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Stereodivergent Synthesis of Enantioenriched 4-Hydroxy-2-cyclopentenones

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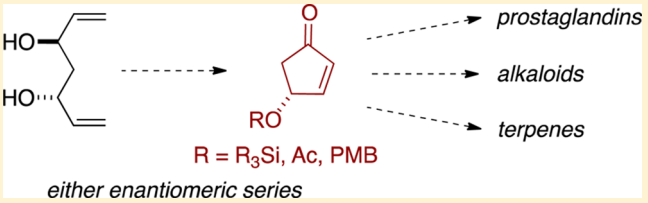
Supporting Information

ABSTRACT: Protected 4-hydroxycyclopentenones (4-HCPs) constitute an important class of intermediates in chemical synthesis. A route to this class of compound has been developed. Key steps include Noyori reduction (which establishes the stereochemistry of the product), ring-closing metathesis, and simple functional group conversions to provide a set of substituted 4-HCPs in either enantiomeric form.



Building blocks based on 4-hydroxycyclopentenone (4-HCP, **1**) are valuable for the synthesis of biologically active molecules.[1] Originally developed for the synthesis of prostaglandins,[2−4] protected 4-HCPs have been converted to numerous natural product structures, including alkaloids,[5−9] terpenes,[10−12] and others[13−20] (Figure 1). This diversity of

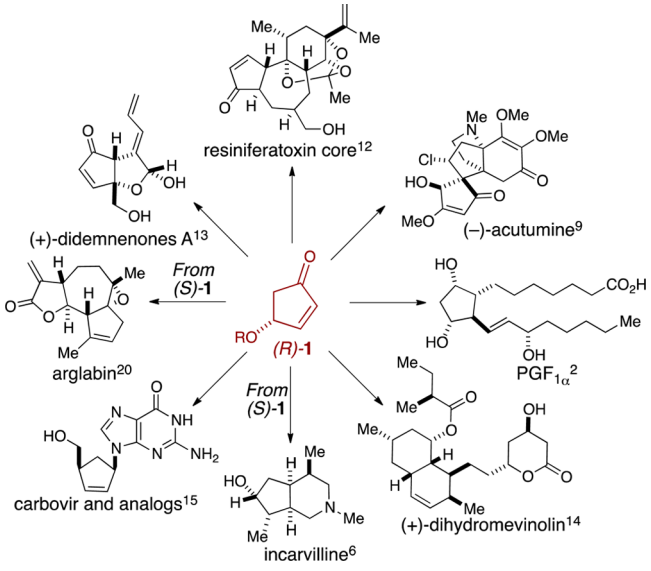


Figure 1. Representative applications of **1** in synthesis. Except where noted, these syntheses used (*R*)-**1** (shown) as starting material.

targets is such that it is reasonable to consider **1** a "privileged building block" for chemical synthesis. As such, means of preparing either (*R*)- or (*S*)-**1** in enantiomerically pure form with a variety of protecting groups has been vigorously pursued. In this Note, we describe a simple synthesis of a C_2-symmetrical diol, in either enantiomeric form, that can be converted to **1** and analogues useful in organic synthesis.

Enantioselective approaches to **1** include chiral pool members like tartaric acid, ribose, or arabinose as starting materials.[1] Figure 2a shows that Ogura's method, which as

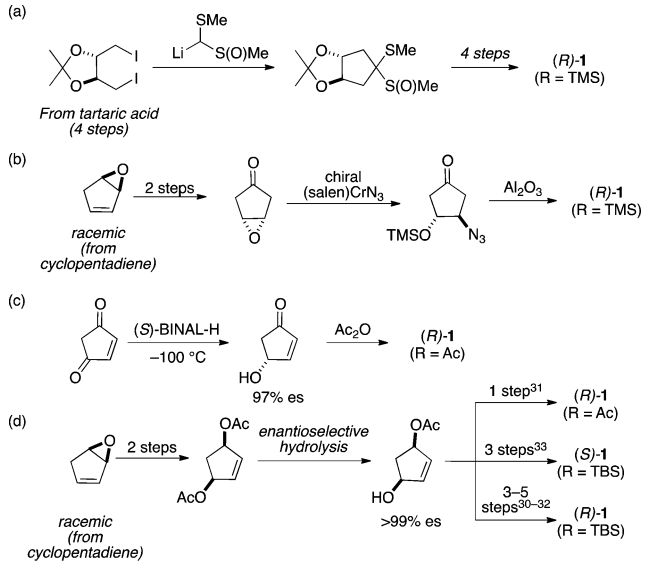


Figure 2. Representative approaches to (*R*)-**1**: (a) from tartaric acid,[21,22] (b) asymmetric epoxide opening,[24] (c) the Noyori reduction,[25] and (d) or enzymatic hydrolysis.[28,30−33]

further developed by Rokach, is the most commonly used method cited in this category.[21,22] Among a number of asymmetric syntheses that have appeared,[1,23] short routes that feature enantioselective ring-opening[24] or Noyori reduction[25] reactions stand out (Figure 2b,c). The latter, while brief, seems to be rarely used to prepare **1**, perhaps due to the requirement

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for severely cryogenic conditions and stoichiometric amounts of chiral reagent.

The preparation of enantiopure **1** by enzymatic catalysis has also been extensively investigated.[1,26,27] In particular, the esterase-promoted desymmetrization of *meso*-cyclopentenediol esters is very commonly cited by researchers using 4-HCPs and is one of the best-known examples of enzymatic reactions in organic synthesis (Figure 2).[28,29] The key step is the stereoselective hydrolysis of an enantiotopic acetate ester,[24] which affords an intermediate that is converted to TBS-protected enone (*R*)-**1**.[30−32] This route can be adapted to the synthesis of the *S*-configured series by modifying the protection/deprotection steps.[33]

Having used existing methods for procuring **1** as a starting material[5] and contemplating further such applications, we sought to develop an alternative enantioselective synthesis of these compounds. We specifically hoped to create a convenient route that would allow ready and equal access to either enantiomer. In seeking to develop such a route, we noticed that the simple step of formally inverting one of the alcohol stereocenters in *cis*-1,2-dihydroxycyclopent-4-ene changes the timing and nature of the stereochemical issues to be considered (Figure 3). In the enzymatic route, it is necessary to carry out

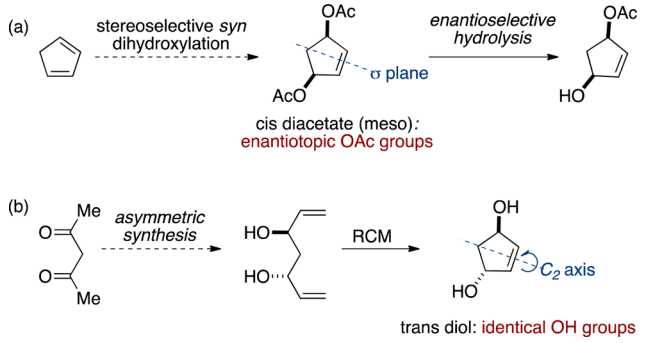
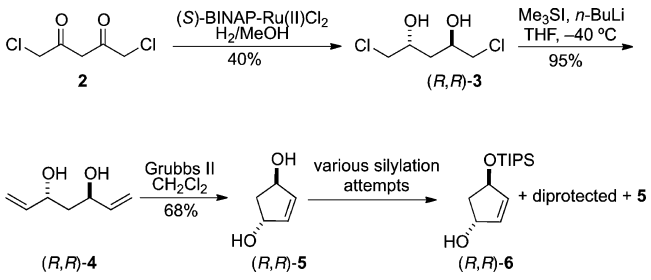


Figure 3. Stereochemical issues encountered en route to (a) a chiral *cis*-acetoxy alcohol and (b) a chiral *trans*-diol.

two stereocontrolled steps: (1) the synthesis of the *meso*-diacetate (i.e., only cis and not trans, generally accomplished from cyclopentadiene by $^1O_2$ chemistry or by epoxidation followed by acetolysis of a derived π-allyl species[34]) and (2) the enzyme-controlled enantioselective hydrolysis (Figure 3a).[24] In contrast, the corresponding *trans*-diol would no longer have planar symmetry but instead be a chiral, C_2-symmetric molecule (Figure 3b). Thus, it would no longer be necessary to differentiate the two identical alcohol groups in future steps. Moreover, we felt that it would be possible to readily prepare this diol using the known asymmetric conversion of diketone **2** to **4**,[35−38] followed by ring-closing metathesis (RCM; Scheme 1). Thus, only a single stereoselective reaction would be required in the entire synthesis.

To make this happen, commerically available 1,5-dichloro-2,4-pentanedione **2** (also readily made from acetylacetone[35]) was reduced as reported by Rychnovsky and co-workers to afford (*R,R*)-**3** in 40% yield and ca. 97% enantioselectivity (es; Scheme 1).[36,37] Following Hanson, treatment of diol **3** with the Corey−Chaykovsky reagent[39] gave diene diol **4** in 95% yield.[38] Various RCM conditions were tried, with the best results being obtained using Grubbs II[40] catalyst, which provided the cyclized product in 68% yield. In this way, diol **5** could be obtained in multigram amounts (enantiopure **5** is also available via

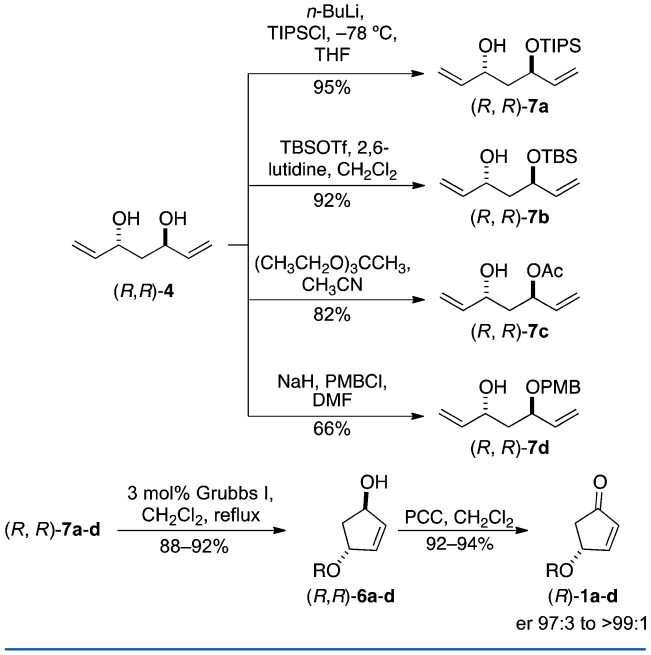
Scheme 1. Synthesis of C_2-Symmetric Diol 5 and Initial Protection Attempts



enzymatic resolution[41]). We were somewhat surprised to find that it was difficult to selectively carry out the monoprotection of **5** to afford ethers like **6**. Although the initial silylation of **5** could be easily accomplished, the monoprotected material seemed to more readily undergo a second reaction with silylating reagent, complicating the route by introducing an inconvenient separation step.

In contrast, the monoprotection of diol **4** proceeded smoothly to provide a set of alcohols (*R,R*)-**7** in moderate to excellent yields (Scheme 2). For example, TIPS-protected

Scheme 2. Monoprotection of Diol and Enone Synthesis



(*R,R*)-**7a** was obtained in 95% yield from diol **4** using *n*-BuLi and TIPSCl at −78 °C. As 4-HCPs appear in different protected guises in synthetic efforts, we prepared TBS-, acyl-, and *p*-methoxybenzyl-protected versions as shown. Here, monoprotected diol (*R,R*)-**7** was cyclized via RCM using Grubbs I catalyst[42] to obtain four examples of (*R,R*)-**6** shown in 88−92% yields. Finally, oxidation of (*R,R*)-**6** with pyridinium chlorochromate provided the targeted *O*-protected 4-hydroxy-2-cyclopentenones (*R*)-**1a−d** in high enantioselectivities. We routinely prepare compound **6** in ca. 5−7 g quantities.

This route can be modified for the synthesis of (*S*)-**1** by simply using (*R*)-BINAP in the hydrogenation step (Scheme 3). Besides no longer requiring different schemes for preparing the two enantiomers, the present route proceeds in acceptable overall yields from commercially available starting materials

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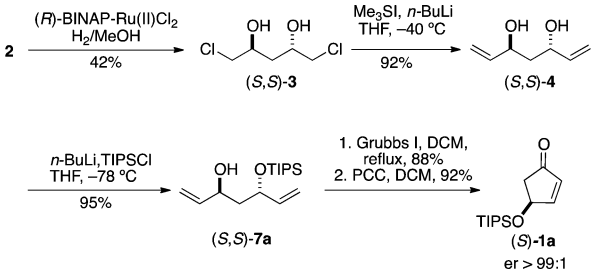
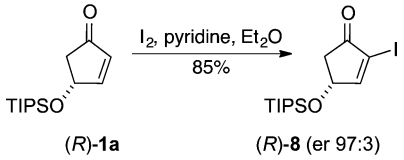
Scheme 3. Synthesis of (*S*)-1a



(26−32%) and compares favorably in number of steps compared to other methods (five steps from **2** to either (*R*)- or (*S*)-**1** as opposed to nine steps for the synthesis shown in Scheme 1a).

Another useful 4-HCP is the α-iodo derivative of enone **1a**, which has found applications in the synthesis of prostaglandins and other natural products (for leading examples, see Roche and Aitken[1]). Thus, we transformed both (*R*)- and (*S*)-**1a** into iodides **8** as shown in Scheme 4.

Scheme 4. Iodination of Enone 1a; (*S*)-8 was Similarly Obtained in ca. 99% es



Just as 4-HCPs have been broadly employed in synthesis,[2−20] the reduced alcohol precursor introduced herein should be of comparable utility. We close by providing a few examples of this potential in Scheme 5. Thus, epoxidation of allylic alcohol **6a** provided **9** exclusively in 66% yield (likely due to a reinforcing combination of Henbest-like delivery of peracid[43] and avoidance of the large OTIPS group). Epoxide opening occurred regioselectively with sodium azide to provide the highly substituted cyclopentane **10** in 69% yield. The stereo- and regiochemistry of the product **10** was confirmed by 2D NMR analysis of the corresponding diacetylated compound (see Supporting Information). In addition, amino-substituted cyclopentane derivatives **12**, **13**, and **14** were made using simple displacement chemistry.

In summary, we have demonstrated a convenient synthesis of 4-HCPs, an important class of privileged building blocks for organic synthesis. The route is scalable for laboratory usage and provides access to multiple analogues in either enantiomeric series of 4-HCPs using the identical route (save choice of catalyst).

EXPERIMENTAL SECTION

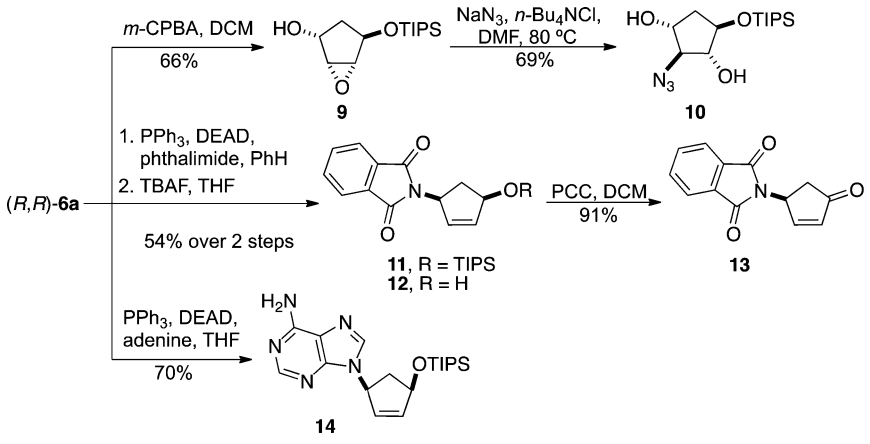
General Methods. All reactions were carried out in oven- or flame-dried glassware under argon atmosphere using standard gastight syringes, cannulas, and septa. Et_2O, THF, and DCM were purified by passage through neutral alumina columns using a commercial solvent purification system. All chemicals were used as received from commercial source without further purification. Flash chromatography was either carried out on a standard grade silica gel (40−63 mm particle size, 230−400 mesh) with compressed nitrogen as a source of positive pressure or on an automated purification system using silica flash column. Infrared (IR) spectra were acquired as thin films. All nuclear magnetic resonance spectra (^{1}H, ^{13}C, COSY, and 1D NOE) were recorded in deutrated chloroform on a 400 MHz instrument with a dual carbon/proton cryoprobe. Chemical shifts are reported in parts per million (ppm) and are referenced to the centerline of the solvent (δ 7.26 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR). High-resolution mass spectra (HRMS) were recorded with a time-of-flight mass spectrometer and an electrospray (ESI) or atmospheric pressure chemical ionization (APCI) ion source. Observed optical rotations were measured at 589 nm. The er values of compounds **1a−c** and compound **8** were determined by gas chromatography using a 5975CVL MSD triple-axis detector. The er value of the compound **1d** was determined by chiral HPLC on an IC column with a 996 UV detector.

Known Compounds. The following compounds were prepared as previously described: **2**,[1] (*R*,*R*)-**3** and its *S*,*S*-enantiomer,[35,36] and (*R*,*R*)-**4** and its *S*,*S*-enantiomer.[37]

*(1R,3R)-Cyclopent-4-ene-1,3-diol (**5**).* A solution of diol **4** (500 mg, 3.91 mmol) in DCM (78.2 mL) and methanol (78.2 mL) was purged with argon for 5 min, and 5 mol % of Grubbs II catalyst (166 mg) was added to it. The reaction mixture was stirred at rt for 6 h and was quenched with DMSO (1 mL). The reaction mixture was stirred under air for 5 min and concentrated. The crude product was purified by silica gel chromatography (100% EtOAc) to afford the product as colorless oil (266 mg, 68%): R_f = 0.20 (100% EtOAc); IR (neat) 3420 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05−6.01 (m, 2H), 5.07 (t, J = 4.8 Hz, 2H), 2.10 (t, J = 5.0 Hz, 2H), 1.56 (br s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 76.4, 44.4; m/z (ESI+) found $[M + H]^+$ 100.0518, $C_5H_8O_2$ requires 100.0524; $[\alpha]_D^{23.6}$ +232 (c 1.0, MeOH) [lit[41] $[\alpha]_D^{27}$ +228.1 (c 1.04, MeOH)].

*(3R,5R)-5-((Triisopropylsilyl)oxy)hepta-1,6-dien-3-ol (**7a**).* To a stirred solution of (*R*,*R*)-**4** (2.7 g, 21.1 mmol) in THF (200 mL) at

Scheme 5. Synthesis of Cyclopentane Derivatives



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−78 °C was added *n*-BuLi (8.4 mL, 2.5 M in hexanes, 21.1 mmol) dropwise. The solution was allowed to stir for 20 min at −78 °C followed by the slow addition of TIPSCl (4.9 mL, 21.1 mmol). After 2 h, the reaction was allowed to slowly warm to rt overnight and was quenched with saturated aqueous NH_4Cl (100 mL). The phases were separated, and the aqueous layer was washed with EtOAc (3 × 100 mL). The combined organic layer was washed with water (100 mL) and brine, dried (Na_2SO_4), filtered, and concentrated. The crude extract was purified by silica gel chromatography (10% EtOAc/hexanes) to afford the product as yellow oil (5.4 g, 96%): R_f = 0.73 (20% EtOAc/hexanes); IR (neat) 3423 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (ddd, J = 17.1, 10.5, 5.9, 1H), 5.83 (ddd, J = 17.1, 10.4, 5.6, 1H), 5.26 (ddd, J = 12.0, 1.5, 1.5 Hz, 1H), 5.22 (ddd, J = 11.8, 1.4, 1.4 Hz, 1H), 5.14 (ddd, J = 10.5, 1.4, 1.4 Hz, 1H), 5.09 (ddd, J = 10.5, 1.5, 1.5 Hz, 1H), 4.62−4.56 (m, 1H), 4.47−4.37 (m, 1H), 3.59 (bs, 1H), 1.87 (ddd, J = 14.0, 9.6, 4.4 Hz, 1H), 1.68 (ddd, J = 14.4, 4.4, 2.8 Hz, 1H), 1.03−1.10 (m, 21H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 140.9, 140.0, 114.9, 114.0, 73.2, 69.6, 43.2, 18.01, 17.99, 12.2; m/z (ESI+) found $[M + H]^+$ 285.2253, $C_{16}H_{32}O_2Si$ requires 285.2255; $[\alpha]_D^{23.6}$ −5.4 (c 1.0, DCM); (3*S*,4*S*)-**7a** $[\alpha]_D^{24.0}$ +5.7 (c 1.5, DCM).

*(3R,5R)-5-((tert-Butyldimethylsilyl)oxy)hepta-1,6-dien-3-ol (**7b**).* To a stirred solution of (*R*,*R*)-**4** (150 mg, 1.17 mmol) and *tert*-butyldimethylsilyltrifluoromethane sulfonate (1.17 mmol, 0.269 mL) in THF (20 mL) at −78 °C was added 2,6-lutidine (1.36 mL, 11.7 mmol) dropwise via syringe. The solution was allowed to stir for 2 h at −78 °C. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic phase was washed with brine, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by silica gel chromatography (10% EtOAc/hexanes) to afford the desired product as colorless oil (260 mg, 92%): R_f = 0.62 (20% EtOAc/hexanes); IR (neat) 3419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.91−5.81 (m, 2H), 5.26 (dt, J = 4.0, 1.6 Hz, 1H), 5.22 (dt, J = 3.6 Hz, 1H), 5.09 (ddt, J = 20.0, 10.4, 1.6 Hz, 2H), 4.51−4.47 (m, 1H), 4.41−4.36 (m, 1H), 3.26 (d, J = 2.8 Hz, 1H), 1.77−1.65 (m, 2H), 0.91 (s, 9H), 0.08 (d, J = 12.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.2, 114.7, 114.0, 72.4, 69.7, 43.3, 25.9, 18.2; m/z (ESI+) found $[M + H]^+$ 243.1780, $C_{13}H_{26}O_2Si$ requires 243.1783; $[\alpha]_D^{23.4}$ −11 (c 8.9, DCM).

*(3R,5R)-5-Hydroxyhepta-1,6-dien-3-yl acetate (**7c**).* To a stirred solution of (*R*,*R*)-**4** (200 mg, 1.56 mmol) in acetonitrile (15 mL) were added triethyl orthoacetate (0.43 mL, 2.34 mmol) and *p*-toluenesulfonic acid (20 mg). The reaction mixture was stirred at rt for 1 h, and a mixture of hydrochloric acid in methanol (0.2 mL of HCl in 1 mL of MeOH) was added to it. The stirring was continued for another 3 h at rt. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and was extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated. Purification via flash column chromatography provided the desired product as colorless oil (213 mg, 82%): R_f = 0.52 (20% EtOAc/hexanes); IR (neat) 3426 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.87−5.75 (m, 2H), 5.48−5.42 (m, 1H), 5.23 (d, J = 17.2 Hz, 2H), 5.10 (dd, J = 23.2, 10.4 Hz, 2H), 4.08 (bs, 1H), 2.73 (s, 1H), 2.06 (s, 3H), 1.85−1.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 140.2, 136.3, 116.6, 114.8, 71.8, 68.7, 42.0, 21.2; m/z (ESI+) found $[M + H]^+$ 171.1017, $C_9H_{14}O_3$ requires 171.1021; $[\alpha]_D^{23.6}$ +16 (c 12.6, DCM).

*(3R,5R)-5-((4-Methoxybenzyl)oxy)hepta-1,6-dien-3-ol (**7d**).* To a 100 mL round-bottom flask containing sodium hydride (83 mg of 50% dispersion, 1.72 mmol, prewashed with hexane) under argon was transferred a solution of (3*R*,5*R*)-hepta-1,6-diene-3,5-diol (200 mg, 1.56 mmol) in THF (20 mL) via syringe at 0 °C. The solution was stirred for 30 min at rt and again cooled to 0 °C by keeping in an ice−water bath. A solution of 4-methoxybenzyl chloride (366 mg in 2 mL of THF, 2.34 mmol) was added via syringe, and the reaction mixture was stirred at rt for overnight. The reaction was quenched with saturated aqueous ammonium chloride solution (10 mL) and was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated. Purification via flash column chromatography provided the desired product as colorless oil (236 mg, 66%): R_f = 0.55 (20% EtOAc/hexanes); IR (neat) 3430 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.93−5.79 (m, 2H), 5.32−5.26 (m, 3H), 5.12 (ddd, J = 10.5, 1.6, 1.6 Hz, 1H), 4.56 (d, J = 11.2 Hz, 1H), 4.47−4.37 (m, 1H), 4.30 (d, J = 11.2 Hz, 1H), 4.16−4.09 (m, 1H), 3.82 (s, 3H), 2.97 (m, 1H), 1.90 (ddd, J = 14.4, 8.4, 3.2 Hz, 1H), 1.73 (ddd, J = 14.8, 8.0, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 140.8, 138.1, 130.2, 129.6, 117.3, 114.1, 113.9, 77.7, 70.2, 69.8, 55.4, 41.8; m/z (ESI+) found $[M + NH_4]^+$ 266.1760, $C_{15}H_{20}O_3$ requires 266.1756; $[\alpha]_D^{23.6}$ +139 (c 6.4, DCM).

General Procedure for the Synthesis of Compounds 6a−d. A solution of starting diene (**7a**−**7d**) in DCM (0.02 M) was purged with argon for 5 min, and Grubbs I catalyst (3 mol %) was added to it under argon. The reaction mixture was stirred for 1 h at 50 °C and quenched with DMSO (1 mL). The solution was stirred under air for 5 min and concentrated. The solvent was evaporated, and the crude reaction mixture was purified by silica gel flash column chromatography to obtain the product (**6a**−**6d**).

*(1R,4R)-4-((Triisopropylsilyl)oxy)cyclopent-2-enol (**6a**).* Following the general procedure above, diene **7a** (5.00 g, 17.6 mmol) provided cyclopentenol **6a** (4.14 g, 92%) as a colorless oil: R_f = 0.41 (20% EtOAc/hexanes); IR (neat) 3322 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.04−5.80 (m, 2H), 5.24−5.06 (m, 1H), 4.98 (d, J = 1.9 Hz, 1H), 2.24−1.96 (m, 3H), 1.17−0.91 (m, 22H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 135.5, 76.6, 76.2, 44.8, 18.1, 18.0, 12.2; m/z (APCI+) found $[M + H]^+$ 243.1780, $C_{13}H_{26}O_2Si$ requires 243.1783; $[\alpha]_D^{23.4}$ +108 (c 2.2, DCM); (1*S*,4*S*)-**6a** $[\alpha]_D^{23.7}$ −103.5 (c 3.0, DCM).

*(1R,4R)-4-((tert-Butyldimethylsilyl)oxy)cyclopent-2-enol (**6b**).* Following the general procedure above, diene **7b** (200 mg, 17.6 mmol) provided cyclopentenol **6b** (156 mg, 88%) as a colorless oil: R_f = 0.44 (20% EtOAc/hexanes); IR (neat) 3327; ^1H NMR (400 MHz, $CDCl_3$) δ 5.95−5.90 (m, 2H), 5.08−5.05 (m, 1H), 5.03−4.97 (m, 1H), 2.08−1.97 (m, 2H), 1.74 (s, 1H), 0.88 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 135.6, 76.7, 76.3, 44.6, 26.0, 18.3, −4.5; m/z (APCI+) found $[M + H]^+$ 243.1780, $C_{13}H_{26}O_2Si$ requires 243.1783; $[\alpha]_D^{23.6}$ +89 (c 5.4, MeOH) [lit[5] $[\alpha]_D^{20}$ +81 (c 0.059, MeOH)].

*(1R,4R)-4-Hydroxycyclopent-2-en-1-yl Acetate (**6c**).* Following the general procedure above, diene **7c** (200 mg, 1.17 mmol) provided cyclopentenol **6c** (147 mg, 88%) as a colorless oil: IR (neat) 3374, 1723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.12−6.06 (m, 1H), 6.01−5.95 (m, 1H), 5.81−5.74 (m, 1H), 5.04−4.97 (m, 1H), 2.49 (br s, 1H), 2.17 (ddd, J = 14.8, 6.8, 2.8 Hz, 1H), 2.06 (ddd, J = 14.8, 7.2, 3.6 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 139.9, 132.8, 79.1, 75.8, 40.6, 21.2; m/z (APCI+) found $[M + H]^+$ 243.1780, $C_{13}H_{26}O_2Si$ requires 243.1783; $[\alpha]_D^{23.2}$ +227 (c 4.9, MeOH) [lit[5] $[\alpha]_D^{20}$ +229 (c 0.027, MeOH)].

*(1R,4R)-4-((4-Methoxybenzyl)oxy)cyclopent-2-enol (**6d**).* Following the general procedure above, diene **7d** (200 mg, 0.81 mmol) provided cyclopentenol **6d** (159 mg, 89%) as a colorless oil: R_f = 0.40 (30% EtOAc/hexanes); IR (neat) 3364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2H), 6.93−6.87 (m, 2H), 6.12−6.03 (m, 2H), 5.08−5.00 (m, 1H), 4.85−4.78 (m, 1H), 4.50 (d, J = 11.2 Hz, 1H), 4.45 (d, J = 11.2 Hz, 1H), 3.82 (s, 3H), 2.22 (ddd, J = 14.4, 6.8, 3.2 Hz, 1H), 2.00 (ddd, J = 14.4, 6.8, 2.8 Hz, 1H), 1.85 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 137.9, 135.1, 130.6, 129.5, 113.9, 82.9, 70.9, 55.4, 41.1; m/z (APCI+) found $[M + H]^+$ 243.1780, $C_{13}H_{26}O_2Si$ requires 243.1783; $[\alpha]_D^{23.4}$ +139 (c 6.4, DCM).

General Procedure for the Synthesis of Compounds 1a−d. To a stirred solution of starting cyclopentenol (**6a**−**6d**) in DCM (0.1 M) was added pyridinium chlorochromate (1.5 equiv) at 0 °C. The reaction mixture was stirred at rt for 6 h followed by filtration over Celite. The Celite bed was washed with diethyl ether. The combined filtrate was concentrated and purified by silica gel flash column chromatography to afford the desired enone (**1a**−**1d**).

*(R)-4-((Triisopropylsilyl)oxy)cyclopent-2-enone (**1a**).* Following above general procedure, cyclopentenol **6a** (2.00 g, 7.81 mmol) provided cyclopentenone **1a** (1.86 g, 94%) as a colorless oil: R_f = 0.30 (10% EtOAc/hexanes); IR (neat) 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 5.7, 2.3 Hz, 1H), 6.16 (dd, J = 5.7, 1.2 Hz, 1H), 2.73 (dd, J = 18.1, 5.9 Hz, 1 H), 2.28 (dd, J = 18.1, 2.2 Hz, 1H), 1.21−0.98 (m, 3H), 1.06 (d, J = 5.4 Hz, 18H); ^{13}C NMR (101 MHz,

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$CDCl_3$) δ 206.5, 163.8, 134.3, 70.9, 45.4, 18.0, 17.9, 12.1; m/z (ESI+) found $[M + H]^+$ 255.1796, $C_{14}H_{26}O_2Si$ requires 255.1798; $[\alpha]_D^{23.8}$ +53 (c 1.05, MeOH). Chiral GC separation: Astec Chiraldex B-DM fused silica capillary column, 30 m × 0.25 mm × 0.12 μm, temperature gradient from 120 °C−140 °C ramping up at 0.25 °C/min, t_R = 37.99 min, t_S = 38.70 min, er 97:3; (S)-**1a** $[\alpha]_D^{23.8}$ −57 (c 2.5, MeOH), er ≥ 99:1 [lit.[5] $[\alpha]_D^{23}$ −58.8 (c 1.05, MeOH)].

*(R)-4-((tert-Butyldimethylsilyl)oxy)cyclopent-2-enone (**1b**).* Following above general procedure, cyclopentenol **6b** (120 mg, 0.56 mmol) provided cyclopentenone **1b** (110 mg, 93%) as a colorless oil: R_f = 0.73 (20% EtOAc/hexanes); IR (neat) 1722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 5.6, 2.4 Hz, 1H), 6.16 (dd, J = 5.6, 1.2 Hz, 1H), 5.10−4.94 (m, 1H), 2.69 (dd, J = 18.4, 6.0 Hz, 1H), 2.22 (dd, J = 18.0, 2.0 Hz, 1H), 0.88 (s, 9H), 0.11 (d, J = 4.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 163.8, 134.4, 70.8, 44.95, 25.7, 18.1, −4.6 (2); m/z (ESI+) found $[M + H]^+$ 213.1315, $C_{11}H_{20}O_2Si$ requires 213.1311; $[\alpha]_D^{23.6}$ +64 (c 1.6, MeOH) [lit.[31] $[\alpha]_D$ +65.3 (c 0.4, MeOH)]. Chiral GC separation: Astec Chiraldex B-DM fused silica capillary column, 30 m × 0.25 mm ×0.12 μm, temperature gradient from 105 to 125 °C ramping up at 1.00 °C/min, t_R = 14.38 min, t_S = 15.11 min, er 97:3.

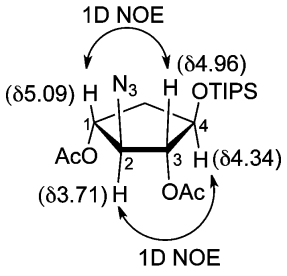
*(R)-4-Oxocyclopent-2-en-1-yl Acetate (**1c**).* Following above general procedure, cyclopentenol **6c** (100 mg, 0.70 mmol) provided cyclopentenone **1c** (91 mg, 92%) as a colorless oil: R_f = 0.73 (20% EtOAc/hexanes); IR (neat) 1720, 1403, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 5.6, 2.4 Hz, 1H), 6.31 (dd, J = 5.6, 1.2 Hz, 1H), 5.85−5.80 (m, 1H), 2.80 (dd, J = 18.7, 6.4 Hz, 1H), 2.30 (dd, J = 18.7, 2.0 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 170.5, 159.0, 137.0, 72.0, 41.0, 20.8; m/z (ESI+) found $[M + H]^+$ 141.0555, $C_7H_9O_3$ requires 141.0552; $[\alpha]_D^{23.8}$ +100 (c 1.4, MeOH) [lit.[31] $[\alpha]_D$ +96.1 (c 0.17, MeOH)]. Chiral GC separation: Astec Chiraldex B-DM fused silica capillary column, 30 m × 0.25 mm ×0.12 μm, temperature gradient from 105 to 110 °C ramping up at 0.25 °C/min, t_R = 9.85 min, t_S = 10.77 min, er 98:2.

*(R)-4-((4-Methoxybenzyl)oxy)cyclopent-2-enone (**1d**).* Following above general procedure, cyclopentenol **6d** (130 mg, 0.59 mmol) provided cyclopentenone **1d** (119 mg, 92%) as a colorless oil: R_f = 0.73 (20% EtOAc/hexanes); IR (neat) 1714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 5.7, 2.3 Hz, 1H), 7.29 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.24 (dd, J = 5.7, 1.2 Hz, 1H), 4.78−4.72 (m, 1H), 4.56 (dd, J = 21.3, 11.3 Hz, 2H), 3.81 (s, 3H), 2.67 (dd, J = 18.4, 6.0 Hz, 1H), 2.34 (dd, J = 18.0, 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 161.3, 159.5, 135.5, 129.5, 129.5, 113.9, 76.5, 71.6, 55.2, 41.8; m/z (ESI+) found $[M + H]^+$ 219.1023, $C_{13}H_{14}O_3$ requires 219.1021; $[\alpha]_D^{23.3}$ +51 (c 3.9, DCM). HPLC (Chiralpak IC column n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, retention time = 38.29 min, er > 99:1).

*(R)-2-Iodo-4-((triisopropylsilyl)oxy)cyclopent-2-enone (**8**).* To a stirred solution of I_2 (10.7 g, 42 mmol) in Et_2O (250 mL) was added pyiridine (2.1 mL, 25 mmol) followed by dropwise addition of (R)-4-((triisopropylsilyl)oxy)cyclopent-2-enone (8.9 g, 35 mmol) at rt. The reaction flask was completely covered with aluminum foil. After 24 h, the reaction was quenched with aqueous $Na_2S_2O_3$ (50 mL). The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated. The resulting oil was purified using silica gel chromatography (10% Et_2O in hexanes) to afford the product as colorless oil (11 g, 85%): R_f = 0.45 (20% EtOAc/hexanes); IR (neat) 1726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 2.5 Hz, 1H), 6.04 (ddd, J = 6.0, 2.3, 2.3, 1H), 2.90 (dd, J = 18.1, 6.0 Hz, 1H), 2.40 (dd, J = 18.1, 2.1 Hz, 1H), 1.30−0.87 (m, 3H), 1.07 (d, J = 5.3 Hz, 18H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 200.4, 169.4, 105.0, 72.4, 43.0, 18.0 (2), 12.1; m/z (ESI+) found $[M + H]^+$ 381.0750, $C_{14}H_{25}IO_2Si$ requires 381.0746; $[\alpha]_D^{23.7}$ +23 (c 4.3, DCM). Chiral GC separation: Astec Chiraldex B-DM fused silica capillary column, 30 m × 0.25 mm × 0.12 μm, temperature 175 °C, t_R = 20.99 min, t_S = 21.84 min, er 97:3; (S)-**8** $[\alpha]_D^{23.7}$ −25 (c 2.7, DCM), er 99:1.

*(1R,2R,4R,5R)-4-((Triisopropylsilyl)oxy)-6-oxabicyclo[3.1.0]hexan-2-ol (**9**).* To a solution of (1*R*,4*R*)-4-((triisopropylsilyl)oxy)cyclopent-2-enol (500 mg, 1.95 mmol) in DCM (20 mL) was added m-CPBA (657 mg, 2.93 mmol) at 0 °C, and the reaction mixture was stirred at rt for 28 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (20 mL) and extracted with DCM (3 × 50 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ and brine and dried (Na_2SO_4). Evaporation of the solvent followed by flash column chromatography (silica gel, 10% EtOAc/hexanes) gave the desired product as colorless oil (350 mg, 66%): R_f = 0.37 (10% EtOAc/hexanes); IR (neat) 3320 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.50 (td, J = 7.9, 0.9 Hz, 1H), 4.42 (d, J = 5.3 Hz, 1H), 3.57−3.51 (m, 1H), 3.43−3.36 (m, 1H), 2.30 (m, 1H), 1.96 (dd, J = 13.7, 8.0 Hz, 1H), 1.47 (ddd, J = 13.5, 8.0, 5.4 Hz, 1H), 1.12−0.94 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 72.3, 71.7, 58.7, 58.6, 39.1, 18.0, 12.1; m/z (ESI+) found $[M + H]^+$ 273.1883, $C_{14}H_{29}O_3Si$ requires 273.1880; $[\alpha]_D^{25.3}$ +26 (c 2.5, DCM).

*(1R,2S,3R,4R)-2-Azido-4-((triisopropylsilyl)oxy)cyclopentane-1,3-diol (**10**).* To a solution of (1*R*,2*R*,4*R*,5*R*)-4-((triisopropylsilyl)oxy)-6-oxabicyclo[3.1.0]hexan-2-ol (150 mg, 0.55 mmol) in DMF (10 mL) were added tetrabutylammonium chloride (153 mg, 0.55 mmol) and sodium azide (358 mg, 5.5 mmol). The reaction mixture was heated at 80 °C for 24 h. The solvent was removed under rediluted pressure, and the residue was diluted with water. The reaction mixture was extracted with ethyl acetate and was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by flash column chromatography (silica gel, 20% EtOAC/hexanes) provided the desired product as colorless oil: R_f = 0.30 (20% EtOAc/hexanes); IR (neat) 3320, 2102 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.24−4.12 (m, 1H), 3.84 (dt, J = 7.8, 4.9 Hz, 1H), 3.53 (t, J = 7.4 Hz, 1H), 2.28 (d, J = 4.6 Hz, 1H), 2.10 (m, 1H), 2.07−2.00 (m, 2H), 1.66 (m, 1H), 1.13−1.00 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.5, 75.1, 72.7, 72.2, 40.2, 17.9, 12.1; m/z (ESI+) found $[M + H]^+$ 316.2055, $C_{14}H_{30}N_3O_3Si$ requires 316.2056; $[\alpha]_D^{25.3}$ −53 (c 0.6, DCM). Stereo- and regiochemistry of the compound **10** was confirmed by 2D HNMR analysis of the corresponding diacetate, which was made by treating the former with acetic anhydride and pyridine: IR (neat) 2104, 1747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.09 (dd, J = 13.2, 6.1 Hz, 1H), 4.96 (t, J = 5.1 Hz, 1H), 4.34 (dd, J = 11.3, 5.7 Hz, 1H), 3.71 (t, J = 5.5 Hz, 1H), 2.33 − 2.18 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03−1.89 (m, 1H), 1.16−0.90 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 170.0, 82.4, 75.8, 73.6, 68.8, 38.0, 21.0, 20.9, 17.82, 17.78, 12.0. Both H1 and H3 show COSY correlation with H2 that confirms the regiochemistry of azide. Further existence of 1D NOE correlation of H1 with H3 and H2 with H4 confirms the stereochemistry of the compound **10**-diacetate, hence confirms the structure of **10** retrospectively.



10-diacetate

*2-((1S,4R)-4-((Triisopropylsilyl)oxy)cyclopent-2-en-1-yl)isoindoline-1,3-dione (**11**).* To a solution of (1*R*,4*R*)-4-((triisopropylsilyl)oxy)cyclopent-2-enol (300 mg, 1.17 mmol) were added dropwise phthaliimide (344 mg, 2.34 mmol) and triphenylphosphine (614 mg, 2.34 mmol) in benzene (10 mL) diethyldiazocarboxylate (0.36 mL, 2.34 mmol) at rt, and the reaction mixture was stirred at rt for 24 h. The reaction mixture was quenched with water (10 mL) and was extracted with diethylether (3 × 30 mL). The combined organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated. Flash column chromatography of the crude provided the desired product as viscous oil (319 mg, 68%): R_f = 0.74 (20% EtOAc/hexanes); IR (neat) 1698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85−7.74 (m, 2H), 7.74−7.62 (m, 2H), 6.01 (ddd, J = 5.6, 2.5, 1.8 Hz, 1H), 5.86 (dt, J = 5.7, 1.7 Hz, 1H), 5.10 (tq, J = 8.4, 2.0 Hz 1H), 4.91 (tq, J

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= 6.9, 1.7 Hz, 1H), 2.75 (dt, J = 12.3, 7.4 Hz, 1H), 2.20−2.05 (ddd, J = 12.4, 8.4, 6.8 Hz, 1H), 1.16−0.95 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 137.1, 134.0, 132.0, 130.8, 123.2, 75.6, 53.4, 40.4, 18.1, 12.21; m/z (ESI+) found $[M + H]^+$ 386.2144, $C_{22}H_{32}NO_3Si$ requires 386.2146; $[\alpha]_D^{24.7}$ −97 (c 5.2, DCM).

*2-((1S,4R)-4-Hydroxycyclopent-2-en-1-yl)isoindoline-1,3-dione (**12**).* To a solution of 2-((1*S*,4*R*)-4-((triisopropylsilyl)oxy)cyclopent-2-en-1-yl)isoindoline-1,3-dione (100 mg, 0.25 mmol) in THF (5 mL) was added dropwise and stirred at rt for 1 h tetrabutylammonium fluoride (0.5 mL of 1 M solution in THF, 0.5 mmol). The reaction mixture was quenched with water (5 mL) and was extracted with ethyl acetate (3 × 30 mL). The combined organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. Flash column chromatography (silica gel, 30% EtOAc/Hexane) of the crude provided the desired product as viscous oil (45 mg, 79%): R_f = 0.20 (20% EtOAc/hexanes); IR (neat) 3315, 1697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.79 (m, 2H), 7.77−7.69 (m, 2H), 6.23 (dt, J = 5.6, 2.0 Hz 1H), 5.75 (dd, J = 5.5, 2.6 Hz, 1H), 5.25 (ddd, J = 9.6, 4.4, 2.2 Hz, 1H), 4.76 (m, 1H), 4.15−4.01 (m, 1H), 2.84 (ddd, J = 15.4, 9.6, 7.8 Hz, 1H), 1.99 (ddd, J = 15.4, 2.0, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 138.6, 134.4, 131.9, 130.3, 123.5, 76.0, 53.1, 38.3; m/z (ESI+) found $[M + H]^+$ 230.0809, $C_{13}H_{12}NO_3$ requires 230.0817; $[\alpha]_D^{25.1}$ −120 (c 3.0, DCM).

*(S)-2-(4-Oxocyclopent-2-en-1-yl)isoindoline-1,3-dione (**13**).* To a solution of 2-((1*S*,4*R*)-4-hydroxycyclopent-2-en-1-yl)isoindoline-1,3-dione (40 mg, 0.18 mmol) in dichloromethane (3 mL) was added pyridiniumchlorochromate (56 mg, 0.26 mmol) at 0 °C. The reaction mixture was stirred at rt for 1 h and was diluted with Et_2O (15 mL). The mixture was filtered through a Celite bed. Evaporation of solvent followed by flash column chromatography (silica gel, 10% EtOAc/hexanes) gave the desired product as colorless oil (36 mg, 91%): IR (neat) 1721, 1698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.81 (m, 2H), 7.80−7.70 (m, 2H), 7.52 (dd, J = 5.7, 2.4 Hz, 1H), 6.44 (dd, J = 5.7, 2.2 Hz, 1H), 5.54 (ddt, J = 6.9, 3.3, 2.3 Hz, 1H), 2.80 (qd, J = 18.3, 5.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 205.3, 167.7, 159.7, 136.3, 134.6, 131.8, 123.7, 49.8, 39.7; m/z (ESI+) found $[M + H]^+$ 228.0659, $C_{13}H_{10}NO_3$ requires 228.0655; $[\alpha]_D^{25.3}$ −224 (c 2.0, DCM) [lit.[23] $[\alpha]_D^{25.3}$ −230.8 (c 1.07, $CHCl_3$)].

*9-((1S,4R)-4-((Triisopropylsilyl)oxy)cyclopent-2-en-1-yl)-9H-purin-6-amine (**14**).* To a solution of (1*R*,4*R*)-4-((triisopropylsilyl)oxy)-cyclopent-2-enol (100 mg, 0.39 mmol), adenine (106 mg, 0.78 mmol), and triphenylphosphine (205 mg, 0.78 mmol) in THF (10 mL) was added diethyldiazocarboxylate (0.12 mL, 0.78 mmol) dropwise at rt, and the reaction mixture was stirred for 24 h. The reaction mixture was quenched with water (5 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated. Flash column chromatography (silica gel, 30% EtOAc/hexanes) of the crude provided the desired product as viscous oil (103 mg, 70%): R_f = 0.35 (30% EtOAc/hexanes); IR (neat) 3360 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.07 (s, 1H), 6.26 (dt, J = 5.6, 2.0 Hz, 1H), 6.23 (m, 2H), 6.00 (dd, J = 5.5, 2.2 Hz, 1H), 5.63 (m, 1H), 5.00 (dt, J = 6.8, 2.0 Hz, 1H), 2.96 (ddd, J = 14.9, 8.2, 6.9 Hz, 1H), 1.88 (dt, J = 14.4, 3.1 Hz, 1H), 1.20−0.99 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 153.0, 149.7, 139.8, 139.3, 131.3, 119.6, 75.6, 56.7, 42.8, 18.1, 12.1; m/z (ESI+) found $[M + H]^+$ 374.2370, $C_{19}H_{32}N_5OSi$ requires 374.2371; $[\alpha]_D^{25.3}$ −53 (c 0.6, DCM).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of all products, and HPLC chromatograms of compounds **1a−c,** and compound **8,** and HPLC chromatogram of compound **1d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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