# Meroterpenoid Synthesis via Sequential Polyketide Aromatization and Cationic Polyene Cyclization: Total Syntheses of (+)-Hongoquercin A and B and Related Meroterpenoids

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S *Supporting Information*
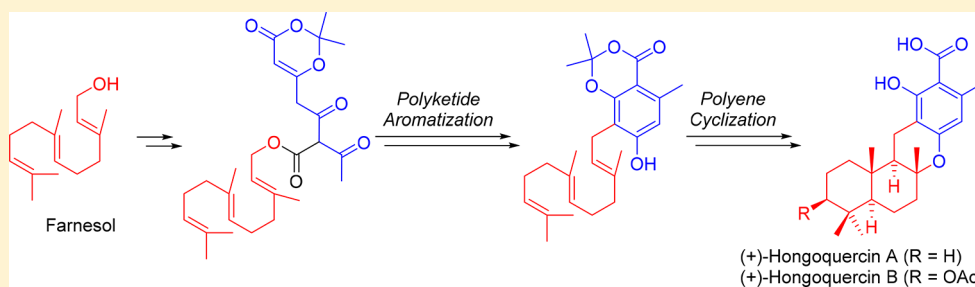
ABSTRACT: (+)-Hongoquercin A and B were synthesized from commercially available *trans,trans*-farnesol in six and eleven steps, respectively, using dual biomimetic strategies with polyketide aromatization and subsequent polyene functionalization from a common farnesyl-resorcylate intermediate. Key steps involve Pd(0)-catalyzed decarboxylative allylic rearrangement of a dioxinone β,δ-diketo ester to a β,δ-diketo dioxinone, which was readily aromatized into the corresponding resorcylate, and subsequent polyene cyclization via enantioselective protonation or regioselective terminal alkene oxidation and cationic cyclization of enantiomerically enriched epoxide to furnish the tetracyclic natural product cores. Analogues of the hongoquercin were synthesized via halonium-induced polyene cyclizations, and the meroterpenoid could be further functionalized via saponification, hydrolytic decarboxylation, reduction, and amidation reactions.

■ INTRODUCTION

(+)-Hongoquercin A (**1**) and B (**2**) were isolated from the fermentation broths produced by an unidentified fungus in 1998 independently by Roll and Abbanat (Figure 1).[1] They exhibited modest antibacterial activity against methicillin-resistant *Staphylococcus aureus* and vancomycin-resistant *Enterococcus faecium*.[1] These natural products are meroterpenoids which have a mixed biosynthetic origin involving polyketide and terpenoid pathways. (−)-Siccanin (**3**) and (−)-austalide K

(**4**) are additional examples of such structurally diverse bioactive meroterpenoids.[2]

Over the last two decades, several total syntheses of hongoquercins **5** have been reported.[3] The common synthetic strategy involves the coupling of two synthons, an enantiopure synthesized drimene **6** coupled with a substituted resorcinol derivative **7** (Scheme 1). However, this conventional approach often requires extensive use of protecting groups on the resorcinol unit **7** and multistep transformations for the synthesis of the precursor drimene **6**. Most of the reported processes for the preparation of the resorcinol rely on extensive derivatization of an aromatic precursor, while alternative synthetic strategies to prepare resorcinol, such as benzannulation, have been shown to be more concise and flexible.[4] Therefore, we considered that a dual biomimetic approach for elaborating the arene ring and tricyclic terpenoid residues from acyclic precursor **9** sequentially via cascade cyclizations would simplify the syntheses of these natural products. Additionally, if the farnesyl residue was functionalized after aromatization to
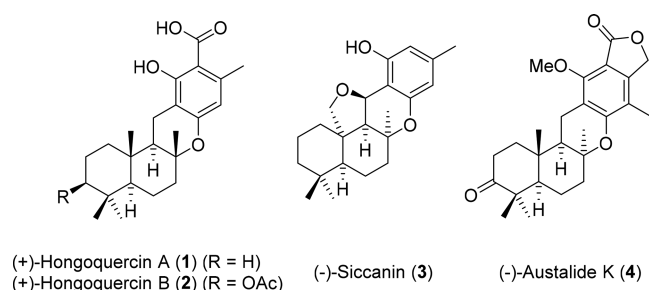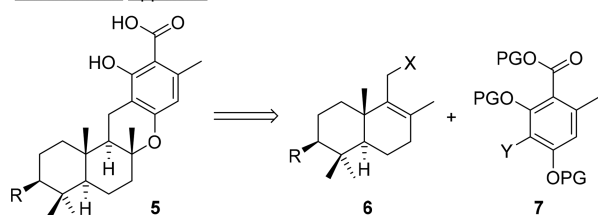

Figure 1. Bioactive meroterpenoid natural products.

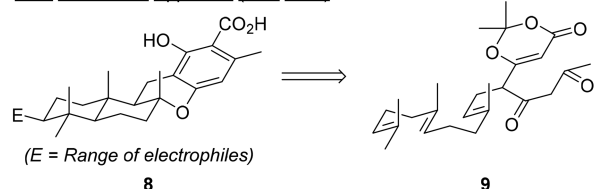**Scheme 1. Synthetic Strategies of the Hongoquercins 5**

construct the resorcylate entity, a diverse range of hongoquercin analogues **8** should be available by variation of the electrophilic reagents used in such derivatizations.

Inspired by the pioneering work of the Harris group and Hyatt group, respectively, on the biomimetic synthesis of β-resorylate and on the generation of acyl ketenes by the thermolysis of dioxinones,[5,6] our group has developed a biomimetic route to β-resorylate natural products that utilizes β,δ-diketo dioxinones as masked triketo ketenes.[7] In 2009, we additionally discovered a regioselective palladium(0)-catalyzed decarboxylative rearrangement during the synthesis of aigialomycin D.[8] Application of this reaction greatly facilitated the synthesis of meroterpenoid resorcylate natural products.[9] More recently, we developed an efficient methodology for the synthesis of dioxinone β-keto esters **12** using dioxane-4,6-dione keto dioxanones **10** as the masked dioxinone acylketene **11** (Scheme 2).[10] Application of this reaction provided an efficient

**Scheme 2. Thermolysis of Dioxane-4,6-dione Ketodioxanones 10**
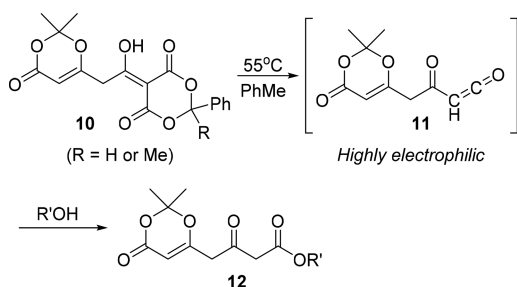
route for the synthesis of β-resorylates, and its utility has been showcased in the total syntheses of several bioactive meroterpenoid natural products.[10] Herein we report further extensive studies on the dual biomimetic total synthesis of the hongoquercins **5**, which we initially published as a communication.[9e]

■ RESULTS AND DISCUSSION

We considered that the key meroterpenoids **13** should be available using a polyene cyclization from resorcylate **14** by enantioselective electrophilic reactions with chiral Brønsted acids (E = H), epoxidation, and subsequent reaction with a

Lewis acid (E = OH) or halogenations with reagents that provide halonium ion intermediates (E = Br and I) (Scheme 3). The common resorcylate intermediate **14** should be

**Scheme 3. Retrosynthetic Analyses of Hongoquercins A (1) and B (2)**
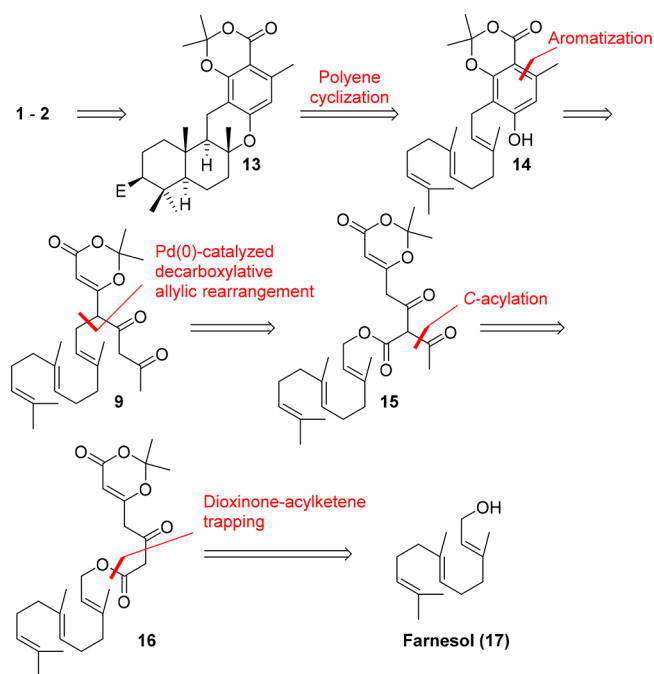
available from the cycloaromatization of β,δ-diketodioxinone **9**, which could be synthesized via palladium(0)-catalyzed decarboxylative allylic rearrangement of dioxinone β,δ-diketo ester **15**. Dioxinone β,δ-diketo ester **15**, in turn, should be available via C-acylation of dioxinone β-keto ester **16**, which, in turn, is available from trapping a dioxinone acylketene with *trans,trans*-farnesol (**17**).[10]

Following our recently published methods,[10] thermolysis of dioxane-4,6-dione keto dioxanone **19** at 55 °C generated the dioxinone acyl ketene **11**, which was trapped with *trans,trans*-farnesol (**17**) to provide dioxinone β-keto ester **21** (79%) (Scheme 4). Magnesium chloride mediated regioselective C-acylation of β-keto ester **21** with acetyl chloride gave dioxinone β,δ-diketo ester **23**, which on reaction with Pd₂(dba)₃ and tri(2-furyl)phosphine resulted in a highly regioselective decarboxylative allylic rearrangement giving the β,δ-diketo dioxinone **9** and readily aromatized in situ to produce farnesyl resorcylate **14** (55% overall from **21**). A geranyl-substituted analogue **24** was also synthesized, using the same reaction sequence, from geraniol (**18**) in three steps with an overall yield of 57%.

We first investigated the synthesis of (+)-hongoquercin A (**1**) via enantioselective protonation of farnesyl resorcylate **14** (Scheme 5) using the Lewis acid enhanced chiral Brønsted acids derived from antimony pentachloride with binol **25** and stannic chloride with binol **26** as introduced by Corey et al.[11] and Yamamoto et al.[12] Enantioselective protonation with SbCl₅·**25** gave a mixture of partially cyclized products from which the desired meroterpenoid **23** was isolated in 15% yield and with an enantiomeric excess of 20% as determined by chiral HPLC. Fortunately, the cyclization using SnCl₄·**26** as the dual Brønsted and Lewis acids was highly enantioselective and

Scheme 4. Synthesis of the Terpene Resorcylates 14 and 24
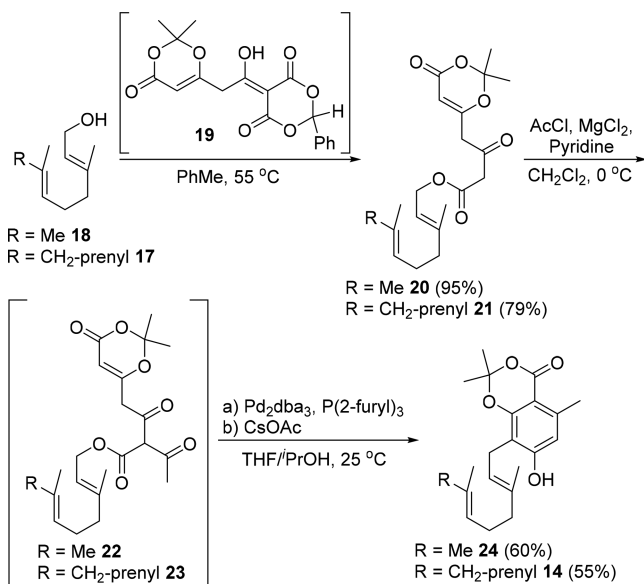
Scheme 5. Total Synthesis of (+)-Hongoquercin A (1)
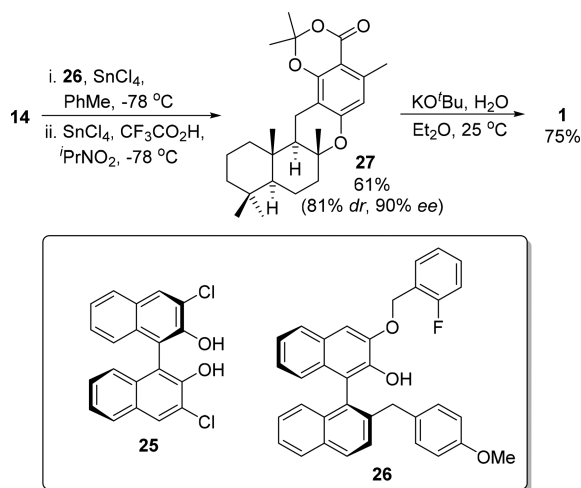
gave the desired meroterpenoid **27** (61%, 81% dr and 90% ee as determined by chiral HPLC) on sequential reaction with SnCl$_4$·**26** and SnCl$_4$ and trifluoroacetic acid. Finally, saponification[13] of meroterpenoid **27** gave (+)-hongoquercin A (**1**) (75%) with an overall yield of 20% over five5 steps from *trans,trans*-farnesol **17**. The spectroscopic data were in full agreement with that reported for the isolated natural product,[1] and the structure was unambiguously confirmed by single-crystal X-ray crystallography.

Next, we focused on the synthesis of (+)-hongoquercin B, which utilized enantioselective epoxidation (Scheme 6). While we had reported the synthesis of this natural product from the farnesyl derivative **33**,[9e] we wished to reinvestigate this synthesis with late-stage oxidation of the terminal alkene on the pendant farnesyl side chain since this should greatly facilitate the synthesis and bioassay of a focused library of novel hongoquercin analogues with the late-stage introduction of terpene structural diversity. In order to effect such electrophilic functionalization of the terminal alkene unit, we needed to suppress phenol-directed oxidation.[14] We found that protection by phenol allylation was suitable for this purpose.

Allylation of farnesyl resorcylate **14** gave allyl ether **28** (77%), which was subjected to dihydroxylation in the presence of the Corey dihydroquinidine ligand **29**, thus producing the (*R*)-diol **30** (58%, 78% brsm, 88% ee as determined by Mosher ester analysis).[15] Diol **30** was subsequently converted into the (*S*)-epoxide **31** (93%) via mesylation and potassium carbonate mediated cyclization. The allyl protecting group was selectively removed by reaction with dimethylbarbituric acid **32** catalyzed by Pd(PPh$_3$)$_4$ to provide epoxide **33** (91%).[16] After screening a variety of different Lewis acids with epoxide **33**, it was found that ferric chloride hydrate was a superior Lewis acid catalyst to boron trifluoride etherate,[9e] which we previously reported for this cyclization of epoxide **33** to provide meroterpenoid **34**. The use of boron trifluoride etherate often led to the formation of undesired byproducts such as bicyclic ethers and partially cyclized products. Such side reactions and irreproducibility were substantially suppressed using ferric chloride hydrate.[17] Thus, treatment of epoxide **33** with FeCl$_3$·6H$_2$O resulted in biomimetic cationic cyclization to give meroterpeonoid **34** (56%, 92% ee as determined by chiral HPLC) as a single diastereoisomer. Saponification of meroterpenoid **34** gave acid **35** (69%),[13] which was subjected to acetylation to provide diacetate **36**. Subsequent selective deacetylation of the phenolic acetate gave (+)-hongoquercin B (66%) with an overall yield of 3.7% over 11 steps. The analytical data for this synthetic material are in full agreement with that reported for the isolated natural product.[1]
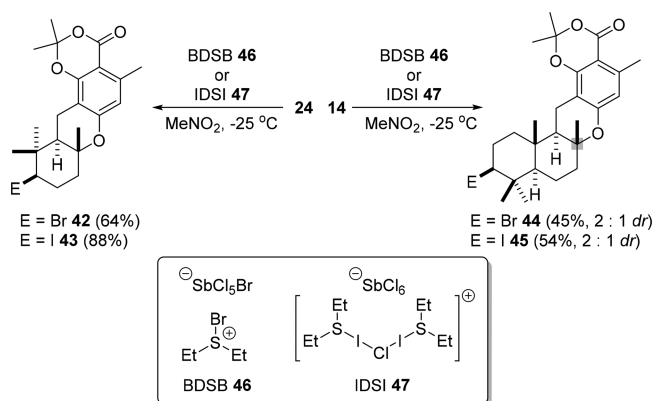
Additional meroterpenoids analogues were prepared via epoxidation (Scheme 7) and halogenations (Scheme 8). First, the geranyl-substituted resorcylate **24** was protected as its silyl ether **37** (76%) and epoxidized with the dioxirane derived from the Shi chiral ketone **38** to give epoxide **39** (69%).[18] Subsequent deprotection gave epoxide **40** (92%), which was cyclized using boron trifluoride etherate to give meroterpenoid **41** (77%, 84% ee as determined by chiral HPLC) as a single diastereoisomer. The (*S*)-enantiomer of meroterpenoid **41** (98% ee as determined by chiral HPLC) was obtained by recrystallization to enhance chiral purity. Second, we examined the halonium-induced polyene cyclization of the resorcylates to produce additional analogues (Scheme 8).[19] Reaction of the geranyl resorcylate **24** with the Snyder reagents Et$_2$SBr·SbCl$_5$Br (BDSB, **46**) and (Et$_2$SI)$_2$Cl·SbCl$_6$ (IDSI, **47**) resulted in bromo- and iodo-cyclizations to produce the racemic bromo-meroterpenoid **42** (64%) and racemic iodo-meroterpenoid **43** (88%) as single diastereoisomers, respectively. Racemic bromide **44** (45%, 2:1 dr) and racemic iodide **45** (54%, 2:1 dr) were also successfully synthesized from farnesyl-substituted resorcylate **14** using the BDSB- (**46**) and IDSI-mediated (**47**) halocyclizations.[20]

The 2,2-dimethyl-1,3-benzodioxan-4-one moiety of the meroterpenoids intermediates was also used in alternative derivatization reactions (Scheme 9). Thus, reaction of the geranyl-substituted resorcylate **24** with boron trifluoride etherate at 25 °C gave the racemic meroterpenoid **48** (89%, 3:1 dr), and the desired pure *trans*-fused ring product was obtained by recrystallization from *n*-hexane.[21] Saponification[13] of meroterpenoid **48** gave racemic carboxylic acid **49** (69%), while hydrolytic decarboxylation gave racemic phenol **50** (97%). Furthermore, reduction of meroterpenoid **48** with LiAlH$_4$ gave racemic diol **51** (95%), and racemic Weinreb amide **52** (96%) was obtained following Grignard reagent mediated amidation.[22]

Scheme 6. Total Synthesis of (+)-Hongoquercin B (2)
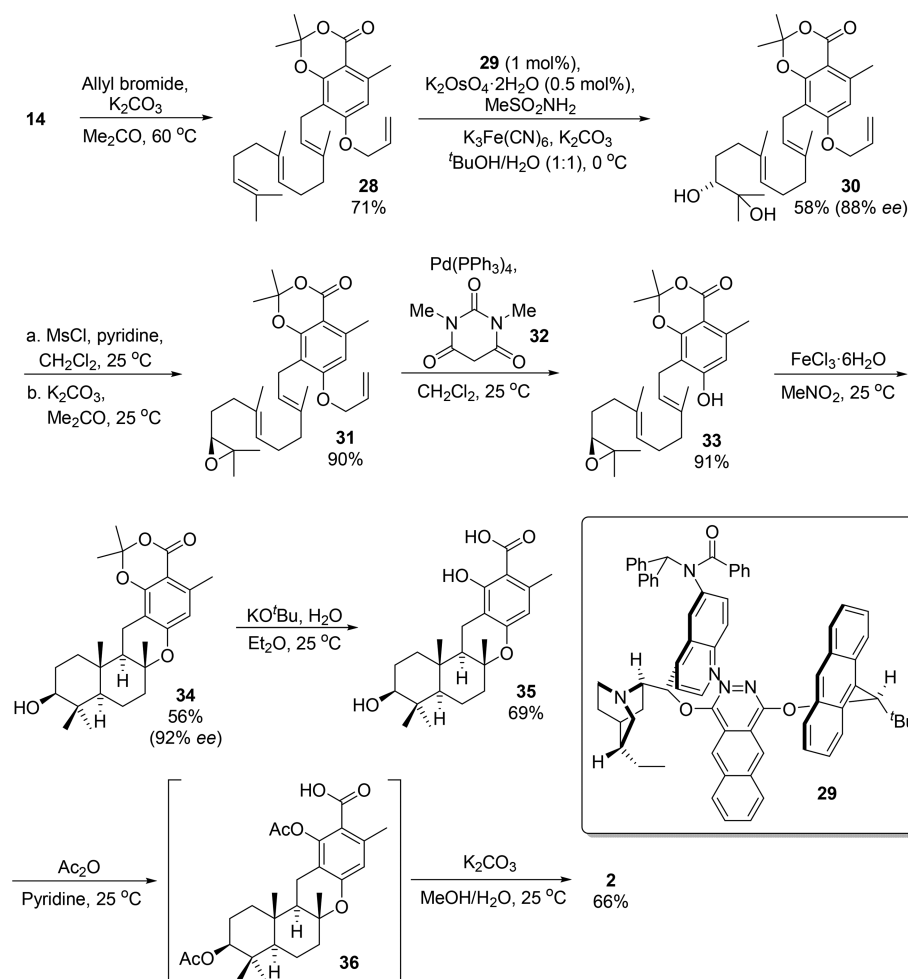
Scheme 7. Synthesis of Meroterpenoid 41
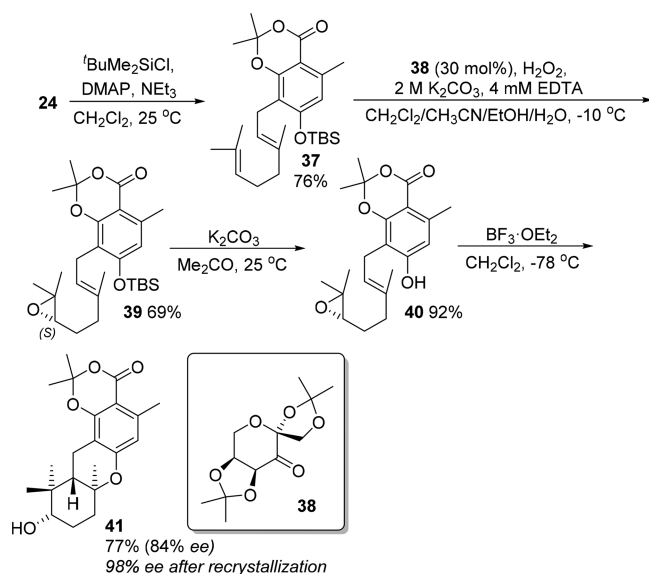
Scheme 8. Halocyclizations To Produce Meroterpenoids 42−45[20]

approach involving sequential polyketide and late-stage electrophile-mediated polyene cyclizations. Several analogues were synthesized by epoxidation or bromo- and iodo-cyclizations. The meroterpenoids were additionally functionalized using saponification, hydrolytic decarboxylation, reduction, and Grignard reagent mediated amidation reactions. Further studies on the synthesis of novel meroterpenoids adopting such dual biomimetic approach are ongoing in our laboratory.
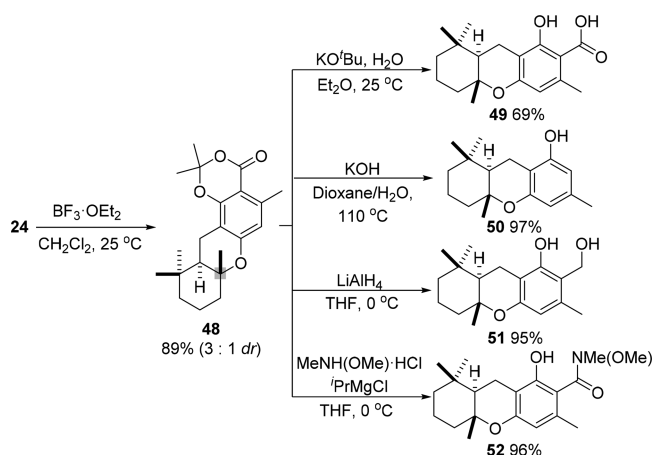
■ CONCLUSION

In conclusion, the total syntheses of (+)-hongoquercins A (**1**) and B (**2**) were completed in five and eleven steps, respectively with an overall yield of 20% and 3.7% via a dual biomimetic

Scheme 9. Synthesis and Functionalization of Meroterpenoid 48

EXPERIMENTAL SECTION

General Methods. All reagents and solvents were used directly without further purification unless otherwise stated. The preparation of malonate and dioxinone acid was performed according to the method of Barrett et al.[10b] Binol 25 and binol 26 were prepared, respectively, according to the procedures reported by Corey et al.[11] and Yamamoto et al.[12] Dihydroquinidine ligand 29 was prepared according to the procedure reported by Corey et al.[15] $Et_2SBr \cdot SbCl_5Br$ (BDSB, 46) and $(Et_2SI)_2Cl \cdot SbCl_6$ (IDSI, 47) were prepared according to the method published by Snyder et al.[19] All solvents were purified and dried by distillation under an atmosphere of N_2 before use. The chiral ketone 38 was prepared from L-fructose according to the established method by Shi et al.[18] Et_2O and THF were redistilled from $Na-Ph_2CO$. CH_2Cl_2, Et_3N, MeOH, $^iPrNO_2$, $MeNO_2$, and pyridine were redistilled from CaH_2, and PhMe was redistilled from Na. All air- and moisture-sensitive reactions were carried out under an atmosphere of N_2 using standard Schlenk techniques in oven-dried glassware equipped with a magnetic stirring bar. The progress of reactions was monitored by analytical thin-layer chromatography (TLC) on silica gel coated aluminum oxide F_{254} plates. Developed TLC was visualized under UV light and stained with acidic vanillin solution. Flash column chromatography was performed by employing silica gel 60 Å, particle size 40−63 μm. The enantiomeric excesses of the compounds were determined by chiral HPLC analysis on Chiralpak IE column with n-hexane and ^iPrOH as the mobile phase. All ^1H and proton-decoupled ^{13}C NMR spectra were recorded at 400 and 101 MHz, respectively, at ambient temperature in deuterated solvent as noted. NMR spectra were referenced to residual solvent peaks ($CDCl_3$: $\delta = 7.26$ for ^1H NMR and $\delta = 77.0$ for ^{13}C NMR; CD_3OD $\delta = 3.31$ and 4.87 for ^1H NMR and $\delta = 49.0$ for ^{13}C NMR; $(CD_3)_2CO$: $\delta = 2.05$ for ^1H NMR and $\delta = 29.8$ for ^{13}C NMR) and chemical shifts were reported in ppm. IR spectra are reported in cm^{-1}. Optical rotations were recorded with a polarimeter with the specified concentration and temperature. Mass spectra were obtained from the Imperial College Mass Spectrometry Service with the use of TOF and magnetic analyzers for ESI and EI techniques, respectively. Melting points are uncorrected. X-ray diffraction data were recorded at the Imperial College X-ray Crystallography Facility.

General Procedures for the Synthesis of Dioxinone β-Keto Esters. 2-Phenyl-1,3-dioxane-4,6-dione (6.91 g, 36.0 mmol), DCC (7.43 g, 36.0 mmol), and DMAP (4.40 g, 36.0 mmol) were dissolved in CH_2Cl_2 (300 mL), and the resulting mixture was stirred for 5 min at 25 °C. 2-(2,2-Dimethyl-4-oxo-4H-1,3-dioxin-6-yl)acetic acid (6.70 g, 36.0 mmol) was added with stirring at 25 °C. After 18 h, the mixture was cooled to 0 °C, and the insoluble solid was filtered off and washed with CH_2Cl_2 (15 mL). The filtrate was washed with aqueous HCl (1 M; 2 × 200 mL), the two phases were separated, and the organic layer was dried $MgSO_4$), filtered, and concentrated under

reduced pressure to give the crude delicate dioxane-4,6-dione keto dioxinone 19 as a yellow foam, which was used directly without further purification. Crude dioxane-4,6-dione keto dioxinone 19 and geraniol (18) or trans,trans-farnesol (17) (20.0 mmol) were dissolved in PhMe (150 mL) and stirred at 55 °C for 4 h. The reaction mixture was concentrated under reduced pressure, and the brown residue was chromatographed (pentane/EtOAc 9:1−4:1) to provide the dioxinone β-keto esters 20 and 21, respectively.

(E)-3,7-Dimethylocta-2,6-dienyl 4-(2,2-dimethyl-4-oxo-4H-1,3-dioxin-6-yl)-3-oxobutanoate (20). Dioxinone β-keto ester 20 (6.92 g, 19.0 mmol, 95%), prepared from geraniol (18) (3.47 mL, 20.0 mmol), was obtained as a pale yellow oil: R_f 0.20 (pentane/EtOAc 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 5.34−5.30 (m, 1H), 5.09−5.04 (m, 1H), 4.67 (d, $J = 7.2$ Hz, 2H), 3.51 (s, 2H), 3.50 (s, 2H), 2.14−2.01 (m, 4H), 1.71 (s, 6H), 1.68 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.6, 166.3, 163.5, 160.4, 143.6, 132.0, 123.5, 117.3, 107.3, 97.1, 62.6, 49.1, 46.9, 39.5, 26.2, 25.6, 25.0, 17.7, 16.5; IR ν_{max} (neat) 1720, 1375, 1272, 1201, 1015 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{29}O_6$ 365.1964, found 365.1977.

(2E,6E)-3,7,11-Trimethyldodeca-2,6,10-trienyl 4-(2,2-dimethyl-4-oxo-4H-1,3-dioxin-6-yl)-3-oxobutanoate (21). Dioxinone β-keto ester 21 (6.81 g, 15.7 mmol, 79%), prepared from trans,trans-farnesol (17) (5.02 mL, 20.0 mmol), was obtained as a pale yellow oil: R_f 0.36 (pentane/Et_2O 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 5.33−5.28 (m, 1H), 5.11−5.02 (m, 2H), 4.65 (d, $J = 7.2$ Hz, 2H), 3.49 (s, 2H), 3.48 (s, 2H), 2.13−1.99 (m, 6H), 1.99−1.91 (m, 2H), 1.69 (s, 6H), 1.66 (s, 3H), 1.65 (s, 3H), 1.57 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.6, 166.3, 163.5, 160.4, 143.5, 135.5, 131.2, 124.2, 123.4, 117.3, 107.2, 97.0, 62.5, 49.0, 46.9, 39.6, 39.4, 26.6, 26.1, 25.6, 24.9, 17.6, 16.4, 15.9; IR ν_{max} (neat) 2922, 1722, 1639, 1375, 1272, 1202, 1015, 901, 806 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{37}O_6$ 433.2590, found 433.2598. Anal. Calcd for $C_{25}H_{36}O_6$: C, 69.42; H, 8.39. Found: C, 69.49; H, 8.24.

General Procedure for the Synthesis of Resorcylates 14 and 24. $MgCl_2$ (476 mg, 5.00 mmol) and pyridine (0.810 mL, 10.0 mmol) were added with stirring to β-keto ester 20 or 21 (5.00 mmol) in CH_2Cl_2 (25 mL) at 0 °C. After 15 min, AcCl (0.540 mL, 7.50 mmol) was added dropwise, and the reaction mixture was further stirred for 1 h at 0 °C. The reaction was quenched by addition of saturated aqueous NH_4Cl (20 mL), and the pH was adjusted to ∼2 with aqueous HCl (1 M). The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the crude dioxinone β,δ-diketo ester 22 or 23. $P(2-furyl)_3$ (232 mg, 1.00 mmol) and Pd_2dba_3 (229 mg, 0.250 mmol) were added sequentially with stirring to this crude material in THF (30 mL) at 25 °C. After 1 h, CsOAc (2.88 g, 15.0 mmol) in ^iPrOH (30 mL) was added, and the resulting mixture was stirred for an dditional 1.5 h. The reaction was quenched with aqueous HCl (1 M; 30 mL), the two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, concentrated under reduced pressure, and chromatographed (pentane/EtOAc 19:1−10:1) to give resorcylate 24 or 14.

(E)-8-(3,7-Dimethylocta-2,6-dienyl)-7-hydroxy-2,2,5-trimethyl-4H-benzo[d][1,3]dioxin-4-one (24). Resorcylate 24 (1.03 g, 3.02 mmol, 60% over two steps), prepared from dioxinone β-keto ester 20 (1.83 g, 5.00 mmol), was obtained as a white solid. An analytically pure sample was obtained by recrystallization from $MeNO_2$: R_f 0.37 (pentane/EtOAc 4:1); mp 102.9−103.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 6.06 (s, 1H), 5.19 (t, $J = 7.4$ Hz, 1H), 5.04 (t, $J = 6.3$ Hz, 1H), 3.33 (d, $J = 7.2$ Hz, 2H), 2.59 (s, 3H), 2.14−1.98 (m, 4H), 1.79 (s, 3H), 1.69 (s, 6H), 1.67 (s, 3H), 1.59 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 161.2, 160.2, 156.0, 142.8, 138.5, 132.0, 123.7, 120.8, 113.7, 112.8, 105.3, 104.8, 39.7, 26.4, 25.7, 25.6, 22.0, 21.9, 17.7, 16.2; IR ν_{max} (neat) 3199, 1694, 1608, 1300, 1282, 1210, 1177, 1106, 1045, 754 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{29}O_4$ 345.2066, found 345.2067. Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.32; H, 8.19. Found: C, 73.35; H, 8.31.

7-Hydroxy-2,2,5-trimethyl-8-((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trienyl)-4H-benzo[d][1,3]dioxin-4-one **(14)**. Resorcylate **14** (1.14 g, 2.75 mmol, 55% over two steps), prepared from dioxinone β-keto ester **21** (2.17 g, 5.00 mmol), was obtained as a yellow oil, which solidified upon standing: R_f 0.24 (pentane/EtOAc 9:1); mp 72.2 °C; ^{1}H NMR (400 MHz, CDCl₃) δ 6.41 (s, 1H), 6.15 (s, 1H), 5.19 (t, J = 6.7 Hz, 1H), 5.13−5.00 (m, 2H), 3.32 (d, J = 7.2 Hz), 2.58 (s, 3H), 2.14−1.90 (m, 8H), 1.79 (s, 3H), 1.68 (s, 6H), 1.67 (s, 3H), 1.58 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.0, 160.0, 156.0, 142.8, 138.6, 135.6, 131.3, 124.3, 123.5, 120.8, 113.6, 112.7, 105.3, 104.8, 39.7, 39.7, 26.7, 26.3, 25.7, 25.7, 22.0, 21.9, 17.7, 16.2, 16.0; IR ν_{max} (neat) 3209, 2971, 2926, 1738, 1704, 1964, 1606, 1590, 1376, 1284, 1217, 1170, 1107, 1046, 858, 751 cm⁻¹; HRMS (ESI) m/z [M + H]⁺ calcd for C₂₆H₃₇O₄ 413.2692, found 413.2680. Anal. Calcd for C₂₆H₃₆O₄: C, 75.69; H, 8.80. Found: C, 75.56; H, 8.96.

(7aR,9aS,13aS,13bR)-2,2,5,7a,10,10,13a-Heptamethyl-7a,8,9a,-10,11,12,13,13a,13b,14-decahydro-4H,9H-benzo[a][1,3]dioxino-[5,4-j]xanthen-4-one **(27)**. SnCl₄ in heptane (1 M; 0.750 mL, 0.750 mmol) was added with stirring to binol **26** (463 mg, 0.900 mmol) in PhMe (9 mL) at 25 °C. After 10 min, the mixture was cooled to −78 °C, when resorcylate **14** (124 mg, 0.300 mmol) in PhMe (1.5 mL) was added dropwise and the reaction mixture was further stirred for 48 h at −78 °C. The reaction was quenched with NaHCO₃ (15 mL) and the mixture diluted with Et₂O (10 mL). The two phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (4 × 15 mL). The combined organic layers were dried (MgSO₄), filtered, concentrated, and chromatographed (pentane/Et₂O 9:1 to PhMe/Et₂O 12:1) to recover the binol **26**. The crude mixture of products was then dissolved in 2-nitropropane (6 mL) and cooled to −78 °C. SnCl₄ in heptane (1 M; 0.750 mL, 0.750 mmol) and CF₃COOH (0.230 mL, 3.00 mmol) were sequentially added dropwise with stirring at −78 °C. After 24 h, the reaction was quenched with saturated aqueous NaHCO₃ (10 mL) and diluted with Et₂O (10 mL). The two phases were separated, and the aqueous layer was extracted with Et₂O (4 × 15 mL). The combined organic layers were dried (MgSO₄), filtered, concentrated, and chromatographed (pentane/Et₂O 9:1) to provide meroterpenoid **27** (78 mg, 0.189 mmol, 63%, 80% dr, 90% ee, measured by chiral HPLC, Chiralpak IE column, n-hexane/ⁱPrOH 19:1, 5 mL/min, t_R = 15.9 [(+)-enantiomer], 14.9 [(−)-enantiomer] min) as a colorless oil containing a mixture of diastereoisomers. An analytical sample was purified by preparative chiral HPLC: R_f 0.75 (pentane/EtOAc 9:1); $[\alpha]_D^{20}$ +80.3 (c 0.57, MeOH); ¹H NMR (500 MHz, CDCl₃) δ 6.33 (s, 1H), 2.57 (s, 3H), 2.53 (dd, 1H), 2.24 (dd, J = 16.8, 13.2 Hz, 1H), 2.08 (dt, J = 12.5, 3.2 Hz, 1H), 1.82−1.77 (m, 1H), 1.77−1.74 (m, 1H), 1.72 (s, 3H), 1.69 (s, 3H), 1.68−1.65 (m, 1H), 1.65−1.62 (m, 1H), 1.53 (d, J = 5.3 Hz, 1H), 1.52−1.45 (m, 1H), 1.45−1.39 (m, 1H), 1.39−1.34 (m, 1H), 1.19 (s, 3H), 1.16 (dd, J = 13.5, 4.3 Hz, 1H), 1.02 (dd, J = 12.2, 2.3 Hz, 1H), 0.98 (dd, J = 12.8, 3.8 Hz, 1H), 0.91 (s, 6H), 0.85 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 160.9, 158.7, 156.1, 142.0, 114.3, 108.3, 104.8, 103.9, 78.4, 56.1, 51.3, 41.8, 40.8, 39.2, 36.9, 33.4, 33.2, 26.2, 25.5, 22.0, 21.6, 20.7, 19.7, 18.5, 16.5, 14.9; IR ν_{max} (neat) 2928, 2867, 1728, 1616, 1575, 1452, 1388, 1285, 1127 cm⁻¹; HRMS (ESI) m/z [M + H]⁺ calcd for C₂₆H₃₇O₄ 413.2696, found 413.2698.

(+)-Hongoquercin A [(4aS,6aR,12aR,12bS)-11-Hydroxy-4,4,6a,9,12b-pentamethyl-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-2H-benzo[a]xanthene-10-carboxylic Acid **(1)**]. H₂O (7 μL, 0.383 mmol) was added with stirring to a suspension of meroterpenoid **27** (79.0 mg, 0.191 mmol) and KOⁱBu (172 mg, 1.53 mmol) in Et₂O (3 mL) at 25 °C. After 2 h, ice was added until two layers were formed, and the two phases were separated. The organic layer was extracted with H₂O (5 × 5 mL), and the combined aqueous layers were acidified with HCl (4 M) to pH ∼1. The two phases were separated, and the aqueous layer was extracted with Et₂O (5 × 5 mL). The combined organic layers were dried (MgSO₄), filtered, concentrated, and chromatographed (pentane/EtOAc/AcOH 9:1:0.01) to afford (+)-hongoquercin A (**1**) (53 mg, 0.142 mmol, 75%) as white solid. An analytical sample was prepared by recrystallization (pentane/CH₂Cl₂): R_f 0.25 (pentane/EtOAc/AcOH 9:1:0.01); mp 146.1−148.5 °C; $[\alpha]_D^{24}$ +90.5 (c 0.57, MeOH); ¹H NMR (400 MHz, CDCl₃)

δ 11.86 (s, 1H), 6.21 (s, 1H), 2.69 (dd, J = 16.9, 5.0 Hz, 1H), 2.51 (s, 3H), 2.29 (dd, J = 16.9, 13.2 Hz, 1H), 2.08 (dt, J = 12.5, 3.1 Hz, 1H), 1.86−1.72 (m, 2H), 1.69 (dd, J = 13.1, 4.8 Hz, 1H), 1.66−1.58 (m, 1H), 1.55 (dd, J = 13.1, 5.0 Hz, 1H), 1.52−1.45 (m, 1H), 1.44−1.42 (m, 1H), 1.42−1.34 (m, 1H), 1.20 (s, 3H), 1.15 (dd, J = 13.4, 4.0 Hz, 1H), 1.03 (dd, J = 12.2, 2.2 Hz, 1H), 1.00−0.94 (m, 1H), 0.92 (s, 3H), 0.91 (s, 3H), 0.85 (s, 3H). ¹H NMR (500 MHz, CD₃OD) δ 6.11 (s, 1H), 2.65 (dd, J = 16.9, 5.0 Hz, 1H), 2.46 (s, 3H), 2.27 (dd, J = 16.7, 13.2 Hz, 1H), 2.05 (dt, J = 12.5, 3.2 Hz, 1H), 1.81−1.76 (m, 2H), 1.72 (dt, J = 13.7, 3.6 Hz, 1H), 1.69−1.61 (m, 1H), 1.52 (dd, J = 13.2, 5.2 Hz, 1H), 1.50−1.40 (m, 3H), 1.26−1.21 (m, 1H), 1.19 (s, 3H), 1.08 (dd, J = 12.2, 2.3 Hz, 1H), 1.05−0.98 (m, 1H), 0.96 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 175.3, 163.9, 158.8, 141.3, 112.6, 108.1, 104.9, 78.4, 56.1, 51.5, 41.8, 40.8, 39.2, 37.0, 33.4, 33.2, 24.1, 21.6, 20.8, 19.7, 18.5, 16.7, 14.9); ¹³C{¹H} NMR (126 MHz, CD₃OD) δ 175.6, 164.5, 158.9, 141.7, 112.8, 108.8, 104.9, 79.0, 57.5, 53.2, 43.0, 42.1, 40.4, 38.1, 34.2, 33.9, 24.2, 22.0, 21.1, 20.8, 19.6, 17.7, 15.4; IR ν_{max} (neat) 2927, 1621, 1574, 1454, 1378, 1262, 1126 cm⁻¹; HRMS (ESI) m/z [M + H]⁺ calcd for C₂₃H₃₃O₄ 373.2383, found 373.2379. Anal. Calcd for C₂₃H₃₂O₄: C, 74.16; H, 8.66. Found: C, 74.22; H, 8.78.

7-(Allyloxy)-2,2,5-trimethyl-8-((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)-4H-benzo[d][1,3]dioxin-4-one **(28)**. Allyl bromide (0.65 mL, 7.50 mmol) was added with stirring to a suspension of K₂CO₃ (1.38 g, 10.0 mmol) and resorcylate **14** (2.06 g, 5.00 mmol) in Me₂CO (50 mL). The resulting suspension was heated to 60 °C with stirring for 18 h, when the mixture was concentrated and diluted with H₂O (50 mL) and CH₂Cl₂ (50 mL). The two phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were dried (MgSO₄), filtered, concentrated, and chromatographed (pentane/Et₂O 9:1) to provide allyl ether **28** (1.61 g, 3.56 mmol, 71%) as a pale yellow oil: R_f 0.33 (pentane/Et₂O 9:1); ¹H NMR (400 MHz, CDCl₃) δ 6.41 (s, 1H), 6.04 (ddt, J = 17.3, 10.3, 5.1 Hz, 1H), 5.42 (dd, J = 17.3, 1.6 Hz, 1H), 5.30 (dd, J = 10.6, 1.4 Hz, 1H), 5.13 (tq, J = 7.3, 1.3 Hz, 1H), 5.07 (tdd, J = 6.9, 3.1, 1.4 Hz, 2H), 4.60 (dt, J = 5.1, 1.6 Hz, 2H), 3.29 (d, J = 7.3 Hz, 2H), 2.63 (s, 3H), 2.10−1.89 (m, 8H), 1.75 (s, 3H), 1.68−1.66 (m, 9H), 1.58 (s, 3H), 1.56 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.9, 155.6, 142.5, 135.2, 134.9, 132.6, 131.2, 124.3, 124.1, 121.6, 117.6, 116.0, 109.3, 105.7, 104.7, 68.9, 39.74, 39.66, 26.7, 26.5, 25.73, 25.66, 22.5, 21.8, 17.6, 16.1, 16.0; IR ν_{max} (neat) 2969, 3925, 2856, 1729, 1606, 1575, 1376, 1278, 1207, 1169, 1115, 1046, 980, 908 cm⁻¹; HRMS (ESI) m/z [M + H]⁺ calcd for C₂₉H₄₁O₄ 453.3005, found 453.2983. Anal. Calcd for C₂₉H₄₀O₄: C, 76.95; H, 8.91. Found: C, 76.84; H, 8.87.

7-(Allyloxy)-8-((R,2E,6E)-10,11-dihydroxy-3,7,11-trimethyldodeca-2,6-dien-1-yl)-2,2,5-trimethyl-4H-benzo[d][1,3]dioxin-4-one **(30)**. Allyl ether **28** (1.53 g, 3.38 mmol) was dissolved in ⁱBuOH (17 mL) and H₂O (17 mL) and cooled to 0 °C. Ligand **29** (35 mg, 33.8 μmol), MeSO₄NH₂ (322 mg, 3.39 mmol), K₃Fe(CN)₆ (3.34 g, 10.1 mmol), K₂CO₃ (1.40 g, 10.1 mmol), and K₂OsO₄·2H₂O (6.3 mg, 17.1 μmol) were added sequentially with stirring at 0 °C. After 24 h, solid Na₂SO₃ (3.00 g) was added, and the mixture was further stirred for 30 min. The reaction mixture was diluted with H₂O (25 mL) and EtOAc (25 mL), the two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried (MgSO₄), filtered, concentrated, and chromatographed (pentane/EtOAc 4:1−1:1 to EtOAc/EtOH 4:1) to afford unreacted allyl ether **28** (400 mg, 0.88 mmol, 26%), tetraol (204 mg, 0.392 mmol, 12%), ligand **29** (33 mg, 32.3 μmol, 96% recovered), and diol **30** (956 mg, 1.96 mmol, 58%, 78% corrected for recovered allyl ether **28**, 88% ee as determined by Mosher ester analysis)[15] as a colorless oil: R_f 0.36 (pentane/EtOAc 1:1); $[\alpha]_D^{23}$ +10.4 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.42 (s, 1H), 6.05 (ddt, J = 17.3, 10.4, 5.1 Hz, 1H), 5.42 (dd, J = 17.3, 1.6 Hz, 1H), 5.30 (dd, J = 10.6, 1.4 Hz, 1H), 5.19−5.10 (m, 2H), 4.61 (dt, J = 5.1, 1.6 Hz, 2H), 3.33 (dd, J = 10.5, 2.0 Hz, 1H), 3.29 (d, J = 7.4 Hz, 2H), 2.63 (s, 3H), 2.25−1.92 (m, 6H), 1.75 (s, 3H), 1.71 (s, 2H), 1.67 (s, 6H), 1.59 (s, 3H), 1.56−1.45 (m, 1H), 1.46−1.32 (m, 1H), 1.18 (s, 3H), 1.14 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.14, 161.08, 155.7,

142.7, 135.2, 135.1, 132.8, 125.1, 121.9, 117.9, 116.1, 109.5, 105.9, 104.9, 78.4, 73.1, 69.1, 39.9, 36.9, 29.8, 26.7, 26.6, 25.9 (2C), 23.4, 22.6, 21.9, 16.2, 16.0; IR ν_{max} (neat) 3443, 2931, 2972, 1729, 1606, 1576, 1451, 1377, 1329, 1281, 1209, 1170, 1117 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{29}$H$_{43}$O$_6$ 487.3060, found 487.3051. Anal. Calcd for C$_{29}$H$_{42}$O$_6$: C, 71.57; H, 8.70. Found: C, 71.69; H, 8.73.

7-(Allyloxy)-8-((2E,6E)-9-((S)-3,3-dimethyloxiran-2-yl)-3,7-dimethylnona-2,6-dien-1-yl)-2,2,5-trimethyl-4H-benzo[d][1,3]dioxin-4-one (31). Pyridine (2.20 mL, 27.3 mmol) and MsCl (0.28 mL, 3.62 mmol) were added sequentially with stirring to diol **30** in CH$_2$Cl$_2$ (20 mL). After 15 h, the mixture was diluted with Me$_2$CO (50 mL), K$_2$CO$_3$ (20.0 g, 0.145 mol) was added, and stirring was continued for 24 h. H$_2$O (30 mL) was added, and the two phases were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 40 mL), and the combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc 19:1 to 5:1) to give epoxide **31** (767 mg, 1.64 mmol, 90%) as a colorless oil: R_f 0.25 (pentane/EtOAc 19:1); $[\alpha]_D^{25}$ −1.8 (c 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.41 (s, 1H), 6.16−5.90 (m, 1H), 5.46−5.36 (m, 1H), 5.32−5.26 (m, 1H), 5.17−5.05 (m, 2H), 4.60 (d, J = 5.0 Hz, 2H), 3.28 (d, J = 7.3 Hz, 2H), 2.66 (t, J = 6.3 Hz, 1H), 2.62 (s, 3H), 2.17−1.91 (m, 6H), 1.74 (s, 3H), 1.66 (s, 6H), 1.57 (s, 3H), 1.67−1.48 (m, 2H), 1.28 (s, 3H), 1.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 160.9 (2C), 155.5, 142.5, 135.0, 134.0, 132.6, 124.7, 121.7, 117.6, 115.9, 109.3, 105.7, 104.6, 68.9, 64.1, 58.2, 39.7, 36.2, 27.4, 26.5, 25.7 (2C), 24.9, 22.4, 21.8, 18.7, 16.1, 15.9; IR ν_{max} (neat) 2961, 2923, 1727, 1606, 1575, 1450, 1376, 1327, 1279, 1207, 1169, 1115 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{29}$H$_{41}$O$_5$ 469.2954, found 469.2960.

8-((2E,6E)-9-((S)-3,3-Dimethyloxiran-2-yl)-3,7-dimethylnona-2,6-dien-1-yl)-7-hydroxy-2,2,5-trimethyl-4H-benzo[d][1,3]dioxin-4-one (33). Dimethylbarbituric acid (**32**) (217 mg, 1.39 mmol) and Pd(PPh$_3$)$_4$ (29 mg, 0.0251 mmol) were added sequentially with stirring to epoxide **31** (589 mg, 1.26 mmol) in CH$_2$Cl$_2$ (10 mL). After 1 h, the reaction mixture was concentrated and purified by chromatography (pentane/EtOAc 4:1) to afford epoxide **33** (491 mg, 1.15 mmol, 91%) as a colorless oil: R_f 0.30 (pentane/EtOAc 4:1); $[\alpha]_D^{26}$ +13.8 (c 1.0, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.90 (s, 1H), 6.42 (s, 1H), 5.19−5.13 (m, 1H), 5.12−5.05 (m, 1H), 3.29 (d, J = 7.3 Hz, 2H), 2.77 (dd, J = 7.4, 4.9 Hz, 1H), 2.58 (s, 3H), 2.19−1.98 (m, 6H), 1.74 (s, 3H), 1.73−1.69 (m, 1H), 1.68 (s, 6H), 1.57 (s, 3H), 1.56−1.49 (m, 1H), 1.33 (s, 3H), 1.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 161.1, 160.4, 155.9, 142.6, 136.8, 134.0, 124.5, 121.9, 113.5, 113.2, 105.0, 104.7, 64.6, 59.5, 39.3, 36.2, 27.0, 25.7, 25.7 (2C), 24.9, 22.0, 21.8, 18.7, 16.0 (2C); IR ν_{max} (neat) 3258, 2964, 2927, 1727, 1693, 1609, 1514, 1452, 1377, 1327, 1276, 1210, 1107 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{26}$H$_{37}$O$_5$ 429.2641, found 429.2645.

(7aR,9aR,11S,13aS,13bR)-11-Hydroxy-2,2,5,7a,10,10,13a-heptamethyl-7a,8,9a,10,11,12,13,13a,13b,14-decahydro-4H,9H-benzo[a][1,3]dioxino[5,4-j]xanthen-4-one (34). FeCl$_3$·6H$_2$O (892 mg, 3.30 mmol) was added with stirring to epoxide **33** (470 mg, 1.10 mmol) in MeNO$_2$ (220 mL), and the resulting mixture was further stirred at 25 °C for 15 min. Saturated aqueous NaHCO$_3$ (150 mL) was added, and the two phases were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 50 mL), and the combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc 3:1) to give meroterpenoid **34** (263 mg, 0.614 mmol, 56%, 92% ee, measured by chiral HPLC, Chiralpak IE column, n-hexane/^{i}PrOH 17:3, 5 mL/min, t_R = 18.9 [(−)-enantiomer], 25.8 [(+)-enantiomer] min) as a white foam: R_f 0.19 (pentane/EtOAc 3:1); $[\alpha]_D^{24}$ +52.2 (c 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.33 (s, 1H), 3.26 (dt, J = 11.0, 5.3 Hz, 1H), 2.56 (s, 3H), 2.56−2.49 (m, 1H), 2.25 (dd, J = 16.7, 13.1 Hz, 1H), 2.10 (dt, J = 12.5, 3.2 Hz, 1H), 1.86−1.76 (m, 2H), 1.72 (s, 3H), 1.68 (s, 3H), 1.73−1.60 (m, 3H), 1.52 (dd, J = 13.1, 5.0 Hz, 1H), 1.47−1.41 (m, 1H), 1.40 (d, J = 5.9 Hz, 1H), 1.19 (s, 3H), 1.12 (td, J = 13.0, 4.3 Hz, 1H), 1.03 (s, 3H), 1.02−0.98 (m, 1H), 0.92 (s, 3H), 0.82 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 160.8, 158.6, 156.1, 142.1, 114.3, 108.0, 104.8,

104.0, 78.6, 78.1, 55.0, 51.1, 40.7, 38.8, 37.4, 36.7, 28.1, 27.1, 26.1, 25.5, 22.0, 20.7, 19.4, 16.5, 15.5, 15.0; IR ν_{max} (neat) 3440, 2930, 2867, 1713, 1616, 1574, 1452, 1388, 1286, 1207, 1126, 1043 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{26}$H$_{37}$O$_5$ 429.2641, found 429.2646.

(3S,4aR,6aR,12aR,12bS)-3,11-Dihydroxy-4,4,6a,9,12b-pentamethyl-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-2H-benzo[a]xanthene-10-carboxylic Acid (35). H$_2$O (10 μL, 0.552 mmol) was added to a suspension of KO^{t}Bu (124 mg, 1.10 mmol) in Et$_2$O (1 mL) at 0 °C and stirred for 5 min. Meroterpenoid **34** (59 mg, 0.138 mmol) in Et$_2$O (1 mL) was added with stirring at 25 °C. After 3 h, ice was added until two layers were formed, and the two phases were separated and diluted with Et$_2$O (2 mL). The pH was adjusted to ∼1 with aqueous HCl (4 M). The two phases were separated, and the aqueous layer was extracted with Et$_2$O (3 × 2 mL). The combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc/AcOH 3:1:0.01) to give the carboxylic acid **35** (37 mg, 0.0952 mmol, 69%) as a white solid: R_f 0.14 (pentane/EtOAc/AcOH 4:1:0.01); mp 153−155 °C; $[\alpha]_D^{24}$ +104.3 (c 0.3, CH$_3$OH); ^{1}H NMR (400 MHz, CD$_3$OD) δ 6.08 (s, 1H), 3.18 (dd, J = 11.3, 5.0 Hz, 1H), 2.61 (dd, J = 16.8, 5.0 Hz, 1H), 2.45 (s, 3H), 2.26 (dd, J = 16.7, 13.0 Hz, 1H), 2.03 (dt, J = 12.4, 3.2 Hz, 1H), 1.84−1.73 (m, 2H), 1.72−1.59 (m, 3H), 1.54−1.41 (m, 2H), 1.16 (s, 3H), 1.15−1.08 (m, 1H), 1.04−1.01 (m, 1H), 1.00 (s, 3H), 0.94 (s, 3H), 0.81 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CD$_3$OD) δ 175.6, 164.4, 158.7, 141.7, 112.7, 108.6, 105.2, 79.4, 78.7, 56.5, 52.9, 42.1, 39.9, 38.8, 37.8, 28.7, 27.9, 24.2, 21.0, 20.5, 17.8, 16.2, 15.5; IR ν_{max} (neat) 3445, 2972, 2934, 2865, 1621, 1579, 1453, 1379, 1265, 1178, 1126, 1038 cm^{-1}; HRMS (ESI) m/z [M − H]$^-$ Calcd for C$_{23}$H$_{31}$O$_5$ 387.2171, found 387.2180.

(+)-Hongoquercin B [(3S,4aR,6aR,12aR,12bS)-3-Acetoxy-11-hydroxy-4,4,6a,9,12b-pentamethyl-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-2H-benzo[a]xanthene-10-carboxylic Acid (2)]. Ac$_2$O (63 μL, 0.666 mmol) was added with stirring to carboxylic acid **35** (37 mg, 0.0952 mmol) in pyridine (0.5 mL) at 25 °C. After 24 h, CH$_2$Cl$_2$ (2 mL) was added, and the pH was adjusted to ∼1 with aqueous HCl (4 M). The two phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 2 mL). The combined organic layers were dried (MgSO$_4$), filtered, and concentrated to give diacetate **36**. Crude diacetate **36** was dissolved in MeOH (2 mL) and H$_2$O (0.2 mL), and K$_2$CO$_3$ (20 mg, 0.143 mmol) was added at 25 °C. The resulting mixture was stirred for 5 h, when CH$_2$Cl$_2$ (2 mL) was added, and the pH was adjusted to ∼1 with aqueous HCl (4 M). The two phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 1 mL). The combined organic layers were dried (MgSO4), filtered, concentrated, and chromatographed (pentane/EtOAc/AcOH 3:1:0.01) to give (+)-hongoquercin B (**2**) (27 mg, 0.0627 mmol, 66% over two steps from carboxylic acid **35**) as white solid: R_f 0.29 (pentane/EtOAc/AcOH 3:1:0.01); mp 155−157 °C; $[\alpha]_D^{30}$ +91.0 (c 0.52, CH$_3$OH); ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.85 (s, 1H), 6.21 (s, 1H), 4.52 (dd, J = 11.6, 4.7 Hz, 1H), 2.66 (dd, J = 16.8, 4.8 Hz, 1H), 2.52 (s, 3H), 2.30 (dd, J = 16.8, 13.1 Hz, 1H), 2.13−2.07 (m, 1H), 2.07 (s, 3H), 1.86 (dt, J = 13.3, 3.6 Hz, 1H), 1.81−1.60 (m, 4H), 1.53 (dd, J = 13.1, 5.0 Hz, 1H), 1.47−1.42 (m, 1H), 1.24−1.18 (m, 1H), 1.20 (s, 3H), 1.10 (dd, J = 12.1, 2.2 Hz, 1H), 0.96 (s, 3H), 0.91 (s, 3H), 0.90 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 175.9, 171.0, 163.8, 158.6, 141.6, 112.6, 107.7, 102.7, 80.4, 78.0, 55.1, 51.3, 40.6, 37.7, 37.1, 36.6, 28.1, 24.1, 23.5, 21.3, 20.7, 19.3, 16.8, 16.7, 15.0; IR ν_{max} (neat) 3063, 2972, 2941, 1731, 1623, 1580, 1454, 1371, 1263, 1178, 1126, 1035, 1007 cm^{-1}; HRMS (ESI) m/z [M − H]$^-$ calcd for C$_{25}$H$_{33}$O$_6$ 429.2277, found 429.2284.

(E)-7-(tert-Butyldimethylsilyloxy)-8-(3,7-dimethylocta-2,6-dien-yl)-2,2,5-trimethyl-4H-benzo[d][1,3]dioxin-4-one (37). NEt$_3$ (1.08 mL, 7.72 mmol) was added with stirring to resorcylate **24** (806 mg, 2.34 mmol) in CH$_2$Cl$_2$ (50 mL) at 25 °C, when ^{t}BuMe$_2$SiCl (1.16 g, 7.72 mmol) and DMAP (5.72 mg, 0.0468 mmol) were added. The resulting mixture was stirred for 2 h, when 10% aqueous citric acid (30 mL) and CH$_2$Cl$_2$ (20 mL) were added. The two phases were separated, and the organic layer was washed with 10% citric acid solution (2 × 30 mL), H$_2$O (30 mL), and brine (30 mL). The organic

layer was dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc 19:1) to give silyl ether **37** (815 mg, 1.78 mmol, 76%) as a colorless oil: R_f 0.59 (pentane/Et$_2$O 10:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.36 (s, 1H), 5.13−5.00 (m, 2H), 3.24 (d, J = 7.0 Hz, 2H), 2.58 (s, 3H), 2.07−1.99 (m, 2H), 1.98−1.90 (m, 2H), 1.73 (s, 3H), 1.65 (s, 6H), 1.63 (s, 3H), 1.55 (s, 3H), 1.01 (s, 9H), 0.28 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 160.9, 158.9, 156.4, 141.7, 134.9, 131.3, 124.1, 121.8, 118.4, 116.1, 105.9, 104.6, 39.6, 26.5, 25.7 (2C), 25.6 (4C), 22.2, 22.1, 18.2, 17.6, 16.2, −4.1 (2C); IR ν_{max} (neat) 2930, 2859, 1733, 1606, 1569, 1292, 1209, 1169, 1044, 841, 782 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{27}$H$_{43}$O$_4$Si 459.2931, found 459.2938. Anal. Calcd for C$_{27}$H$_{42}$O$_4$Si: C, 70.70; H, 9.23. Found: C, 70.52; H, 9.10.

(S,E)-7-((tert-Butyldimethylsilyl)oxy)-8-(5-(3,3-dimethyloxiran-2-yl)-3-methylpent-2-en-1-yl)-2,2,5-trimethyl-4H-benzo[d][1,3]-dioxin-4-one (39). Silyl ether **37** (334 mg, 0.75 mmol) and the chiral ketone **38** (58 mg, 0.225 mmol) were dissolved in CH$_2$Cl$_2$ (6 mL), CH$_3$CN (3 mL), EtOH (3 mL), and aqueous buffer (2 M K$_2$CO$_3$; 4 × 10^{-3} M EDTA; 6 mL) and cooled to 0 °C. H$_2$O$_2$ (0.42 mL) was added dropwise with stirring. After 15 h, Na$_2$SO$_3$ (200 mg) was added, and the phases were separated. The aqueous layer was extracted with Et$_2$O (3 × 15 mL), and the combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc 10:1) to afford epoxide **39** (244 mg, 0.514 mmol, 69%) as a colorless oil: R_f 0.22 (pentane/EtOAc 19:1); $[\alpha]_D^{23}$ +2.8 (c 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.35 (s, 1H), 5.12 (tq, J = 7.1, 1.3 Hz, 1H), 3.24 (d, J = 7.0 Hz, 2H), 2.65 (t, J = 6.2 Hz, 1H), 2.58 (s, 3H), 2.20−1.98 (m, 2H), 1.74 (s, 3H), 1.65 (s, 6H), 1.61−1.53 (m, 2H), 1.24 (s, 3H), 1.21 (s, 3H), 1.00 (s, 9H), 0.28 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 160.8, 158.9, 156.3, 141.9, 134.1, 122.5, 118.1, 116.1, 105.9, 104.6, 64.0, 58.2, 36.2, 27.3, 25.8 (2C), 25.6 (3C), 24.8, 22.2, 22.1, 18.6, 18.3, 16.2, −4.0 (2C); IR ν_{max} (neat) 2959, 2930, 2859, 1732, 1605, 1570, 1279, 842 cm^{-1}; HRMS (FTMS + p APCI) m/z [M + H]$^+$ calcd for C$_{27}$H$_{43}$O$_5$Si 475.2874, found 475.2870. Anal. Calcd for C$_{27}$H$_{42}$O$_5$Si: C, 68.31; H, 8.92. Found: C, 68.21; H, 9.03.

(S,E)-8-(5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-yl)-7-hydroxy-2,2,5-trimethyl-4H-benzo[d][1,3]dioxin-4-one (40). K$_2$CO$_3$ (2.33 g, 16.9 mmol) was added with stirring to epoxide **39** (160 mg, 0.337 mmol) in Me$_2$CO (20 mL) at 25 °C. After 2 h, CH$_2$Cl$_2$ (30 mL) and H$_2$O (50 mL) were added, and the two phases were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc 5:1) to give epoxide **40** (112 mg, 0.311 mmol, 92%) as a colorless oil: R_f 0.29 (pentane/EtOAc 5:1); $[\alpha]_D^{24}$ −9.4 (c 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.40 (s, 1H), 6.17 (s, 1H), 5.30−5.15 (m, 1H), 3.31 (dd, J = 7.0, 2.1 Hz, 2H), 2.69 (dd, J = 6.8, 5.6 Hz, 1H), 2.58 (s, 3H), 2.26−2.07 (m, 2H), 1.80 (s, 3H), 1.68 (s, 6H), 1.69−1.55 (m, 2H), 1.28 (s, 3H), 1.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 160.9, 159.8, 156.0, 142.8, 136.8, 121.7, 113.6, 113.0, 105.4, 104.8, 64.2, 58.6, 36.5, 27.2, 25.8, 25.7, 24.8, 22.0, 21.8, 18.7, 16.2; IR ν_{max} (neat) 3235, 2928, 1727, 1696, 1609, 1277 cm^{-1}; HRMS (FTMS + p APCI) m/z [M + H]$^+$ calcd for C$_{21}$H$_{29}$O$_5$ 361.2010, found 361.2016.

(7aS,10S,11aS)-10-Hydroxy-2,2,5,7a,11,11-hexamethyl-7a,8,-10,11,11a,12-hexahydro-4H,9H-[1,3]dioxino[4,5-a]xanthen-4-one (41). BF$_3$OEt$_2$ (0.2 mL, 0.139 mmol) was added with stirring to epoxide **40** (110 mg, 0.305 mmol) in CH$_2$Cl$_2$ (30 mL) at −78 °C. After 5 min, Et$_3$N (5 mL) and H$_2$O (20 mL) were added, the mixture was allowed to warm to 25 °C, and the two phases were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 30 mL), and the combined organic layers were dried (MgSO$_4$), filtered, concentrated, and purified by chromatography (pentane/EtOAc 5:2) to give the meroterpenoid **41** (85 mg, 0.236 mmol, 77%, 84% ee, measured by chiral HPLC, Chiralpak IE column, n-hexane/^{i}PrOH 9:1, 5 mL/min, t_R = 22.0 [(−)-enantiomer], 26.6 [(+)-enantiomer] min) as a white foam: R_f 0.29 (pentane/EtOAc 5:2); $[\alpha]_D^{24}$ −71.0 (c 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.33 (s, 1H), 3.41 (dd, J = 11.4, 4.2 Hz, 1H), 2.63 (dd, J = 16.8, 4.9 Hz, 1H), 2.56 (s, 3H), 2.31 (dd, J = 16.9, 13.2 Hz, 1H), 2.00 (dt, J = 12.5, 3.3 Hz, 1H), 1.91−1.81 (m, 1H),

1.78−1.74 (m, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.64−1.52 (m, 2H), 1.20 (s, 3H), 1.12 (s, 3H), 0.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 160.8, 158.6, 156.0, 142.2, 114.3, 107.9, 104.8, 104.1, 77.8, 77.6, 46.1, 38.5, 37.4, 28.1, 27.3, 26.1, 25.4, 21.9, 19.8, 17.2, 14.3; IR ν_{max} (neat) 3433, 2942, 1708, 1617, 1573, 1287, 1128 cm^{-1}; HRMS (ESI) m/z [M − H]$^−$ calcd for C$_{21}$H$_{27}$O$_5$ 359.1858, found 359.1853. Anal. Calcd for C$_{21}$H$_{28}$O$_5$: C, 69.98; H, 7.83. Found: C, 69.86; H, 7.94.

General Procedure for BDSB (46)-Induced Halocyclization. BDSB (**46**) (604 mg, 1.10 mmol) was added with stirring to resorcylate **24** or **14** (1.00 mmol) in MeNO$_2$ (50 mL) at −25 °C. After 10 min, saturated aqueous NaHCO$_3$ (15 mL) and aqueous Na$_2$SO$_3$ (0.5 M; 5 mL) were added, and stirring was continued for 15 min. The two phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/Et$_2$O 9:1) to give the bromo-meroterpenoid **42** or **44**.

10-Bromo-2,2,5,7a,11,11-hexamethyl-7a,8,10,11,11a,12-hexahydro-4H,9H-[1,3]dioxino[4,5-a]xanthen-4-one (42). Bromide **42** (272 mg, 0.642 mmol, 64%), prepared from resorcylate **24** (344 mg, 1.00 mmol), was obtained as a white solid: R_f 0.29 (pentane/Et$_2$O 9:1); mp 225.3−225.7 °C; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 6.36 (s, 1H), 4.26 (dd, J = 11.8, 4.8 Hz, 1H), 2.80−2.77 (m, 1H), 2.52 (s, 3H), 2.50−2.43 (m, 1H), 2.30−2.13 (m, 2H), 2.00 (dt, J = 13.0, 3.5 Hz, 1H), 1.90−1.79 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.27 (s, 3H), 1.19 (s, 3H), 1.06 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, (CD$_3$)$_2$CO) δ 160.7, 159.1, 157.0, 142.6, 115.1, 109.3, 105.8, 105.4, 78.2, 66.9, 47.9, 41.0, 40.1, 32.3, 29.9, 26.3, 25.6, 22.1, 20.2, 19.5, 17.4; IR ν_{max} (neat) 2975, 2924, 2865, 1715, 1616, 1575, 1380, 1286, 1128, 1044 cm^{-1}; HRMS (EI) m/z [M]$^{\bullet+}$ calcd for C$_{21}$H$_{27}$BrO$_4$ 422.1093, found 422.1110. Anal. Calcd for C$_{21}$H$_{27}$BrO$_4$: C, 59.58; H, 6.43. Found: C, 59.45; H, 6.57.

11-Bromo-2,2,5,7a,10,10,13a-heptamethyl-7a,8,9a,10,11,12,-13,13a,13b,14-decahydro-4H,9H-benzo[a][1,3]dioxino[5,4-j]-xanthen-4-one (44). Bromide **44** (219 mg, 0.446 mmol, 45%, 2:1 dr), prepared from resorcylate **14** (413 mg, 1.00 mmol), was obtained as a white solid containing a minor amount of a diastereoisomer: R_f 0.24 (pentane/Et$_2$O 9:1); mp 234.0−237.4 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.33 (s, 1H), 4.00 (dd, J = 12.6, 4.7 Hz, 1H), 2.57 (s, 3H), 2.51 (dd, J = 16.8, 5.1 Hz, 1H), 2.37−2.13 (m, 3H), 2.13−2.07 (m, 1H), 1.91−1.84 (m, 1H), 1.84−1.78 (m, 1H), 1.72 (s, 3H), 1.71−1.69 (m, 1H), 1.69 (s, 3H), 1.59−1.46 (m, 2H), 1.20 (s, 3H), 1.20−1.11 (m, 2H), 1.12 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 160.8, 158.5, 156.1, 142.2, 114.3, 107.8, 104.8, 104.1, 77.8, 68.4, 56.3, 51.1, 40.7, 40.5, 39.6, 37.0, 30.7, 30.6, 26.1, 25.5, 22.0, 21.1, 20.6, 18.3, 16.5, 14.9; IR ν_{max} (neat) 2949, 1718, 1613, 1575, 1376, 1288, 1131, 1042, 902, 844, 693 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{26}$H$_{36}$BrO$_4$ 491.1797, found 491.1807. Anal. Calcd for C$_{26}$H$_{35}$BrO$_4$: C, 63.54; H, 7.18. Found: C, 63.49; H, 7.07.

General Procedure for IDSI (47)-Induced Halocyclization. IDSI (**47**) (884 mg, 1.10 mmol) was added with stirring to resorcylate **24** or **14** (1.00 mmol) in MeNO$_2$ (50 mL) at −25 °C. After 10 min, saturated aqueous NaHCO$_3$ (15 mL) and aqueous Na$_2$SO$_3$ (0.5 M; 5 mL) were added, and stirring was continued for 15 min. The two phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/Et$_2$O 9:1) to give the iodo-meroterpenoid **43** or **45**.

10-Iodo-2,2,5,7a,11,11-hexamethyl-7a,8,10,11,11a,12-hexahydro-4H,9H-[1,3]dioxino[4,5-a]xanthen-4-one (43). Iodide **43** (415 mg, 0.882 mmol, 88%), prepared from resorcylate **24** (344 mg, 1.00 mmol), was obtained as a white solid: R_f 0.29 (pentane/Et$_2$O 9:1); mp 221.6−222.4 °C; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 6.36 (s, 1H), 4.46 (dd, J = 11.9, 4.8 Hz, 1H), 2.82 (dd, J = 23.3, 6.7 Hz, 1H), 2.52 (s, 3H), 2.50−2.44 (m, 1H), 2.46−2.30 (m, 2H), 1.91 (dd, J = 13.2, 5.0 Hz, 1H), 1.87−1.82 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.28 (s, 3H), 1.16 (s, 3H), 1.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, (CD$_3$)$_2$CO) δ 160.5, 158.9, 156.7, 142.4, 114.9, 109.3, 105.6, 105.2, 78.2, 50.1, 46.2, 42.5, 39.6, 34.9, 32.3, 26.1, 25.4, 21.9, 20.3, 20.0,

19.9; IR ν_{max} (neat) 2970, 1715, 1616, 1575, 1379, 1285, 1127, 1044, 902 cm^{-1}; HRMS (EI) m/z [M]$^{\bullet+}$ Calcd for C$_{21}$H$_{27}$IO$_4$ 470.0954, found 470.0947. Anal. Calcd for C$_{21}$H$_{27}$IO$_4$: C, 53.63; H, 5.79. Found: C, 53.55; H, 5.86.

11-Iodo-2,2,5,7a,10,10,13a-heptamethyl-7a,8,9a,10,11,12,-13,13a,13b,14-decahydro-4H,9H-benzo[a][1,3]dioxino[5,4-j]-xanthen-4-one (45). Iodide **45** (293 mg, 0.544 mmol, 54%, 2:1 dr), prepared from resorcylate **14** (413 mg, 1.00 mmol), was obtained as a white solid containing a minor diastereoisomer: R_f 0.24 (pentane/Et$_2$O 9:1); mp 189.5−192.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.33 (s, 1H), 4.24 (dd, J = 13.0, 3.2 Hz, 1H), 2.57 (s, 3H), 2.50 (dd, J = 16.4, 5.0 Hz, 1H), 2.46−2.29 (m, 2H), 2.24 (dd, J = 16.8, 13.1 Hz, 1H), 2.10−2.03 (m, 1H), 1.95−1.87 (m, 1H), 1.72 (s, 3H), 1.69 (s, 3H), 1.68−1.55 (m, 2H), 1.55−1.51 (m, 1H), 1.51−1.45 (m, 1H), 1.26−1.20 (m, 1H), 1.20 (s, 3H), 1.20−1.10 (m, 1H), 1.10 (s, 3H), 1.01 (s, 3H), 0.98 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 160.8, 158.5, 156.1, 142.2, 114.3, 107.8, 104.8, 104.1, 77.3, 54.9, 52.9, 51.2, 42.2, 40.8, 39.3, 37.3, 33.6, 33.2, 26.1, 25.5, 22.2, 22.0, 21.1, 20.6, 16.5, 14.9; IR ν_{max} (neat) 2946, 1726, 1615, 1576, 1371, 1285, 1124, 1038, 902 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{26}$H$_{36}$IO$_4$ 539.1658, found 539.1664.

2,2,5,7a,11,11-Hexamethyl-7a,8,10,11,11a,12-hexahydro-4H,9H-[1,3]dioxino[4,5-a]xanthen-4-one (48). BF$_3$·OEt$_2$ (0.31 mL, 2.50 mmol) was added dropwise with stirring to resorcylate **24** (172 mg, 0.50 mmol) in CH$_2$Cl$_2$ (50 mL) at −78 °C. The resulting mixture was warmed to 25 °C and further stirred for 1.5 h, when saturated aqueous NaHCO$_3$ (25 mL) and H$_2$O (25 mL) were added and the phases were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 25 mL), and the combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/Et$_2$O 9:1) to provide meroterpenoid **48** (154 mg, 0.447 mmol, 89%, 3:1 dr) as a white solid containing a minor diastereoisomer. Recrystallization from *n*-hexane provided the pure *trans*-fused ring product: R_f 0.48 (pentane/EtOAc 19:1); mp 139.5−141.3 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.34 (s, 1H), 2.62 (dd, J = 16.8, 4.8 Hz, 1H), 2.57 (s, 3H), 2.22 (dd, J = 16.8, 13.3 Hz, 1H), 2.01−1.94 (m, 1H), 1.74 (s, 3H), 1.70 (s, 3H), 1.68−1.64 (m, 1H), 1.60 (dd, J = 13.4, 4.8 Hz, 1H), 1.60−1.55 (m, 2H), 1.54−1.47 (m, 1H), 1.37−1.28 (m, 1H), 1.21 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 160.9, 158.8, 156.0, 142.1, 114.4, 108.6, 104.8, 104.0, 78.7, 47.4, 41.4, 39.7, 33.5, 32.1, 26.2, 25.5, 22.0, 20.6, 19.8, 19.7, 17.3; IR ν_{max} (neat) 2969, 2901, 2921, 1720, 1618, 1576, 1390, 1286, 1043 cm^{-1}; HRMS (ESI) m/z [M]$^{\bullet+}$ calcd for C$_{21}$H$_{28}$O$_4$ 344.1988, found 344.1990. Anal. Calcd for C$_{21}$H$_{28}$O$_4$: C, 73.32; H, 8.19. Found: C, 73.17; H, 8.22.

8-Hydroxy-1,1,4a,6-tetramethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene-7-carboxylic Acid (49). H$_2$O (8 μL, 0.4 mmol) was added with stirring to a suspension of KO^{t}Bu (180 mg, 1.60 mmol) in Et$_2$O (3 mL) at 0 °C. After 5 min, meroterpenoid **48** (69 mg, 0.200 mmol) was added, and the resulting mixture was further stirred at 25 °C for 2 h. The pH was adjusted to ∼2 with aqueous HCl (1 M), the two phases were separated, and the aqueous layer was extracted with Et$_2$O (3 × 10 mL). The combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc/AcOH 9:1:0.01) to give the carboxylic acid **49** (42 mg, 0.138 mmol, 69%) as a white solid: R_f 0.30 (pentane/EtOAc/AcOH 9:1:0.01); mp 176.7−178.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.84 (s, 1H), 11.17 (s, 1H), 6.22 (s, 1H), 2.77 (dd, J = 17.0, 4.8 Hz, 1H), 2.52 (s, 3H), 2.28 (dd, J = 16.9, 13.4 Hz, 1H), 2.01−1.94 (m, 1H), 1.72−1.64 (m, 1H), 1.64−1.55 (m, 3H), 1.55−1.45 (m, 1H), 1.40−1.27 (m, 1H), 1.22 (s, 3H), 1.04 (s, 3H), 0.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 175.5, 163.7, 158.9, 141.4, 112.7, 108.4, 102.4, 78.7, 47.6, 41.5, 39.7, 33.6, 32.1, 24.1, 20.6, 19.8, 19.7, 17.6; IR ν_{max} (neat) 2694, 2919, 2865, 1619, 1578, 1454, 1268, 1151, 1100 cm^{-1}; HRMS (EI) m/z [M]$^{\bullet+}$ Calcd for C$_{18}$H$_{24}$O$_4$ 304.1675, found 304.1679. Anal. Calcd for C$_{18}$H$_{24}$O$_4$: C, 71.03; H, 7.95. Found: C, 71.17; H, 8.11.

1,1,4a,6-Tetramethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthen-8-ol (50). Aqueous KOH (5 M; 1 mL) was added with stirring to meroterpenoid **48** (69 mg, 0.200 mmol) in 1,4-dioxane (2 mL), and the resulting mixture was heated at 110 °C for 23 h. After the reaction mixture was cooled to 25 °C, the pH was adjusted to ∼2 with aqueous

HCl (4 M). The two phases were separated, and the aqueous layer was extracted with Et$_2$O (3 × 10 mL). The combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc 15:1) to give the phenol **50** (40 mg, 0.194 mmol, 97%) as a white foam: R_f 0.33 (pentane/EtOAc 15:1); ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 8.00 (s, 1H), 6.21 (s, 1H), 6.05 (s, 1H), 2.71 (dd, J = 16.7, 5.0 Hz, 1H), 2.26 (dd, J = 16.6, 13.5 Hz, 1H), 2.12 (s, 3H), 1.92−1.81 (m, 1H), 1.68−1.53 (m, 4H), 1.52−1.44 (m, 1H), 1.40−1.27 (m, 1H), 1.17 (s, 3H), 1.01 (s, 3H), 0.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, (CD$_3$)$_2$CO) δ 156.2, 155.0, 137.2, 109.7, 107.7, 107.6, 77.0, 48.8, 42.3, 40.8, 34.0, 21.3, 20.9, 20.4, 20.0, 18.6; IR ν_{max} (neat) 3398, 2935, 2866, 1627, 1587, 1516, 1457, 1101, 1063, 1040 cm^{-1}; HRMS (EI) m/z [M]$^{\bullet+}$ calcd for C$_{17}$H$_{24}$O$_2$ 260.1776, found 260.1786.

7-(Hydroxymethyl)-1,1,4a,6-tetramethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthen-8-ol (51). LiAlH$_4$ in THF (1 M; 0.8 mL, 0.800 mmol) was added with stirring to meroterpenoid **48** (69 mg, 0.200 mmol) in THF (4 mL) at 0 °C. After 1 h, H$_2$O (65 μL) and NaOH (1 M; 150 μL) were added dropwise sequentially, and the mixture was further stirred for 30 min. Solid NH$_4$Cl (100 mg) was added, and the solids were filtered and eluted with Et$_2$O (5 mL). The filtrate was concentrated and chromatographed (pentane/EtOAc 4:1) to afford diol **51** (55 mg, 0.189 mmol, 95%) as white foam: R_f 0.22 (pentane/EtOAc 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (s, 1H), 6.19 (s, 1H), 4.88 (s, 2H), 2.75 (dd, J = 16.6, 5.0 Hz, 1H), 2.37−2.27 (m, 1H), 2.17 (s, 3H), 1.99−1.90 (m, 1H), 1.69−1.54 (m, 4H), 1.52−1.40 (m, 1H), 1.38−1.25 (m, 1H), 1.20 (s, 3H), 1.02 (s, 3H), 0.92 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 155.0, 153.4, 133.6, 113.6, 110.2, 109.0, 77.1, 60.8, 47.8, 41.6, 39.9, 33.5, 32.1, 20.6, 19.8, 19.6, 19.2, 17.7; IR ν_{max} (neat) 3344, 2934, 2865, 1627, 1583, 1102 cm^{-1}; HRMS (ESI) m/z [M − H]$^-$ calcd for C$_{18}$H$_{25}$O$_3$ 289.1804, found 289.1807. Anal. Calcd for C$_{18}$H$_{26}$O$_3$: C, 74.45; H, 9.02. Found: C, 74.59; H, 9.13.

8-Hydroxy-N-methoxy-N,1,1,4a,6-pentamethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene-7-carboxamide (52). MeNH(OMe)·HCl (59 mg, 0.605 mmol) was added dropwise with stirring to meroterpenoid **48** (69 mg, 0.200 mmol) in THF (4 mL) and cooled to 0 °C, followed by dropwise addition of ^{i}PrMgCl in THF (2 M; 0.6 mL, 1.20 mmol). The resulting mixture was stirred at 0 °C for 3 h, when the reaction was quenched with saturated NH$_4$Cl (2 mL) and the mixture was acidified to pH ∼ 1 with aqueous HCl (1 M). The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (MgSO$_4$), filtered, concentrated, and chromatographed (pentane/EtOAc 7:3) to give the amide **52** (67 mg, 0.193 mmol, 96%) as a white solid: R_f 0.43 (pentane/EtOAc 7:3); mp 178.9−182.7 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.20 (s, 1H), 3.57 (s, 3H), 3.33 (s, 3H), 2.74 (dd, J = 16.7, 5.0 Hz, 1H), 2.28 (dd, J = 16.7, 13.4 Hz, 1H), 2.23 (s, 3H), 1.98−1.93 (m, 1H), 1.71−1.64 (m, 1H), 1.61 (dd, J = 13.2, 4.9 Hz, 1H), 1.59−1.54 (m, 2H), 1.54−1.45 (m, 1H), 1.37−1.24 (m, 1H), 1.20 (s, 3H), 1.02 (s, 3H), 0.92 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 169.9, 155.5, 154.5, 135.3, 111.1, 110.7, 108.5, 77.7, 61.3, 47.7, 41.6, 39.9, 34.2, 33.5, 32.1, 20.6, 19.9, 19.8, 19.7, 17.8; IR ν_{max} (neat) 3110, 2933, 1616, 1578, 1456, 1389, 1120, 732 cm^{-1}; HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{20}$H$_{30}$NO$_4$ 348.2175, found 348.2188. Anal. Calcd for C$_{20}$H$_{29}$NO$_4$: C, 69.14; H, 8.41; N, 4.03. Found: C, 69.11; H, 8.49; N, 3.97.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b02095.

> ^{1}H and ^{13}C NMR spectra for (+)-hongoquercin A (**1**), (+)-hongoquercin B (**2**), and compounds **14**, **20**, **21**, **24**, **27**, **28**, **30**, **31**, **33−35**, **37**, **39−41**, **42−45**, and **48−52** (PDF)

> X-ray structural data for compounds **1**, **34**, **41−45**, and **48** (PDF)

X-ray structural data for compounds **1, 34, 41–45**, and **48** (CIF)

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Notes
The authors declare no competing financial interest.

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