.

Characterization:

R_f = (hexanes/EtOAc 3:1): 0.34; IR (neat) ν = 3575, 3468, 2940, 2843, 1744, 1628, 1595, 1500, 1480, 1460, 1431, 1410, 1371, 1331, 1252, 1222, 1195, 1148, 1107 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.71 (s, 1H), 6.54 (s, 1H), 6.01 (d, *J* = 1.4 Hz, 1H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.63 (s, 1H), 5.07 (d, *J* = 6.9 Hz, 1H), 4.77 (d, *J* = 1.4 Hz, 1H), 4.75 (d, *J* = 6.9 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.65 (s, 3H), 3.05 (d, *J* = 1.9 Hz, 1H), 2.83 (s, 3H), 2.11 (q, *J* = 7.2 Hz, 1H), 2.03 (s, 1H), 1.56 (s, 3H), 1.43 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.0, 152.1, 151.7, 149.0, 141.2, 138.3, 138.1, 134.4, 133.1, 122.9, 122.2, 110.5, 104.5, 102.0, 98.8, 86.0, 83.8, 75.2, 60.9, 60.6, 56.6, 56.4, 42.0, 29.1, 20.6, 17.3; [α]_D²³ -115.6°, (c = 1.0, CHCl₃); HRMS: Calcd. for C₂₆H₃₂O₁₁ [M+Na]⁺ = 543.1837 m/z, found = 543.1820 m/z.

Compound SI-10

Procedure: The literature procedure was followed with slight modifications.¹⁰ A 50 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-9** (0.71 mmol, 370.3 mg, 1.0 equiv). The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of THF (10 mL). It was cooled to 0 °C in an ice bath, at which point angelic anhydride (**34**) (1.07 mmol, 191.0 µL, 1.5 equiv) was then added, followed by dropwise addition a solution of LiHMDS (0.85 mmol, 1M in THF, 853.0 µL, 1.2 equiv) by syringe. The resulting solution was then stirred for 1 h at 0 °C and quenched by the addition of NH₄Cl (saturated, 10 mL). The mixture was then extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (2:1 hexanes/EtOAc) to provide **SI-10** (335.8.0 mg, 0.557 mmol, 78%) as a white solid.

Characterization:

R_f = (hexanes/EtOAc 2:1): 0.29; IR (neat) ν = 3530, 2973, 2941, 1731, 1712, 1647, 1626, 1595, 1501, 1478, 1459, 1432, 1413, 1369, 1335, 1269, 1250, 1224, 1145, 1106 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.81 (s, 1H), 6.49 (s, 1H), 5.98 (qq, *J* = 7.2, 1.4 Hz, 1H), 5.94 (d, *J* = 1.4 Hz, 1H), 5.92 (d, *J* = 1.4 Hz, 1H), 5.84 (s, 1H), 5.71 (s, 1H), 4.88 (d, *J* = 5.7 Hz, 1H), 4.84 (d, *J* = 5.7 Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 3.63 (s, 3H), 3.06 (s, 3H), 2.13 (q, *J* = 7.3 Hz, 1H), 2.12 (s, 1H), 1.86 (dq, *J* = 7.3, 1.5

Hz, 3H), 1.59 (s, 3H), 1.33 (quint, $J = 1.5$ Hz, 3H), 1.31 (s, 3H), 1.26 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.9, 165.9, 152.0, 151.5, 148.7, 141.3, 140.3, 138.0, 136.9, 132.8, 130.3, 127.1, 122.3, 121.9, 110.7, 103.3, 101.4, 97.2, 84.1, 83.7, 74.2, 60.7, 60.6, 56.6, 56.2, 43.0, 28.8, 20.7, 19.7, 17.2, 15.8; $[\alpha]_D^{23}$ -16.8°, ($c = 1.0$, CHCl_3); HRMS: Calcd. for $\text{C}_{31}\text{H}_{38}\text{O}_{12}$ $[\text{M}+\text{K}]^+ = 641.1995$ m/z , found = 641.1985 m/z .

2-(Trimethylsilyl)ethyl bromoacetate (**35**)

Procedure: A 100 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with 2-(trimethylsilyl)ethanol (20 mmol, 2.87 mL, 1.0 equiv), pyridine (30 mmol, 2.42 mL, 1.5 equiv) and dissolved in CH_2Cl_2 (40 mL). It was cooled to 0 °C in an ice bath, at which point bromoacetyl bromide (20 mmol, 1.74 mL, 1.0 equiv) was added dropwise via syringe. The resulting mixture was stirred at 0 °C for 1 h, and quenched by the addition of HCl (1M, 50 mL). The mixture was then extracted with CH_2Cl_2 (3 $\times$ 50 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified on silica gel (20:1 hexanes/EtOAc) to provide **35** (4.72 g, 19.7 mmol, 99%) as a colorless oil.

Characterization:

^1H NMR (500 MHz, CDCl_3) δ 4.31 – 4.23 (m, 2H), 3.81 (s, 2H), 1.08 – 0.99 (m, 2H), 0.06 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.5, 64.9, 26.2, 17.4, -1.4. Our characterization data matches the data reported previously.¹¹

Compound 36

Procedure: The literature procedure was followed for the first step with slight modifications.⁹ A 25 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **SI-10** (0.20 mmol, 120.5 mg, 1.0 equiv) and $\text{NaHSO}_4 \cdot \text{SiO}_2$ (200 mg). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of CH_2Cl_2 (4 mL). The resulting mixture was stirred vigorously at rt for 3 h, filtered through celite, and concentrated *in vacuo*. To the crude product was added Cs_2CO_3 (0.40 mmol, 130.3 mg, 2.0 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of DMSO (2 mL). 2-(Trimethylsilyl)ethyl bromoacetate (**35**) (0.30 mmol, 59.0 μL , 1.5 equiv) was then added via syringe, and the resulting mixture was stirred at rt for 2 h. A solution of $\text{TBAF} \cdot 3 \text{H}_2\text{O}$ (0.60 mmol, 189.3 mg, 3.0 equiv) in THF (1 mL) was added, and the resulting solution was stirred for another 2 h. It was then diluted

with 1 M HCl (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with H₂O (50 mL) and brine (20 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (3:1 hexanes/EtOAc to 10:1 EtOAc/MeOH) to provide **36** (89.8 mg, 0.146 mmol, 73%) as a white solid.

Characterization:

R_f = (EtOAc/MeOH 10:1): 0.14; **IR** (neat) ν = 3590, 2943, 1744, 1716, 1624, 1596, 1502, 1479, 1459, 1432, 1412, 1369, 1335, 1223, 1197, 1147, 1104 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 10.50 (br s, 1H), 6.90 (s, 1H), 6.47 (s, 1H), 6.02 (qq, *J* = 7.1, 1.2 Hz, 1H), 5.93 (d, *J* = 1.2 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 5.64 (s, 1H), 5.62 (s, 1H), 5.08 (d, *J* = 16.4 Hz, 1H), 4.44 (d, *J* = 16.4 Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 3.55 (s, 3H), 2.22 (s, 1H), 2.12 (q, *J* = 7.2 Hz, 1H), 1.84 (dq, *J* = 7.2, 1.4 Hz, 3H), 1.57 (s, 3H), 1.39 (quint, *J* = 1.2 Hz, 3H), 1.37 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.6, 168.8, 165.6, 152.5, 149.4, 149.1, 141.5, 140.0, 137.1, 133.8, 133.8, 131.3, 126.9, 120.7, 118.5, 111.6, 102.8, 101.7, 84.7, 83.6, 73.8, 67.8, 61.1, 60.8, 56.2, 43.2, 28.9, 20.6, 19.9, 17.2, 15.8; **[α]_D²³** -24.8°, (*c* = 1.1, CHCl₃); **HRMS**: Calcd. for C₃₁H₃₆O₁₃ [M+Na]⁺ = 639.2048 m/z, found = 639.2039 m/z.

Compound 3 (heteroclitin J)

Procedure: A 100 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar and a rubber septum was charged with **33** (0.50 mmol, 369.4 mg, 1.0 equiv) and *N*-hydroxyphthalimide (NHPI, 0.55 mmol, 89.7 mg, 1.1 equiv). The flask was evacuated and refill with N₂ (repeat 3 times), prior to the addition of CH₂Cl₂ (5 mL), followed by *N,N'*-diisopropylcarbodiimide (DIC, 0.60 mmol, 94.0 μ L, 1.2 equiv) via microsyringe. The resulting mixture was stirred for 12 h at rt under N₂, and diluted by the addition of DMF (40 mL). A solution of Ru(bpy)₃(PF₆)₂ (0.005 mmol, 4.30 mg, 1.0 mol%) in DMF (5 mL) was added, followed by NEt₃ (1.0 mmol, 139.4 μ L, 2.0 equiv). The resulting solution was then irradiated with 25W blue LEDs at rt for 3 h with a cooling fan (See the picture below). It was then poured on a mixture of H₂O (100 mL) and H₃PO₄ (2 M, 5 mL), and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with H₂O (2 × 100 mL) and brine (50 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (4:1 to 1:1 hexanes/EtOAc) to provide **3** (255.7 mg, 0.44 mmol, 88%) as a yellow solid. Single crystals for X-ray diffraction were crystallized by slow evaporation from MeOH.

Characterization:

R_f = (hexanes/EtOAc 1:1): 0.32; **IR** (neat) ν = 3570, 3416, 2937, 1742, 1716, 1642, 1627, 1601, 1583, 1557, 1504, 1488, 1451, 1418, 1398, 1372, 1315, 1286, 1262, 1235, 1176, 1148, 1126, 1110 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 7.51 (tt, *J* = 7.1, 1.6 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 6.51 (d, *J* = 1.2 Hz, 1H), 6.50 (s, 1H), 5.93 (d, *J* = 1.4 Hz, 1H), 5.89 (d, *J* = 1.1 Hz, 1H), 5.88 (d, *J* = 1.5 Hz, 1H), 5.88 (s, 1H), 4.68 (d, *J* = 9.0 Hz, 1H), 4.06 (s, 3H), 4.05 (d, *J* = 9.0 Hz, 1H), 3.75 (s, 3H), 2.54 (s, 1H), 2.24 (q, *J* = 7.2 Hz, 1H), 1.86 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.25 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 196.1, 168.7, 165.1, 155.7, 150.2, 143.5, 141.8, 133.9, 131.9, 130.4, 129.8, 129.3, 128.3, 128.2, 123.1, 120.4, 102.0, 101.2, 82.4, 81.5, 78.9, 75.2, 63.3, 59.0, 58.9, 44.2, 28.5, 20.4, 17.8; **HPLC** (Chiralpak® IC analytical column, eluent

65:35 *i*PrOH:hexanes, 1 mL/min) t_R 17.6 min (major), 21.2 min (minor), > 99% *e.e.*; $[\alpha]^{23}_D$ -140.0°, (*c* = 0.50, MeOH) [lit.¹ $[\alpha]^{20}_D$ -60.5°, (*c* = 0.16, MeOH)]; **HRMS**: Calcd. for $C_{31}H_{30}O_{11}$ $[M+Na]^+$ = 601.1680 *m/z*, found = 601.1677 *m/z*.

Photoredox setup with blue LED light:

HPLC trace of the racemic mixture:

Signal 1: DAD1 A, Sig=328,2 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.557	BB	1.0132	1449.48254	20.29629	49.9270
2	21.245	BB	1.0583	1453.71899	18.42894	50.0730

HPLC trace of the chiral product:

Signal 1: DAD1 A, Sig=328,2 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.560	BB	1.0541	1567.51233	21.31283	100.0000

Compounds 5a (taiwankadsurin A) and 5b (taiwankadsurin B)

Procedure: A 50 mL flame-dried round bottom flask equipped with a Teflon-coated stir bar was charged with **3** (0.10 mmol, 57.9 mg, 1.0 equiv) and dissolved in CH_2Cl_2 (20 mL). A solution of Sudan red 7B (color indicator, 1 mg/mL in CH_2Cl_2 , 20 μ L) was added, the resulting red solution was cooled to $-78^\circ C$, and bubbled with N_2 for 5 min. The N_2 stream was then removed, and a stream of O_3/O_2 was then introduced to the head space of the flask until the faint of the red color in the solution (~ 5 s). The O_3/O_2 stream was then quickly replaced by the N_2 stream, and bubble for another 5 min. Me_2S (2 mL) was then added, and the resulting solution was capped by a rubber septum, warmed to rt and stirred for another 1 h under N_2 , and then concentrated *in vacuo*. The crude product was purified on silica gel (2:1 hexanes/EtOAc) to provide the major diastereomer (**5a**) (38.2 mg, 0.063 mmol, 63%) as an off-white solid and the minor diastereomer (**5b**) (4.1 mg, 0.007 mmol, 7%) as an off-white solid.

Characterization:

Major diastereomer, taiwankadsurin A: R_f = (hexanes/EtOAc 2:1): 0.29; IR (neat) ν = 3440, 2989, 2951, 1726, 1650, 1601, 1503, 1486, 1451, 1434, 1411, 1391, 1372, 1244, 1214, 1175, 1153 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 7.2 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 6.69 (d, J = 3.0 Hz, 1H), 6.60 (s, 1H), 6.49 (d, J = 2.7 Hz, 1H), 6.08 (d, J = 2.7 Hz, 1H), 6.02 (d, J = 1.4 Hz, 1H), 5.99 (d, J = 1.4 Hz, 1H), 5.00 (d, J = 10.2 Hz, 1H), 4.54 (d, J = 10.2 Hz, 1H), 3.96 (s, 3H), 3.57 (s, 3H), 3.51 (s, 1H), 2.37 (qd, J = 6.8, 3.3 Hz, 1H), 2.21 (s, 3H), 1.34 (s, 3H), 1.05 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 169.2, 165.7, 165.5, 150.5, 150.4, 144.3, 134.2, 130.7, 129.5, 129.0, 128.5, 127.9, 118.2, 117.4, 102.0,

99.1, 97.7, 80.6, 79.4, 73.4, 70.6, 57.1, 53.8, 51.9, 45.3, 28.4, 21.4, 8.9; $[\alpha]^{23}_D +35.0^\circ$, ($c = 1.0$, CH_2Cl_2) [lit.³ $[\alpha]^{26}_D +20^\circ$, ($c = 0.5$, CH_2Cl_2)]; **HRMS**: Calcd. for $\text{C}_{31}\text{H}_{30}\text{O}_{13}$ $[\text{M}+\text{K}]^+ = 649.1318$ m/z, found = 649.1287 m/z.

Minor diastereomer, taiwankadsurin B: R_f = (hexanes/EtOAc 2:1): 0.33; **IR** (neat) $\nu = 3440, 2920, 1725, 1652, 1502, 1485, 1451, 1434, 1412, 1390, 1371, 1249, 1211, 1171, 1138$ cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3) δ 8.32 (d, $J = 7.2$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 2H), 6.90 (d, $J = 2.7$ Hz, 1H), 6.79 (d, $J = 3.0$ Hz, 1H), 6.60 (s, 1H), 6.17 (d, $J = 2.7$ Hz, 1H), 5.96 (d, $J = 1.3$ Hz, 1H), 5.95 (d, $J = 1.4$ Hz, 1H), 4.98 (d, $J = 10.0$ Hz, 1H), 4.86 (s, 1H), 4.63 (d, $J = 10.0$ Hz, 1H), 3.61 (s, 3H), 3.56 (s, 3H), 2.39 (qd, $J = 6.8, 3.3$ Hz, 1H), 2.21 (s, 3H), 1.38 (s, 3H), 1.04 (d, $J = 6.8$ Hz, 3H); **^{13}C NMR** (126 MHz, CDCl_3) δ 170.3, 169.3, 165.8, 150.0, 149.7, 142.8, 134.0, 130.7, 129.2, 128.9, 128.8, 127.9, 120.8, 118.6, 101.8, 99.5, 97.9, 78.71, 78.69, 73.5, 70.5, 58.9, 54.3, 51.9, 45.5, 28.8, 21.4, 8.6; $[\alpha]^{23}_D +41.3^\circ$, ($c = 0.4$, CH_2Cl_2) [lit.³ $[\alpha]^{26}_D +62^\circ$, ($c = 0.4$, CH_2Cl_2)]; **HRMS**: Calcd. for $\text{C}_{31}\text{H}_{30}\text{O}_{13}$ $[\text{M}+\text{K}]^+ = 649.1318$ m/z, found = 649.1315 m/z.

Compound 38

Procedure: A one-dram vial equipped with a Teflon-coated stir bar and a screw cap with septum was charged with **36** (0.020 mmol, 12.3 mg, 1.0 equiv) and *N*-hydroxyphthalimide (NHPI, 0.022 mmol, 3.6 mg, 1.1 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of CH_2Cl_2 (0.2 mL), followed by *N,N'*-diisopropylcarbodiimide (DIC, 0.024 mmol, 3.8 μL , 1.2 equiv) via microsyringe. The resulting mixture was stirred for 12 h at rt under N_2 . A solution of $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (0.0002 mmol, 0.2 mg, 1.0 mol%) and DIPEA (0.040 mmol, 7.0 μL , 2.0 equiv) in DMF (1.8 mL) was then added. The resulting solution was then irradiated with 25W blue LEDs at rt for 30 min with a cooling fan (See the picture above for the preparation of **3**). It was then poured on a mixture of H_2O (20 mL) and H_3PO_4 (2 M, 1 mL), and extracted with EtOAc (3×20 mL). The combined organic layers were washed with H_2O (2×20 mL) and brine (20 mL), dried over MgSO_4 , filtered and concentrated *in vacuo*. The mixture was then analyzed by ^1H -NMR with ethylene carbonate as the internal standard, showing 30% yield of **38** (5:1 *d.r.* mixture) and 27% yield of **39**. Analytically pure **38** was prepared using a different method, which will be described in a follow-up manuscript.

Characterization:

R_f = (hexanes/EtOAc 2:1): 0.30; **IR** (neat) $\nu = 3573, 2940, 1732, 1626, 1595, 1500, 1478, 1456, 1430, 1409, 1367, 1332, 1251, 1223, 1195, 1147, 1106$ cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3) *major diastereomer* δ 6.82 (s, 1H), 6.49 (s, 1H), 6.04 (d, $J = 1.1$ Hz, 1H), 5.93 (d, $J = 1.1$ Hz, 1H), 5.85 (s, 1H), 5.53 (s, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.79 (dd, $J = 12.4, 4.0$ Hz, 1H), 3.53 (s, 3H), 3.50 (dd, $J = 12.5, 6.5$ Hz, 1H), 2.45 (s, 1H), 2.35 (qd, $J = 7.1, 4.7$ Hz, 1H), 2.19 – 2.11 (m, 1H), 1.98 (q, $J = 7.1$ Hz, 1H), 1.50 (s, 3H), 1.32 (s, 3H), 1.28 (d, $J = 7.2$ Hz, 3H), 0.98 (d, $J = 7.1$ Hz, 3H), 0.90 (d, $J = 7.3$ Hz, 3H); **^{13}C NMR** (126 MHz, CDCl_3) *major diastereomer* δ 174.9, 168.8, 152.3, 151.6, 148.2, 141.8, 139.1, 138.6, 132.9, 131.7, 122.15, 122.07, 111.0, 103.0, 101.6, 85.2, 84.1, 73.8, 73.2, 60.75, 60.70, 56.3, 43.9, 40.8, 36.1, 28.4, 20.5, 17.8, 14.6, 12.7; $[\alpha]^{23}_D -3.9^\circ$, ($c = 0.4$, CHCl_3); **HRMS**: Calcd. for $\text{C}_{30}\text{H}_{36}\text{O}_{11}$ $[\text{M}+\text{Na}]^+ = 595.2150$ m/z, found = 595.2138 m/z.

Crude ^1H -NMR of the reaction:

Compound 39

Procedure: A 20 mL flame-dried test tube equipped with a Teflon-coated stir bar and a rubber septum was charged with **36** (0.10 mmol, 61.7 mg, 1.0 equiv) and *N*-hydroxyphthalimide (NHPI, 0.11 mmol, 17.9 mg, 1.1 equiv). The flask was evacuated and refill with N_2 (repeat 3 times), prior to the addition of CH_2Cl_2 (1.0 mL), followed by *N,N'*-diisopropylcarbodiimide (DIC, 0.12 mmol, 18.8 μ L, 1.2 equiv) via microsyringe. The resulting mixture was stirred for 12 h at rt under N_2 . K_2CO_3 (0.12 mmol, 16.6 mg, 1.2 equiv) was then added, the mixture was then purged with N_2 for 5 min, and diluted by the addition of DMA (*N,N*-dimethylaminoacetamide, 8 mL). A solution of $Pd(PPh_3)_2Cl_2$ (0.010 mmol, 7.0 mg, 10 mol%), Xantphos (0.012 mmol, 6.9 mg, 12 mol%) and H_2O (0.10 mmol, 1.8 μ L, 1.0 equiv) in DMA (1 mL) was added. The resulting solution was then irradiated with 25W blue LEDs at rt for 8 h with a cooling fan (See the picture above for the preparation of **3**). It was then poured on a mixture of H_2O (50 mL) and H_3PO_4 (2 M, 1 mL), and extracted with EtOAc (3 $\times$ 50 mL). The combined organic layers were washed with H_2O (2 $\times$ 50 mL) and brine (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (5:1 to 2:1 hexanes/EtOAc) to provide the **39** (30.2 mg, 0.0527 mmol, 53%) as an off-white foam. Starting material **36** (14.8 mg, 0.0240 mmol, 24%) was also recovered.

Characterization:

R_f = (hexanes/EtOAc 2:1): 0.30; IR (neat) ν = 3567, 2942, 1746, 1723, 1677, 1628, 1593, 1500, 1479, 1458, 1430, 1408, 1367, 1331, 1294, 1221, 1196, 1151, 1105 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 6.81 (s, 1H), 6.51 (s, 1H), 6.06 (s, 1H), 6.03 (d, J = 1.2 Hz, 1H), 5.94 (d, J = 1.2 Hz, 1H), 5.85 (s, 1H), 5.54 (s, 1H), 5.32 (s, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.59 (dd, J = 11.7, 4.3 Hz, 1H), 3.56 (s, 3H), 3.54 (dd, J = 11.7, 6.3 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.50 (s, 1H), 2.00 (q, J = 7.2 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 3H), 1.29 (d, J = 7.2 Hz, 3H), 1.18 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 168.0, 152.3, 151.8, 148.2, 143.3, 142.0, 140.5, 138.2, 133.2, 131.1, 123.0, 122.33, 122.26, 111.3, 103.9, 101.7, 85.9, 84.2, 74.8, 74.0, 60.8, 60.7, 56.3, 43.7, 35.7, 28.2, 20.5, 17.8, 16.3; $[\alpha]^{23}_D$ +3.7 $^\circ$, (c = 1.0, $CHCl_3$); HRMS: Calcd. for $C_{30}H_{34}O_{11}$ $[M+Na]^+$ = 593.1993 m/z , found = 593.2006 m/z .

Compounds 4 (kadsuphilin N) and SI-11

Procedure: A 20 mL flame-dried Radley tube equipped with a Teflon-coated stir bar and a sealed cap was charged with **39** (0.091 mmol, 51.9 mg, 1.0 equiv) and Mn(dpm)₃ (0.0045 mmol, 2.8 mg, 5 mol%), and dissolved in ⁱPrOH (1 mL) and 1,2-DCE (1 mL). The mixture was cooled to 0 °C, at which point PhSiH₃ (0.455 mmol, 56.1 μL, 5.0 equiv) was added via micro-syringe. The resulting mixture was connected to a tank of O₂ and pressurized to 1 atm. Under a constant pressure of O₂ (1 atm), the reaction was vented 3 times for 10 s to remove N₂, and stirred for 4 h at 0 °C under O₂ (1 atm). It was then depressurized, and PPh₃ (0.137 mmol, 35.9 mg, 1.5 equiv) was added as solid, and the resulting mixture was stirred at rt for another 30 min. It was then poured on Na₂S₂O₃ (20 mL) and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified on silica gel (2:1 to 1:1 hexanes/EtOAc) to provide a 5:1 *d.r.* mixture of the product, which was further separated by preparatory TLC using 2% MeOH/CHCl₃ as the eluent to afford **4** (35.0 mg, 0.0595 mmol, 65%) as an off-white foam, and **SI-11** (7.0 mg, 0.0119 mmol, 13%) as a pale-yellow oil.

Characterization:

Major diastereomer, kadsuphilin N: *R_f* = (hexanes/EtOAc 1:1): 0.32; IR (neat) ν = 3565, 3490, 2942, 1734, 1624, 1595, 1500, 1477, 1457, 1431, 1410, 1367, 1334, 1249, 1221, 1196, 1149, 1104 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.84 (s, 1H), 6.48 (s, 1H), 6.03 (d, *J* = 1.1 Hz, 1H), 5.94 (d, *J* = 1.0 Hz, 1H), 5.76 (s, 1H), 5.48 (s, 1H), 4.17 (dd, *J* = 12.4, 4.3 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.63 (dd, *J* = 12.4, 4.5 Hz, 1H), 3.46 (s, 3H), 2.59 (s, 1H), 1.97 (q, *J* = 7.2 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.80 (s, 1H), 1.49 (s, 3H), 1.34 (s, 3H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.24 (s, 3H), 0.97 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 172.5, 168.8, 152.4, 151.6, 148.7, 141.9, 139.1, 137.6, 132.9, 130.9, 121.8, 121.3, 111.0, 102.6, 101.7, 86.7, 84.0, 76.8, 73.9, 72.5, 60.8, 60.6, 56.3, 44.2, 42.6, 28.5, 21.5, 20.4, 18.0, 12.9; [α]²³_D +24.9° (c = 1.0, CH₂Cl₂) [lit.² [α]²⁶_D -2.4°, (CH₂Cl₂)]; HRMS: Calcd. for C₃₀H₃₆O₁₂ [M+Na]⁺ = 611.2099 m/z, found = 611.2102 m/z.

Minor diastereomer: *R_f* = (hexanes/EtOAc 1:1): 0.33; IR (neat) ν = 3563, 3507, 2919, 1732, 1622, 1596, 1501, 1471, 1457, 1432, 1411, 1369, 1335, 1223, 1177, 1148, 1105 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.85 (s, 1H), 6.47 (s, 1H), 6.04 (d, *J* = 1.3 Hz, 1H), 5.93 (d, *J* = 1.3 Hz, 1H), 5.71 (s, 1H), 5.46 (s, 1H), 4.03 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.73 (dd, *J* = 12.2, 6.0 Hz, 1H), 3.46 (s, 3H), 3.22 (s, 1H), 2.62 (s, 1H), 1.90 (q, *J* = 7.2 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.50 (s, 3H), 1.32 (s, 3H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.25 (s, 3H), 1.02 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 177.7, 168.8, 152.5, 151.6, 148.6, 142.0, 138.6, 137.7, 133.1, 130.5, 121.9, 121.4, 110.8, 102.2, 101.6, 88.4, 83.9, 74.4, 74.0, 72.6, 60.8, 60.6, 56.3, 44.5, 37.7, 28.6, 25.2, 20.4, 18.1, 11.5; [α]²³_D -5.5° (c = 0.6, CHCl₃); HRMS: Calcd. for C₃₀H₃₆O₁₂ [M+Na]⁺ = 611.2099 m/z, found = 611.2112 m/z.

4. X-ray Crystallographic Data

General Experimental

A suitable crystal was selected and mounted on a Cryoloop on a Bruker Venture Metaljet diffractometer. The crystal was kept at 150 K during data collection. Using Olex2,¹² the structure was solved with the XT¹³ structure solution program using Intrinsic Phasing and refined with the XL¹⁴ refinement package using Least Squares minimization.

Figure S1. ORTEP representations of **Compounds 29** (top left), **SI-8** (top right), **3** (bottom).

Table S5. Crystal data and structure refinement for **compounds 29, SI-8 and 3.**

Identification code	Compound 29	Compound SI-8	Compound 3
Empirical formula	C ₃₃ H ₅₀ BBrO ₁₀ Si	C ₃₈ H ₄₀ O ₁₃	C ₃₁ H ₃₀ O ₁₁
Formula weight	725.54	704.70	578.55
Temperature/K	150	150	150
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁
a/Å	13.7600(4)	9.4729(3)	11.9339(7)
b/Å	13.7821(4)	18.1648(6)	8.9903(5)
c/Å	19.4436(5)	20.2360(7)	12.6917(7)
α/°	90	90	90
β/°	90	90	93.929(2)
γ/°	90	90	90
Volume/Å ³	3687.32(18)	3482.1(2)	1358.48(13)
Z	4	4	2
ρ _{calc} /g/cm ³	1.307	1.344	1.414
μ/mm ⁻¹	1.493	0.541	0.576
F(000)	1528.0	1488.0	608.0
Crystal size/mm ³	0.25 × 0.06 × 0.05	0.4 × 0.32 × 0.27	0.24 × 0.24 × 0.19
Radiation	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)
2θ range for data collection/°	6.846 to 121.408	5.688 to 110.178	6.072 to 121.416
Index ranges	-17 ≤ h ≤ 17 -17 ≤ k ≤ 17 -24 ≤ l ≤ 25	-10 ≤ h ≤ 10 -22 ≤ k ≤ 22 -24 ≤ l ≤ 24	-15 ≤ h ≤ 15 -11 ≤ k ≤ 11 -16 ≤ l ≤ 16
Reflections collected	48391	29780	37181
Independent reflections	8458 [R _{int} = 0.0310, R _{sigma} = 0.0195]	6514 [R _{int} = 0.0349, R _{sigma} = 0.0221]	6241 [R _{int} = 0.0257, R _{sigma} = 0.0174]
Data/restraints/parameters	8458/3/436	6514/0/478	6241/1/386
Goodness-of-fit on F ²	1.080	1.099	1.150
Final R indexes [I>=2σ (I)]	R ₁ = 0.0263 wR ₂ = 0.0682	R ₁ = 0.0353 wR ₂ = 0.0861	R ₁ = 0.0398 wR ₂ = 0.0933
Final R indexes [all data]	R ₁ = 0.0273 wR ₂ = 0.0691	R ₁ = 0.0358 wR ₂ = 0.0867	R ₁ = 0.0399 wR ₂ = 0.0934
Largest diff. peak/ hole / e Å ⁻³	0.49/-0.23	0.32/-0.25	0.28/-0.43
Flack parameter	-0.037(4)	-0.04(4)	-0.02(5)

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Mimicking Noncanonical Oxidations with Redox-Neutral Photocatalysis

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Analytical Data

¹H-NMR of **compound 3** (heteroclitin J)

¹³C-NMR of **compound 3** (heteroclitin J)

^1H , ^1H -COSY of **compound 3** (heteroclitin J)

^1H , ^1H -NOESY of **compound 3** (heteroclitin J)

^1H , ^{13}C -HSQC of **compound 3** (heteroclitin J)

^1H , ^{13}C -HMBC of **compound 3** (heteroclitin J)

¹H-NMR of **compound 4** (kadsuphilin N)

¹³C-NMR of **compound 4** (kadsuphilin N)

~172.47
~168.78
~152.41
~151.62
~148.72
~141.89
~139.13
~137.63
~132.94
~130.88
~121.75
~121.31
~111.04
~102.60
~101.66
86.70
83.97
77.41
77.16
76.91
76.83
73.94
72.55
60.80
60.61
56.28
44.24
42.64
28.51
21.54
20.41
17.98
12.93

kadsuphilin N
¹³C-NMR
126 MHz in CDCl₃

^1H , ^1H -COSY of **compound 4** (kadsuphilin N)

kadsuphilin N
 ^1H , ^1H -COSY

^1H , ^1H -NOESY of **compound 4** (kadsuphilin N)

^1H , ^{13}C -HSQC of **compound 4** (kadsuphilin N)

kadsuphilin N
 ^1H , ^{13}C -HSQC

^1H , ^{13}C -HMBC of **compound 4** (kadsuphilin N)

¹H-NMR of **compound 5a** (taiwankadsurin A)

¹³C-NMR of **compound 5a** (taiwankadsurin A)

^1H , ^1H -COSY of **compound 5a** (taiwankadsurin A)

^1H , ^1H -NOESY of **compound 5a** (taiwankadsurin A)

^1H , ^{13}C -HSQC of **compound 5a** (taiwankadsurin A)

^1H , ^{13}C -HMBC of **compound 5a** (taiwankadsurin A)

¹H-NMR of **compound 5b** (taiwankadsurin B)

¹³C-NMR of **compound 5b** (taiwankadsurin B)

^1H , ^1H -COSY of **compound 5b** (taiwankadsurin B)

^1H , ^1H -NOESY of **compound 5b** (taiwankadsurin B)

Taiwankadsurin B
 ^1H , ^1H -NOESY

^1H , ^{13}C -HSQC of **compound 5b** (taiwankadsurin B)

^1H , ^{13}C -HMBC of **compound 5b** (taiwankadsurin B)

¹H-NMR of **compound 22**

¹³C-NMR of **compound 22**

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of **compound SI-1**

¹³C-NMR of **compound SI-1**

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound SI-2

¹³C-NMR of compound SI-2

—154.23 —149.83 —141.06 —132.25 —119.52 —111.98 —103.11

77.41 77.16 76.91

~63.97 ~60.55 ~56.14

—25.78 18.43 17.93 17.92 12.11

—-4.56

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of **compound 24**

¹³C-NMR of **compound 24**

¹H-NMR of **compound 26**

¹³C-NMR of **compound 26**

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound 27

¹³C-NMR of **compound 27**

¹H-NMR of **compound 28**

¹³C-NMR of **compound 28**

~153.37
~148.90
~140.51
~137.71
~137.07
~135.92
~135.18

~114.98
~109.91
~106.18
~103.70
~101.81
~97.23

~80.54
~79.87
~77.41
~77.16
~76.91
~74.53

~60.60
~57.49
~56.16

~45.05

~25.81
~21.57
~18.46
~18.28
~18.09
~12.73
~12.30

~-4.58

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound *epi-28*

¹³C-NMR of compound *epi-28*

153.19
148.93
148.76
140.41
138.58
137.69
136.29
135.92

115.55
109.79
106.39
103.52
101.88
97.17

79.71
79.16
77.41
77.16
76.91
75.71

60.57
57.45
56.13

47.28

25.77
21.99
18.38
18.16
18.09
12.70
12.50

4.63
4.68

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of **compound SI-3**

¹³C-NMR of compound SI-3

~153.15
~149.08
~148.19
~140.04
~138.13
~136.44
~136.10
~135.21

~114.68
~110.46
~106.48
~102.97
~102.00
~97.22

~79.59
~77.41
~77.16
~76.91
~73.62

~60.59
~57.55
~55.89

~42.74

~25.81
~20.69
~18.46
~18.31
~18.20
~12.94
~12.07

~0.86
~4.58
~4.63

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound SI-4

¹³C-NMR of compound SI-4

153.08
152.74
151.97
148.46
141.56
137.06
135.18
135.13

124.66

108.56
104.54
101.40
99.54
96.56

87.92
81.88
77.62
77.41
77.16
76.91

61.20
56.96
56.01

41.10

22.40
18.24
18.16
13.21
12.77

1.05

¹H-NMR of compound 29

¹³C-NMR of compound 29

152.99
152.68
151.13
145.99
141.53
136.26
135.67
135.11

124.66

106.36
103.36
101.38
99.57
96.55

87.72
78.84
78.31
77.41
77.16
76.91

61.33
56.97
56.00

41.54

22.78
18.23
18.00
13.69
12.71

1.01

¹H-NMR of **compound 30**

¹³C-NMR of compound 30

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound SI-5

¹³C-NMR of compound SI-5

¹H-NMR of compound SI-6

¹³C-NMR of compound SI-6

¹H-NMR of compound 31

¹³C-NMR of **compound 31**

¹H-NMR of compound SI-7

¹³C-NMR of compound SI-7

¹H-NMR of **compound 32**

¹³C-NMR of **compound 32**

¹H-NMR of compound SI-8

¹³C-NMR of compound SI-8

168.87
168.39
164.61

152.17
151.02
148.69

135.61
134.94
133.11
132.99
131.91
129.86
129.57
129.41
128.03
118.21
115.95
109.75
102.72
101.23

85.20
83.33
77.41
77.16
76.91
74.11
73.79
68.24
65.18
60.74
56.13

43.25

28.95

20.61
17.20

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of **compound 33**

¹³C-NMR of compound 33

169.06
168.65
164.66
152.02
148.83
146.15
134.85
133.39
130.31
129.33
129.18
128.23
120.56
119.51

108.61
103.25
101.48

85.65
82.92
77.41
77.16
76.91
74.02
67.58

60.47
56.09

43.64

29.01

20.80
17.18

6.61
5.36

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound SI-9

¹³C-NMR of compound SI-9

¹H-NMR of compound SI-10

¹³C-NMR of compound SI-10

¹H-NMR of **compound 35**

¹³C-NMR of compound 35

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound 36

¹³C-NMR of compound 36

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound 38

¹³C-NMR of **compound 38**

¹H-NMR of compound 39

¹³C-NMR of compound 39

¹³C-NMR
126 MHz in CDCl₃

¹H-NMR of compound SI-11

¹³C-NMR of compound SI-11