An Exceptionally Short and Simple Enantioselective Total Synthesis of Pentacyclic Triterpenes of the β-Amyrin Family

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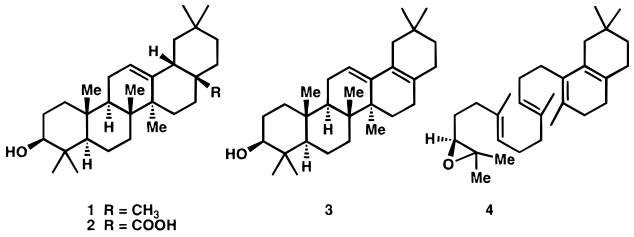
Abstract: A new and very direct enantioselective total synthesis of members of the β-amyrin family of pentacyclic triterpenes has been developed starting with acylsilane **5**, 2-propenyllithium, and cyclohexenylmethyl bromide **6**, which were assembled to form tetraene **7**. Cationic cyclization of **7** and silylation afforded **8,** which after vinyl triflate formation was cyclized via a Cu(I) intermediate (Scheme 2) to form the TBS ether of aegiceradienol **10**, a versatile intermediate that is readily converted into natural β-amyrins such as β-amyrin (**1**) and oleanolic acid (**2**). The C(14)-diastereomer (**13**) of aegiceradienol was also synthesized from the C(14)-diastereomer of **8** using an intramolecular Stille reaction for the closure of ring D (Scheme 4).

Some time ago we reported the first enantioselective synthesis of the parent pentacyclic triperpene β-amyrin (**1**) and other members of the family, including oleanolic acid (**2**), from a common intermediate, the naturally occurring nor-triterpene aegiceradienol (**3**).[1] A key step in this synthesis was the transformation of the chiral epoxide **4** to **3** by a diastereoselective cation-π tricyclization reaction, a process that resembles the biosynthetic pathway to triterpenoids, including steroidal precursors, from (*S*)-2,3-oxidosqualene.[2,3] Since the first synthesis of the β-amyrin family, no other enantioselective routes to this major class of natural products have been reported. Described herein is a new, very short, and enantiocontrolled synthesis of the versatile triterpenoid intermediate **3**. In this synthesis, the components **5**, 2-propenyllithium, and **6** were

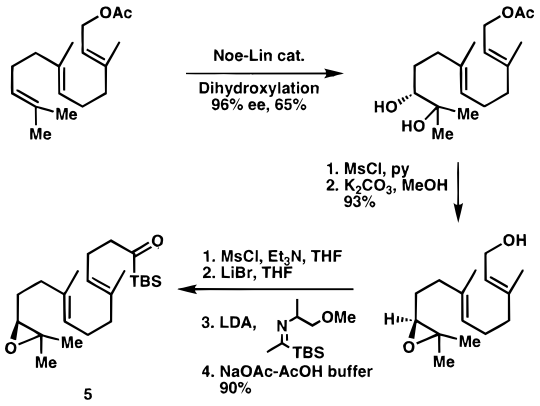


assembled in a single step to form the chiral epoxide **7** from which the target molecule **3** was produced by sequential cation-π tricyclization and organocopper-promoted closure of the final ring (Scheme 2).

The acylsilane component **5** was synthesized as shown in Scheme 1, and detailed in the Experimental Section. The route of synthesis had previously been developed and applied in this laboratory in connection with the total synthesis of dammarenediol.[4,5]

The three-component coupling of **5**, 2-propenyllithium, and **6** (Scheme 2) involved the following sequence: (1) addition of acylsilane **5** (TBS = *tert*-butyldimethylsilyl) to 2-propenyllithium, which resulted in 1,2-carbonyl addition, (2) addition of a solution of BaI_2 in tetrahydrofuran (THF),[6] which effects Brook rearrangement to a chelated *Z*-allylic organobarium intermediate,[4,7] and (3) coupling of the *Z*-allylic barium reagent so formed with the allylic bromide **6** to produce the chiral epoxy tetraene **7** in excellent overall yield and stereoselectivity (>95% of the *Z*-olefin by ^{1}H NMR analysis). Cation-π tricyclization of the monocyclic epoxy tetraene **7** to form the tetracyclic ketone **8** was effected in 52% isolated yield (after silylation and silica gel chromatography) using methylaluminum dichloride as catalyst in 3:1 hexane−CH_2Cl_2 as solvent at −78 °C. A more polar isomer was obtained as byproduct in 23% yield which was shown to be the C(14) diastereomer of tetracyclic ketone **8** (i.e., tetracylic ketone **11**) by the experiments described below. Vinyl triflate **9** was then prepared from ketone **8** via the lithium enolate as outlined in Scheme 2.

Scheme 1



The final ring of **3** was closed by the two-step conversion of **9** to the corresponding vinylcopper reagent and internal coupling with the vinyl bromide subunit. The experimental sequence for this novel ring closure was as follows: (1) replacement of the triflate group of **9** by trimethylstannyl group using the method of Wulff[8] (hexamethyldistannane, Pd(0) catalyst) and (2)

(1) Corey, E. J.; Lee, J. *J. Am. Chem. Soc.* **1993**, *115*, 8873.
(2) Corey, E. J.; Cheng, H.; Baker, C. H.; Matsuda, S. P. T.; Li, D.; Song, X. *J. Am. Chem. Soc.* **1997**, *119*, 1289.
(3) For other approaches to the synthesis of pentacyclic triterpenoids (racemic) using cation-π cyclization see: Fish, P. V.; Johnson, W. S. *J. Org. Chem.* **1994**, *59*, 2324.
(4) Corey, E. J.; Lin, S. *J. Am. Chem. Soc.* **1996**, *118*, 8765.
(5) Corey, E. J.; Noe, M. C.; Lin, S. *Tetrahedron Lett.* **1995**, *36*, 8741.
(6) Anhydrous BaI_2 in THF was prepared by reaction of I_2 with barium metal strips (prepared by hammering mineral oil covered Ba chunks into <1 mm thick sheets and cutting by scissors).
(7) Corey, E. J.; Lin, S.; Luo, G. *Tetrahedron Lett.* **1997**, *38*, 5771.

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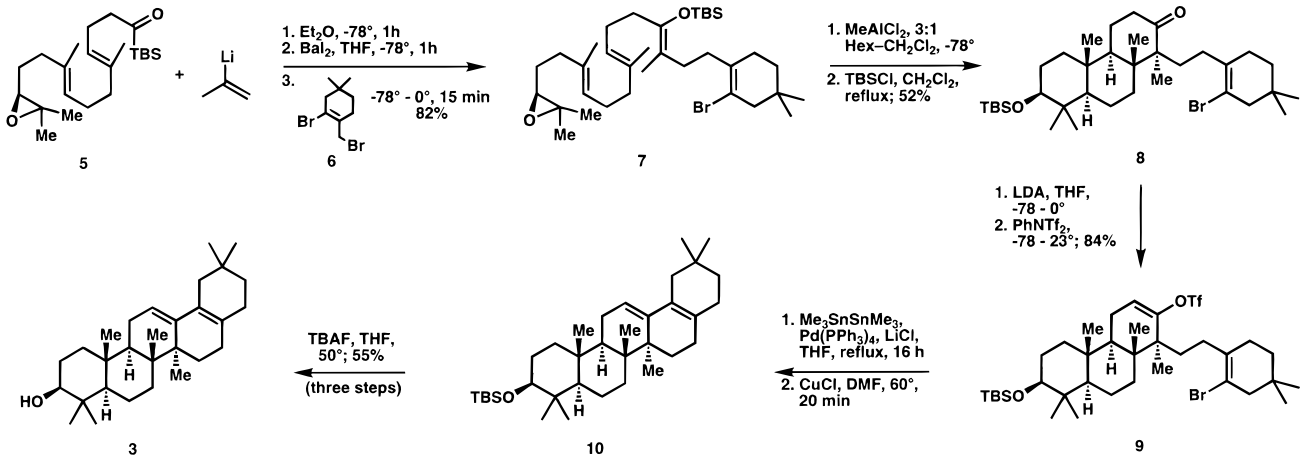
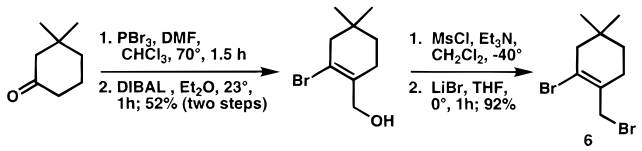
Scheme 2



transmetalation using CuCl in dimethylformamide at 60 °C, which also resulted in ring closure to generate the TBS ether **10**, which was purified chromatographically and desilylated by tetra-*n*-butylammonium fluoride (TBAF) to form aegiceradienol (**3**) in 55% overall yield from vinyl triflate.[9−11] Comparison of synthetic TBS ether **10** with an authentic sample revealed identity with respect to ^{1}H and ^{13}C NMR spectra, melting point, mixture melting point, optical rotation, and IR, UV, and mass spectra. In addition, synthetic and authentic samples of **10** showed identical TLC behavior.

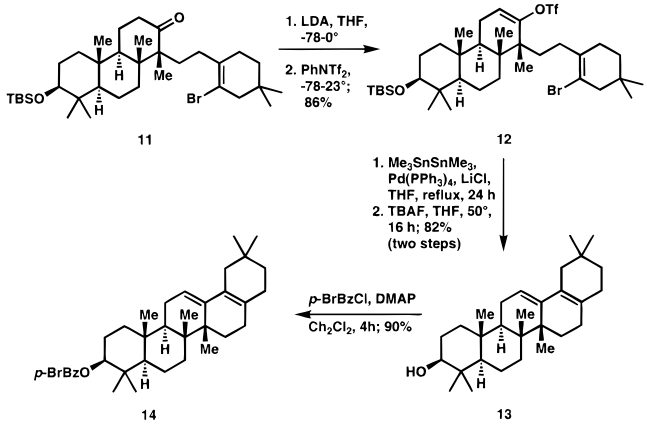
The allylic bromide **6**, which was utilized in the three-component coupling outlined above (Scheme 2), was readily prepared from 3,3-dimethylcyclohexanone[12] as shown in Scheme 3.[13]

Scheme 3



The byproduct in the cyclization reaction **7** → **8** (Scheme 2) was identified as **11** by the chemical conversions outlined in Scheme 4. In a sequence resembling that used for the synthesis of aegiceradienol **3** from tetracyclic ketone **8**, **11** was transformed via the vinyl triflate **12** into the corresponding vinyltrimethyltin derivative by reaction with hexamethyldistannane in the presence of $Pd(Ph_3P)_4$ and LiCl as catalysts in THF at reflux. The vinyltin intermediate was not isolated because under the conditions for its formation it underwent internal Stille coupling to produce directly the 3-TBS ether of the C(14) diastereomer of aegiceradienol. The structure of this product was demonstrated after desilylation to **13**, conversion to the *p*-bromobenzoate **14**, and single-crystal X-ray crystallographic analysis.[14] The internal Stille cyclization reaction to form **13** was efficient (82% yield over two steps, stannylation and cyclization) and much more facile than that with the C(14)-isomeric substrate **9** (which did not undergo any Stille cyclization under the same conditions).

Scheme 4



In summary, a new approach for the enantioselective synthesis of pentacyclic triterpenes of the β-amyrin family has been developed, which is remarkably direct as compared to previously known routes to this type of structure. Each synthetic intermediate was obtained in >95% purity by 400 MHz ^{1}H NMR analysis. Key steps include the asymmetric synthesis of the chiral epoxide **5**, its use in a three-component coupling to generate **7** stereospecifically, and finally the sequence of cation-π triple cyclization and internal cuprous chloride promoted ring closure which generates the pentacyclic target.

Experimental Section

(10*R*)-(2*E*,6*E*)-10,11-Dihydroxy-10,11-dihydrofarnesyl Acetate. A mixture of Noe-Lin catalyst (17 mg, 15 μmol),[5] $K_2OsO_4 \cdot H_2O$ (2.8 mg, 7.5 μmol), $K_3Fe(CN)_6$ (1.48 g, 4.5 mmol), K_2CO_3 (0.62 g, 4.5 mmol), $CH_3SO_2NH_2$ (143 mg, 1.5 mmol), and 2,6-*E*,*E*-farnesyl acetate (396 mg, 1.5 mmol) in 15 mL of 1:1 *t*-BuOH−H_2O was stirred at 7 °C for 32 h. The reaction was quenched with 6 mL of saturated Na_2SO_3 and 6 mL of saturated $Na_3S_2O_3$ at 0 °C, and was then allowed to warm to 23 °C and stirred for 45 min. After removal of *t*-BuOH under reduced pressure, the reaction mixture was extracted four times with 25 mL of ether. The combined extract was washed with 5 mL of 3 M NaOH,

(8) Wulff, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277.

(9) For examples of copper(I) mediated cyclization of vinyl iodides see: Piers, E.; Wong, T. *J. Org. Chem.* **1993**, *58*, 3609.

(10) Attempts to effect the ring closure of the trimethylstannyl derivative from **9** to pentacycle **10** by intramolecular Stille ring closure were not successful. See: Mori, M.; Kaneta, N.; Shibasaki, M. *J. Org. Chem.* **1991**, *56*, 3486.

(11) Success in the CuCl-mediated ring closure to form **10** depends critically on removal of Pd species and LiCl from the vinyl tin substrate (readily accomplished by filtration of the crude material through a column of basic alumina).

(12) Cormier, R. *Synth. Commun.* **1981**, *11*, 295.

(13) See: Rajamannar, T.; Balasubramanian, K. K. *Tetrahedron Lett.* **1988**, *29*, 5789.

(14) Detailed X-ray crystallographic data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

followed by 5 mL of brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel chromatography (20−50% EtOAc in hexanes) to give 290 mg of (10*R*)-10,11-dihydroxy-10,11-dihydrofarnesyl acetate (65%). A total of 67 mg (17%) of unreacted farnesyl acetate was also recovered. Further elution of the column with 20% EtOH in EtOAc removed a mixture of tetraol byproducts. Finally, eluting the column with 10:1:0.1 CH_2Cl_2−MeOH−NH_4OH gave 11.2 mg (66%) of the Noe-Lin catalyst.

Analytical data for (10*R*)-10,11-dihydroxy-10,11-dihydrofarnesyl acetate: $R_f = 0.60$ (EtOAc); $[\alpha]^{23}_D$ +20.8 (*c* 0.72, MeOH); FTIR (film) 3440, 2974, 2930, 1740, 1723, 1446, 1383 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.33 (dt, $J = 7.0$, 1.2 Hz, 1H), 5.16 (dt, $J = 6.8$, 0.9 Hz, 1H), 4.58 (d, $J = 7.0$ Hz, 2H), 3.34 (dd, $J = 10.5$, 1.8 Hz, 1H), 2.23 (m, 1 H), 2.14 (m, 2H), 2.09 (s, 3H), 2.05 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H), 1.57 (m, 1H), 1.42 (m, 1H), 1.39 (s, 3H), 1.17 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 142.0, 135.4, 124.4, 118.5, 78.1, 73.0, 61.5, 39.4, 36.7, 29.6, 26.4, 26.0, 23.3, 21.1, 16.4, 15.9 ppm; HRMS (CI, M + NH_4^+) calculated for $[C_{17}H_{30}O_4 + NH_4]^+$ 316.2488, found 316.2496.

The enantiomeric excess of (10*R*)-10,11-dihydroxy-10,11-dihydrofarnesyl acetate was determined as 96% by ^1H NMR analysis of its corresponding mono-(*S*)-MTPA ester: ^1H NMR (500 MHz, C_6D_6): δ 3.54 (s, 3H) for the *S* enantiomer; δ 3.47 (s, 3H) for the *R* enantiomer, corresponding to the methyl group on the α-methoxy group of the ester. The following is the procedure used for conversion of (10*R*)-10,11-dihydroxy-10,11-dihydrofarnesyl acetate to its mono-MTPA ester. A mixture of (10*R*)-10,11-dihydroxy-10,11-dihydrofarnesyl acetate (6 mg, 0.02 mmol), (*S*)-(+)-methoxy-α-(trifluoromethyl)phenylacetyl chloride (7.5 μL, 0.04 mmol) and DMAP (10 mg, 0.08 mmol) in dry CH_2Cl_2 (0.8 mL) was stirred at 23 °C for 1 h. The reaction mixture was then passed through a short column of silica gel, which was further eluted with 10 mL of ether. The eluent was concentrated to give the desired (*S*)-MTPA ester as a colorless oil, which is used directly for ^1H NMR analysis.

(10*S*)-(2*E*,6*E*)-10,11-Oxidofarnesol. To a solution of (10*R*)-10,11-dihydroxy-10,11-dihydrofarnesyl acetate (371 mg, 1.24 mmol) and pyridine (1.5 mL, 18.5 mmol) in 3 mL of dry CH_2Cl_2 at 0 °C was added MsCl (154 μL, 2.0 mmol). After the reaction mixture was stirred at 23 °C for 12 h, it was diluted with 17 mL of MeOH and treated with K_2CO_3 (1.7 g, 12 mmol), and stirring was continued for 5 h. The reaction mixture was diluted with 17 mL of water, and the volatile materials were removed in vacuo. The product was extracted three times with 25 mL of EtOAc. The combined extract was washed twice with 40 mL of aqueous $CuSO_4$ (to remove pyridine), followed by brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel chromatography (20% EtOAc in hexanes) to give 275 mg of pure (10*S*)-(2*E*,6*E*)-10,11-oxidofarnesol (93%) as a colorless oil. R_f = 0.56 (50% EtOAc in hexanes); $[\alpha]^{23}_D$ −5.2 (*c* 1.0, MeOH), lit.[14] $[\alpha]^{23}_D$ −2.0 (*c* 1.0, MeOH); FTIR (film) 3419, 2962, 2925, 2859, 1448, 1403, 1379, 1250 cm^{-1}; ^1H NMR (400 M Hz, $CDCl_3$) δ 5.39 (br t, J = 6.9 Hz, 1H), 5.14 (br t, $J = 6.7$ Hz, 1H), 4.13 (d, $J = 6.8$ Hz, 2H), 2.69 (t, $J = 6.2$ Hz, 1H), 2.02−2.16 (m, 6H), 1.66 (s, 3H), 1.62 (m, 2H), 1.61 (s, 3H), 1.29 (s, 3H), 1.25 (s, 3H) ppm; ^{13}C NMR (101 M Hz, $CDCl_3$) δ 139.4, 134.4, 124.6, 123.7, 64.2, 59.4, 58.4, 39.4, 36.4, 27.3, 26.2, 24.9, 18.8, 16.3, 16.0 ppm; HRMS (CI, M + NH_4^+) calculated for $[C_{15}H_{26}O_2 + NH_4]^+$ 256.2277, found 256.2271.

(12*S*)-(4*E*,8*E*)-1-*tert*-Butyldimethylsilyl-12,13-oxido-5,9,13-trimethyl-4,8-tetradecadien-1-one (5). To a solution of (10*S*)-(2*E*,6*E*)-10,11-oxidofarnesol (238 mg, 1.0 mmol) and Et_3N (0.2 mL, 1.4 mmol) in 5 mL of dry THF at −42 °C was added MsCl (101 μL, 1.3 mmol) and the mixture was stirred at this temperature for 45 min. The reaction mixture was warmed to 0 °C. A 2 M solution of LiBr (2.5 mL, 5.0 mmol) in THF was added. After the reaction mixture was stirred at 0 °C for 1 h, it was partitioned between 25 mL of hexane and 20 mL of ice cold water. The organic phase was separated. The aqueous phase was extracted three times with 20 mL of hexanes. The combined hexanes extract was successively washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo to give 285 mg (95%) of (10*S*)-(2*E*,6*E*)-10,11-oxidofarnesyl bromide, which was dried azeotropically with toluene and used in the next step without further purification. $R_f = 0.49$ (30% ether in hexanes); FTIR (film) 2961, 2925, 1449, 1378 cm^{-1}; ^1H NMR (400 M Hz, $CDCl_3$) δ 5.53 (dt, $J = 8.5$, 1.3 Hz, 1H), 5.13 (m, 1H), 4.02 (d, $J = 8.5$ Hz, 2H), 2.70 (t, $J = 6.2$ Hz, 1H), 2.06−2.16 (m, 7H), 1.73 (s, 3H), 1.65 (m, 2H), 1.64 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H) ppm; ^{13}C NMR (101 M Hz, $CDCl_3$) δ 143.5, 134.8, 124.0, 120.7, 64.2, 58.4, 39.5, 36.4, 29.7, 27.5, 26.1, 25.0, 18.8, 16.1, 16.0 ppm.

To a solution of LDA (prepared by addition of 1.0 mL of a 1.6 M solution of BuLi in hexanes to a solution of 1.76 mmol of diisopropylamine in 5 mL of THF) was added at −30 °C the imine, (1-*tert*-(butyldimethylsilyl)ethylidene)(2-methoxy-1-methylethyl)amine (0.45 mL, 1.5 mmol) via syringe. The resulting yellow solution was warmed to 0 °C for 30 min, and then cooled to −30 °C. A solution of (10*S*)-(2*E*,6*E*)-10,11-oxidofarnesyl bromide (285 mg, 0.95 mmol) in 2.0 mL of dry THF was added via cannula. The reaction mixture was slowly warmed to −10 °C over 1 h, and quenched with 3.5 mL of saturated NH_4Cl at −78 °C. The mixture was partitioned between 25 mL of ether and 25 mL of brine. The organic phase was separated and the aqueous phase was extracted three times with 20 mL of ether. The combined ether extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was dissolved in 6 mL of pentane, and treated with 6 mL of NaOAc−AcOH buffer (prepared by dissolving 3.3 g of NaOAc and 7 mL of AcOH in 30 mL of water). After the reaction mixture was stirred vigorously at 23 °C for 2 h, it was diluted with 30 mL of water and extracted three times with 30 mL of hexanes. The combined hexanes extract was successively washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel chromatography (6% ether in hexanes) to give acylsilane **5** (340 mg, 90% from oxidofarnesol). $R_f = 0.48$ (2:1 hexanes−ether); $[\alpha]^{23}_D$ −2.4 (*c* 0.54, MeOH); FTIR (film) 2958, 2929, 2858, 1641, 1463, 1378 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 5.21 (m, 2H), 2.56 (t, $J = 6.0$ Hz, 1H), 2.51 (m, 2H), 2.37 (m, 2H), 2.12 (m, 2H), 2.03 (m, 2H), 1.52−1.62 (m, 2H), 1.59 (s, 3H), 1.55 (s, 3H), 1.15 (s, 3H), 1.10 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (101 M Hz, C_6D_6) δ 244.3, 135.5, 134.4, 125.0, 124.1, 63.5, 57.3, 50.3, 40.0, 36.8, 28.0, 27.0, 26.5, 25.0, 21.1, 18.9, 16.6, 16.02, 16.00, −7.0 ppm; HRMS (CI, M + NH_4^+) calculated for $[C_{23}H_{42}SiO_2 + NH_4]^+$ 396.3298, found 396.3293.

(15*S*)-(3*Z*,7*E*,11*E*)-1-(2-Bromo-4,4-dimethyl-1-cyclohexenyl)-4-*tert*-butyldimethylsiloxy-15,16-oxido-3,8,12,16-tetramethyl-3,7,11-pentadecatriene (7). To a solution of *t*-BuLi (1.94 mL of a 1.7 M solution in pentane, 3.3 mmol) in 2.0 mL of Et_2O at −78 °C was added 2-bromopropene (200 mg, 1.65 mmol) via syringe. After the mixture was stirred at −78 °C for 30 min, it was warmed to 0 °C for 30 min and recooled to −78 °C. A solution of (12*S*)-(4*E*,8*E*)-1-*tert*-butyldimethylsilyl-12,13-oxido-5,9,13-trimethyl-4,8-tetradecadien-1-one (**5**, 500 mg, 1.32 mmol,) in 2.0 mL of Et_2O, precooled to −78 °C, was added via cannula. After 1 h of stirring at −78 °C, a 0.2 M solution of BaI_2 in THF (10 mL, 2.0 mmol) was added via syringe. The resulting yellow slurry was stirred at −78 °C for 1 h. 2-Bromo-1-bromomethyl-4,4-dimethyl-1-cyclohexene (**6**, 558 mg, 2.0 mmol) was added via syringe. After the mixture was stirred at −78 °C for 1h, it was warmed to 0 °C to give a clear solution. After the reaction was stirred at 0 °C for 30 min, it was quenched by the addition of 15 mL of a 0.5 M pH 7 phosphate buffer followed by warming to 23 °C. The mixture was filtered through a pad of Celite. The filtrate was extracted three times with hexanes. The combined hexanes extract was dried over Na_2SO_4 and evaporated in vacuo to give the crude product as a clear oil, which was purified by silica gel chromatography (1−1.5% EtOAc in hexanes) to give 691 mg of pure **7** (84%) as a clear oil. $[\alpha]^{23}_D$ −2.74 (*c* 0.73, benzene); R_f = 0.27 (10% EtOAc in hexanes; ceric ammonium molybdate, CAM); FTIR (film) 2957, 2928, 2858, 1670, 1459, 1452, 1381, 1254 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.31 (t, $J = 7.0$ Hz, 1H), 5.25 (t, $J = 6.8$ Hz, 1H), 2.56 (t, $J = 6.2$ Hz, 1H), 2.47−2.29 (m, 6H), 2.26 (br s, 2H), 2.26−2.18 (m, 9H), 1.74 (s, 3H), 1.66 (s, 3H), 1.63−1.47 (m, 3H), 1.19 (t, $J = 6.3$ Hz, 2H), 1.15 (s, 3H), 1.10 (s, 3H), 1.04 (s, 9H), 0.78 (s, 6H), 0.17 (s, 6H) ppm; ^{13}C NMR (101 MHz, C_6D_6) δ 145.0, 135.4, 134.8, 134.4, 125.1, 124.3, 118.3, 113.2, 63.5, 57.3, 50.5, 40.2, 36.9, 35.5, 35.3, 32.8, 32.0, 29.5, 28.8, 28.0, 27.8, 27.1, 26.6, 26.2, 25.0, 18.9, 18.6, 16.7, 16.2, 16.1, −3.6 ppm. HRMS (FAB, M + Na^+) calculated for $[C_{35}H_{61}O_2SiBr + Na]^+$ 643.3522, found 643.3554.

(1*S*,4a*R*,4b*R*,7*S*,8a*R*,10a*R*)-1-[2-(2-Bromo-4,4-dimethylcyclohex-1-enyl)ethyl]-7-*tert*-butyldimethylsiloxy-1,4b,8,8,10a-pentamethyldodecahydrophenanthren-2-one (8). A solution of **7** (30 mg, 48 μmol) dissolved in a mixture of 3.6 mL of hexanes and 1.2 mL of CH_2Cl_2 was cooled to −78 °C. A solution of 1.0 M $MeAlCl_2$ (56 μL, 56 μmol) in hexanes was diluted in a mixture of 2.1 mL of hexanes and 0.70 mL of CH_2Cl_2 and also cooled to −78 °C. The diluted solution of $MeAlCl_2$ was added to the solution of **7** via cannula. After the addition was complete, the mixture was stirred at −78 °C for another 30 min. Et_3N (57 mg, 0.56 mmol) was added, followed by 0.5 mL of 4:1 MeOH−H_2O. The mixture was warmed to room temperature and poured into 5 mL of water. After separation of the layers, the aqueous phase was extracted three times with 5 mL of ether. The combined organic extract was washed with brine, dried over Na_2SO_4, and evaporated in vacuo to give the crude product as a white foam, which was azeotropically dried by evaporating with toluene. To a solution of the dried crude product in 1.0 mL of CH_2Cl_2 was added TBSCl (11 mg, 72 μmol) and imidazole (6.6 mg, 96 μmol). The resulting mixture was refluxed for 20 h. After the mixture had been cooled to 23 °C, the whole was passed through a short column of silica gel, which was further eluted with 20 mL of CH_2Cl_2. The eluent was concentrated in vacuo to give the crude product as a white foam, which was purified by preparative TLC (eluted with benzene) to give two pure products.

Analytical data for **8**: 15.6 mg (52%) of white solid; mp 210−211 °C (recrystalized from CH_2Cl_2−pentane); $[\alpha]^{23}_D$ +12.8 (*c* 1.04, benzene); R_f = 0.47 (benzene, CAM); FTIR (film) 2947, 1706, 1466, 1433, 1389, 1252 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (dd, *J* = 11.4, 4.7 Hz, 1H), 2.54 (td, *J* = 13.4, 7.0 Hz, 1H), 2.36 (dt, *J* = 17.7, 5.6 Hz, 1H), 2.28−2.01 (m, 4H), 2.23 (br s, 2H), 1.95−1.42 (m, 12H), 1.40−1.31 (m, 1H), 1.38 (t, *J* = 6.3 Hz, 2H), 1.20 (s, 3H), 1.02 (m, 1H), 0.91 (br s, 6H), 0.89 (s, 3H), 0.88 (s, 9H), 0.86 (s, 3H), 0.82 (s, 3H), 0.71 (s, 3H), 0.02 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.1, 135.9, 117.4, 79.2, 55.5, 55.2, 50.7, 50.2, 44.5, 39.5, 39.1, 38.1, 37.6, 35.5, 34.2, 32.7, 32.2, 28.5, 27.8, 27.4, 27.0, 26.0, 22.9, 18.5, 18.2, 17.9, 16.8, 16.7, 16.0, −3.7, −4.9 ppm. HRMS (FAB, M + Na^+) calculated for $[C_{35}H_{61}O_2SiBr + Na]^+$ 643.3522, found 643.3513.

The byproduct is **(1*R*,4a*R*,4b*R*,7*S*,8a*R*,10a*R*)-1-[2-(2-Bromo-4,4-dimethylcyclohex-1-enyl)ethyl]-7-*tert*-butyldimethylsiloxy-1,4b,8,8,-10a-pentamethyldodecahydrophenanthren-2-one (11)**: 6.9 mg (23%) of a colorless oil; $[\alpha]^{23}_D$ −6.35 (*c* 0.63, benzene); R_f = 0.30 (benzene, CAM); FTIR (film) 2952, 2899, 2857, 1708, 1466, 1390, 1363, 1253 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.23 (dd, *J* = 11.4, 4.7 Hz, 1H), 2.57 (td, *J* = 13.7, 7.1 Hz, 1H), 2.33−2.21 (m, 3H), 2.12−1.99 (m, 3H), 1.88−1.69 (m, 5H), 1.65−1.30 (m, 10H), 1.06 (td, *J* = 13.0, 3.5 Hz, 1H), 0.93 (s, 3H), 0.92 (s, 3H), 0.91 (s, 6H), 0.88 (s, 3H), 0.87 (s, 9H), 0.83 (s, 3H), 0.72 (s, 3H), 0.03 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 134.2, 118.8, 79.2, 56.7, 55.4, 50.2, 50.0, 43.7, 39.5, 39.1, 39.0, 37.6, 35.4, 34.6, 32.13, 32.08, 31.4, 28.7, 28.5, 28.3, 27.8, 27.6, 26.0, 22.3, 18.4, 18.2, 18.0, 16.8, 16.1, 13.7, −3.7, −4.8 ppm. HRMS (FAB, M + Na^+) calculated for $[C_{35}H_{61}O_2SiBr + Na]^+$ 643.3522, found 643.3530.

1,1,1-Trifluoromethanesulfonic Acid (1*S*,4a*R*,4b*R*,7*S*,8a*R*,10a*R*)-1-[2-(2-Bromo-4,4-dimethylcyclohex-1-enyl)ethyl]-7-*tert*-butyldimethylsiloxy-1,4b,8,8,10a-pentamethyl-1,4,4a,4b,5,6,7,8,8a,9,-10,10a-dodecahydrophenanthren-2-yl Ester (9). To a solution of **8** (45 mg, 72 μmol) in 0.36 mL of THF cooled at −78 °C was added a freshly prepared 0.50 M LDA solution in THF (220 μL, 0.11 mmol,). After the mixture was stirred at −78 °C for 30 min, it was warmed to 0 °C and stirred for another 1 h. The solution was cooled to −78 °C, and solid $PhNTf_2$ (41 mg, 0.12 mmol, 1.6 equiv) was added. After the mixture was stirred at −78 °C for 30 min, it was warmed to 23 °C and stirred at that temperature for 1.5 h. The reaction was quenched by the addition of 3 mL of water. After the aqueous phase was extracted three times with 10 mL of hexanes, the combined hexanes extract was dried over $MgSO_4$, passed through a short column of silica gel, and concentrated in vacuo to give crude **9** as a yellow solid, which was purified by preparative TLC (eluted with 3% EtOAc in hexanes) to give 46 mg of pure **9** (84%) as a white foam. $[\alpha]^{23}_D$ +1.43 (*c* 0.63, benzene); R_f = 0.59 (5% EtOAc in hexanes, CAM); FTIR (film) 2954, 2930, 2857, 1413, 1390, 1247 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63 (t, *J* = 4.1 Hz, 1H), 3.17 (dd, *J* = 11.2, 4.5 Hz, 1H), 2.29 (m, 1H), 2.24 (br s, 2H), 2.19−2.03 (m, 5H), 1.66−1.43 (m, 9H), 1.43−1.31 (m, 4H), 1.15 (s, 3H), 0.98 (s, 3H), 0.97 (m, 1H), 0.93 (s, 3H), 0.91 (s, 6H), 0.89 (s, 3H), 0.87 (s, 9H), 0.73 (s, 3H), 0.02 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 135.1, 118.4 (q, *J* = 321 Hz), 118.3, 115.2, 79.2, 55.3, 50.2, 47.8, 46.0, 42.1, 39.4, 38.9, 37.1, 35.4, 34.4, 33.6, 32.1, 30.1, 28.6, 28.4, 28.1, 27.7, 27.6, 26.0, 21.8, 20.2, 18.4, 18.2, 16.7, 16.2, −3.7, −4.9 ppm.

Aegiceradienol (3). To a solution of **9** (30 mg, 40 μmol) and Pd-$(PPh_3)_4$ (0.9 mg, 0.80 μmol) in 1.0 mL of THF was added 0.48 mL of a 0.5 M LiCl solution in THF (0.24 mmol), followed by $Me_3SnSnMe_3$ (26 mg, 80 μmol) via syringe. The resulting light yellow solution was heated at reflux for 16 h. The reaction mixture was cooled to room temperature. Et_3N (0.10 mL) and cyclohexane (7 mL) were added with stirring. The resulting mixture was then filtered through a short column of basic alumina (0.8 × 3 cm), which was further eluted with 20 mL of cyclohexane. The eluent was concentrated in vacuo to give the crude product as a white foam, which was dried azeotropically by evaporating with toluene.

To the above crude product was added 3.0 mL of DMF and the mixture was heated to 60 °C to give a clear solution. A suspension of CuCl (12 mg, 0.12 mmol) in 1.5 mL of DMF was also heated to 60 °C. This suspension of CuCl was added to the warm solution of crude product via cannula. The resulting mixture was stirred at 60 °C for 20 min and cooled to room temperature. A 1:1 mixture of concentrated NH_4OH and saturated NH_4Cl (2 mL) was added. The mixture was stirred open to air for 1 h. The mixture was further diluted with 10 mL of water and extracted three times with 10 mL of cyclohexane. The combined organic extract was washed once with 10 mL of brine, dried over Na_2SO_4, and concentrated in vacuo to give the crude product as a white foam, which was purified by preparative TLC impregnated with $AgNO_3$, eluted with pentane, to give 12.5 mg (60%) of **10** as a white solid. Mp 196.2−197.5 °C; $[\alpha]^{23}_D$ +71.8 (*c* 0.11, benzene); UV λ_{max} = 244 nm; R_f = 0.33 (hexanes, CAM); FTIR (film) 2934, 2904, 2877, 2856, 2835, 1465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (m, 1H), 3.19 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.15−1.83 (m, 7H), 1.78−1.18 (m, 15H), 0.97 (s, 3H), 0.96 (s, 3H), 0.910 (s, 3H), 0.906 (s, 3H), 0.89 (s, 9H), 0.88 (s, 3H), 0.86 (s, 6H), 0.74 (s, 3H), 0.02 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 129.1, 125.4, 116.7, 79.5, 55.6, 47.5, 41.2, 39.6, 39.4, 38.9, 38.7, 37.0, 35.3, 34.0, 29.5, 29.4, 28.9, 28.6, 28.45, 28.37, 27.8, 27.3, 23.6, 21.1, 18.6, 18.2, 16.9, 16.2, 16.1, −3.7, −4.8 ppm. HRMS (FAB, M^+) calculated for $[C_{35}H_{60}OSi]^+$ 524.4414, found 524.4410. These are identical with the data obtained from an authentic sample.

The product obtained above was dissolved in 0.10 mL of a 1.0 M solution of TBAF in THF (0.10 mmol) and stirred at 50 °C for 14 h. The solution was cooled to room temperature. NH_4Cl (20 mg) was added. After the mixture was stirred at room temperature for another 15 min, it was diluted with 5 mL of EtOAc. The whole was filtered through a short column of silica gel, which was further eluted with 10 mL of EtOAc. The eluent was concentrated in vacuo to give the crude product as a white foam, which was purified by preparative TLC and eluted with 20% EtOAc in hexanes to give 9.0 mg (92%) of pure aegiceradienol (**3**) as a white solid. Mp 191−192 °C [lit.[15] mp 185−188 °C]; $[\alpha]^{23}_D$ +74.3 (*c* 0.33, benzene) [lit. $[\alpha]^{23}_D$ +74 (*c* 0.83)];[15] R_f = 0.31 (20% EtOAc in hexanes, CAM); FTIR (film) 3327, 3053, 2945, 2931, 2904, 2874, 2834, 1451, 1264 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (m, 1H), 3.20 (dd, *J* = 10.8, 5.7 Hz, 1H), 2.08−1.82 (m, 7H), 1.74−1.20 (m, 16H), 0.98 (s, 3H), 0.95 (s, 3H), 0.94 (s, 3H), 0.88 (s, 3H), 0.85 (s, 6H), 0.77 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 129.1, 125.3, 116.6, 79.0, 55.5, 47.4, 41.2, 39.6, 38.8, 38.6, 37.1, 35.3, 33.9, 29.5, 29.3, 28.9, 28.4, 28.3, 28.1, 27.35, 27.30, 23.5, 21.1, 18.4, 16.9, 16.0, 15.7 ppm. HRMS (EI, M^+) calculated for $[C_{29}H_{46}O]^+$ 410.3549, found 410.3533. These are identical in all aspects with the authentic sample.

2-Bromo-1-hydroxymethyl-4,4-dimethyl-1-cyclohexene. PBr_3 (23.2 g, 86 mmol) was added dropwise to a solution of DMF (6.95 g, 95 mmol) in 25 mL of chloroform at 0 °C. The white suspension was warmed to 70 °C for 30 min. 3,3-Dimethylcyclohexanone (4.0 g, 32

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mmol) was added dropwise over a 30 min period via syringe. The resulting brown solution was stirred at 70 °C for another 1.5 h. The mixture was poured into 40 mL of 4 M NaOAc solution. Solid NaOH was added until the aqueous layer reached pH 7.

The mixture was extracted five times with 30 mL of hexanes. The combined hexanes extract was dried over Na_2SO_4, filtered, and concentrated to give the crude product, 2-bromo-4,4-dimethyl-1-cyclohexenecarboxaldehyde, as a light yellow oil, which was used in the subsequent reaction without further purification. An analytically pure sample was obtained by preparative TLC (eluted with 10% EtOAc in hexanes) as a clear oil. $R_f = 0.60$ (20% EtOAc in hexanes, $KMnO_4$); FTIR (film) 2957, 2928, 2868, 2855, 1680, 1621, 1224 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 2.51 (t, $J = 2.2$ Hz, 2H), 2.28 (tt, $J = 6.4$, 2.2 Hz, 2H), 1.44 (t, $J = 6.4$ Hz, 2H), 0.95 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 142.7, 134.0, 52.4, 33.9, 32.3, 27.8, 22.7 ppm; HRMS (EI, M^+) calculated for $[C_9H_{13}BrO]^+$ 216.0150, found 216.0140.

The crude product obtained above was dissolved in 60 mL of Et_2O and cooled to 0 °C. A 1.0 M solution of DIBAL in toluene (32 mL, 32 mmol) was added dropwise over 30 min. The resulting colorless solution was warmed to 23 °C and stirred for 1 h. The reaction was quenched by addition of 32 g of ground $Na_2SO_4 \cdot 10H_2O$ and stirring for 14 h. The mixture was then filtered. The solids were washed 4 times with 50 mL of Et_2O. The combined filtrate was concentrated in vacuo to give crude product as a colorless oil. Silica gel chromatography (5−7% EtOAc in hexanes) afforded 3.6 g (52%) of desired product as a colorless oil. $R_f = 0.27$ (20% EtOAc in hexanes, $KMnO_4$); FTIR (film) 3316, 2954, 2939, 2921, 2871, 2851, 1452, 1430, 1366 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.22 (s, 2H), 2.28 (br s, 2H), 2.26 (m, 2H), 1.9−1.4 (br, 1H), 1.42 (t, $J = 6.2$ Hz, 2H), 0.93 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.9, 120.5, 66.0, 50.2, 34.9, 32.1, 27.8, 26.8 ppm; HRMS (EI, M^+) calculated for $[C_9H_{15}BrO]^+$ 218.0306, found 218.0309.

2-Bromo-1-bromomethyl-4,4-dimethyl-1-cyclohexene (6). To a solution of 2-bromo-1-hydroxymethyl-4,4-dimethyl-1-cyclohexene (3.60 g, 16.4 mmol) in 33 mL of THF at −40 °C was added Et_3N (2.66 g, 26.3 mmol) and MsCl (2.45 g, 21.4 mmol) sequentially. After the mixture was stirred at −40 °C for 30 min, a 2 M solution of anhydrous LiBr in THF (25 mL, 49 mmol) was added via syringe. The mixture was warmed to 0 °C and stirred for 1 h. The reaction mixture was poured into a sepratory funnel containing 80 g of ice and 80 mL of hexanes. After separation, the aqueous layer was washed twice with 50 mL of hexanes. The combined hexanes extract was dried over Na_2SO_4 and passed through a short silica gel column that was further eluted with hexanes. The eluent was concentrated in vacuo to give 4.26 g of **6** (92%) as a colorless oil, which was pure and used in subsequent reactions without further purification. $R_f = 0.45$ (hexanes, $KMnO_4$); FTIR (film) 2956, 2922, 2870, 1649, 1432, 1366, 1344 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.11 (s, 2H), 2.30 (m, 4H), 1.45 (t, $J = 6.6$ Hz, 2H), 0.93 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.2, 123.9, 50.4, 36.3, 34.9, 32.2, 27.8, 27.1 ppm; HRMS (EI, M^+) calculated for $[C_9H_{14}Br_2]^+$ 279.9462, found 279.9469.

(1*R*,4a*R*,4b*R*,7*S*,8a*R*,10a*R*)-1-[2-(2-Bromo-4,4-dimethylcyclohex-1-enyl)ethyl]-7-*tert*-butyldimethylsiloxy-1,4b,8,8,10a-pentamethyl-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydrophenanthren-2-yl Trifluoromethanesulfonate (12) To a solution of **11** (98 mg, 0.16 mmol, 1.0 equiv) in 0.40 mL of THF cooled at −78 °C was added a freshly prepared 0.50 M LDA solution in THF (410 μL, 0.20 mmol, 1.3 equiv). After the mixture was stirred at −78 °C for 30 min, it was warmed to 0 °C and stirred for another 1 h. The solution was cooled to −78 °C, and $PhNTf_2$ (84 mg, 0.24 mmol, 1.5 equiv) was added as a solid. After the mixture was stirred at −78 °C for 30 min, it was warmed to 23 °C and stirred at that temperature for 1.5 h. The reaction was quenched by the addition of 3 mL of water. After the aqueous phase was extracted three times with 10 mL of hexanes, the combined hexanes extract was dried over $MgSO_4$, passed through a short column of silica gel, and concentrated in vacuo to give crude **12** as a yellow oil, which was purified by preparative TLC to give 102 mg of pure **12** (86%) as a white solid. Mp 141−142 °C; $[\alpha]^{23}_D$ +21.4 (*c* 1.68, benzene); $R_f = 0.58$ (5% EtOAc in hexanes, CAM); FTIR (film) 2954, 2933, 2859, 1466, 1409, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.74 (t, $J = 4.0$ Hz, 1H), 3.19 (dd, $J = 11.3$, 4.7 Hz, 1H), 2.27 (br s, 2H), 2.21 (m, 1H), 2.14−1.98 (m, 5H), 1.72−1.45 (m, 7H), 1.42−1.32 (m, 4H), 1.02 (s, 3H), 0.98 (m, 1H), 0.95 (s, 3H), 0.94 (m, 1H), 0.93 (m, 9H), 0.89 (s, 3H), 0.87 (s, 9H), 0.73 (s, 3H), 0.02 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 134.6, 118.7, 118.4 (q, $J = 320$ Hz), 106.7, 79.1, 55.2, 50.2, 47.1, 46.2, 41.8, 39.4, 38.9, 37.1, 35.8, 35.4, 33.8, 33.7, 32.1, 28.6, 28.0, 27.8, 27.7, 26.0, 22.0, 18.4, 18.2, 17.7, 16.9, 16.2, −3.7, −4.8 ppm.

(3*S*,4a*R*,6a*R*,6b*S*,14a*R*,14b*R*)-4,4,6a,6b,11,11,14b-Heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,9,10,11,12,14,14a,14b-octadecahydropicen-3-ol (13) To a solution of **12** (20 mg, 27 μmol, 1.0 equiv) and $Pd(PPh_3)_4$ (3.1 mg, 2.7 μmol, 0.10 equiv) in 1.5 mL of THF was added 0.32 mL of a 0.5 M LiCl solution in THF (0.16 mmol, 6.0 equiv), followed by $Me_3SnSnMe_3$ (39 mg, 0.12 mmol, 4.5 equiv) via syringe. The resulting light yellow solution was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and diluted with 10 mL of cyclohexane. The resulting mixture was passed through a short column of silica gel, which was further eluted with 20 mL of cyclohexane. The eluent was concentrated in vacuo to give a crude product as white solid, which was used in the next step without further purification.

The crude product obtained above was dissolved in 1.5 mL of THF. A 1.0 M solution of TBAF in THF was added (0.40 mL, 0.40 mmol, 5.0 equiv). The mixture was stirred at 50 °C for 18 h. After the mixture was cooled to 23 °C, it was diluted with 10 mL of ether and washed with 10 mL of water. The aqueous wash was extracted twice with 10 mL of ether. The combined ether extract was dried over Na_2SO_4 and concentrated in vacuo to give crude product as a white solid, which was purified with preparative TLC to give 11.4 mg (82%) of the desired product, **13**, as a white solid; mp 213-214 °C; $[\alpha]^{23}_D$ +36.1 (*c* 0.57, benzene); $R_f = 0.21$ (20% EtOAc in hexanes, CAM); FTIR (film) 3416, 2939, 2870, 2834, 1459, 1384 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.47 (dd, $J = 6.4$, 1.4 Hz, 1H), 3.18 (ddd, $J = 10.6$, 5.5, 5.5 Hz, 1H), 2.16 (br d, $J = 16.3$ Hz, 2H), 2.10−1.80 (m, 6H), 1.73−1.48 (m, 8H), 1.40−1.30 (m, 3H), 1.26 (d, $J = 5.7$ Hz, 1H), 1.17 (dd, $J = 11.9$, 4.2 Hz, 1H), 1.00−0.85 (m, 2H), 0.97 (s, 3H), 0.95 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H), 0.84 (s, 9H), 0.78 (s, 3H), 0.77 (s, 3H), 0.69 (dd, $J = 11.5$, 1.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 128.5, 126.7, 116.5, 79.0, 55.6, 48.9, 42.5, 40.6, 39.1, 38.8, 38.7, 37.1, 35.6, 34.9, 30.6, 30.3, 29.4, 29.2, 28.3, 27.8, 27.4, 26.3, 22.9, 18.5, 18.3, 16.7, 16.6, 15.9 ppm. HRMS (ES, M + H^+) calculated for $[C_{29}H_{46}O + H]^+$ 411.3627, found 411.3646.

(3*S*,4a*R*,6a*R*,6b*S*,14a*R*,14b*R*)-4,4,6a,6b,11,11,14b-Heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,9,10,11,12,14,14a,14b-octadecahydropicen-3-yl *p*-Bromobenzoate (14). To a solution of **13** (10 mg, 24 μmol, 1.0 equiv) in 250 μL of CH_2Cl_2, was added DMAP (7.4 mg, 61 μmol, 2.5 equiv) and *p*-bromobenzoyl chloride (10.7 mg, 49 μmol, 2.0 equiv). The mixture was stirred at 23 °C for 4 h. The mixture was diluted with 1 mL of CH_2Cl_2, and passed through a short column of silica gel, which was further eluted with another 10 mL of CH_2Cl_2. The eluent was concentrated in vacuo to give the crude product as a white solid, which was purified by preparative TLC (eluted with 20% benzene in hexanes) to give 13 mg (90%) of pure **14** as a white solid. Mp 233−234 °C; $[\alpha]^{23}_D$ +32.6 (*c* 0.27, benzene); $R_f = 0.35$ (20% benzene in hexanes, CAM); FTIR (film) 2945, 2873, 1717, 1590, 1460, 391, 1275 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.6$ Hz, 2H), 5.48 (d, $J = 6.2$ Hz, 1H), 4.70 (dd, $J = 9.3$, 5.5 Hz, 1H), 2.17 (br d, $J = 16.4$ Hz, 1H), 2.04 (m, 3H), 2.00−1.80 (m, 3H), 1.78−1.50 (m, 8H), 1.43−1.30 (m, 3H), 1.24 (m, 2H), 1.17−1.03 (m, 2H), 1.02 (s, 3H), 0.99 (s, 3H), 0.95 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.85 (s, 3H), 0.80 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 165.6, 144.8, 131.7, 131.1, 130.0, 127.9, 126.8, 116.3, 82.0, 55.8, 48.8, 42.6, 40.7, 39.1, 38.8, 38.2, 37.1, 35.7, 34.9, 34.5, 30.6, 30.3, 29.4, 29.2, 28.4, 27.8, 26.4, 23.8, 22.9, 18.5, 18.3, 17.3, 16.8, 16.6 ppm. HRMS (FAB, M + Na^+) calculated for $[C_{29}H_{46}O + H]^+$ 615.2816, found 615.2806. An X-ray crystal structure was also obtained to determine the absolute conformation of the stereocenters.

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