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Regioselective Semihydrogenation of Dienes

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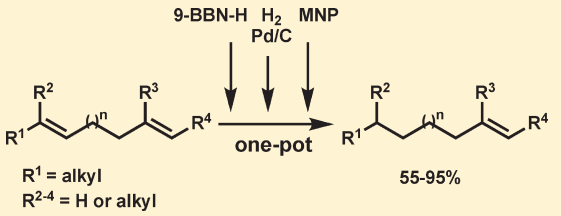
Supporting Information

ABSTRACT: A one-pot, three-step strategy for the regioselective semihydrogenation of dienes is described. This procedure uses 9-BBN-H as a temporary protective group for alkenes. Yields range from 55% to 95%, and the reaction is tolerant of a variety of common functional groups. Additionally, the final elimination step of the sequence can be replaced with a peroxide-mediated alkylborane oxidation, generating regioselectively semihydrogenated product alcohols.



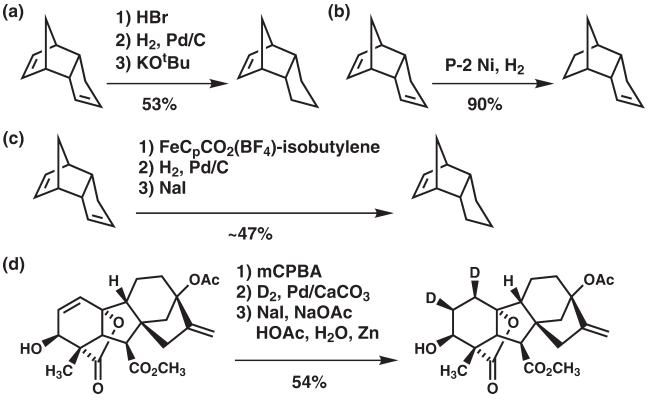
Development of strategies for the catalytic hydrogenation of polyenes "has attracted substantial attention over the past three decades."[1] In particular, the selective semihydrogenation (monohydrogenation) of dienes to monoenes has recently been described as being "of fundamental importance"[2a] and "important from both practical and theoretical aspects."[2b] For example, selective diene and polyene hydrogenation[2b] is widely used in many industrial processes, including the synthesis of petrochemicals[3a] and polymers,[3b] and in fine chemical synthesis including natural products (vide infra) and synthetic oligomers such as telomere derivatives.[3c]

Whereas strategies exist for the direct regioselective semihydrogenation of the less substituted alkene of a differentially substituted diene,[1,4,5] there have been no corresponding reports of the direct regioselective semihydrogenation of dienes that are selective for the more highly substituted alkene of a differentially substituted diene.

There are, however, scattered ad hoc examples where one alkene of a diene has been selectively masked followed by hydrogenation of the remaining alkene and removal of the masking group. Schleyer et al. hydrobrominated the more strained alkene of dicyclopentadiene, hydrogenated the remaining alkene, and then eliminated hydrogen bromide to reveal the original alkene (Scheme 1a).[6] This strategy was necessary because catalytic hydrogenation alone had been shown to selectively hydrogenate the more strained alkene (Scheme 1b).[7] Nicholas accomplished the same transformation by coordinating a metal complex to the more strained alkene, hydrogenating the remaining alkene, then displacing the metal complex to reveal the original alkene (Scheme 1c).[8] MacMillan et al. epoxidized the more sterically accessible alkene of a diene, hydrogenated the remaining alkene, then reduced the epoxide to reveal the original alkene (Scheme 1d).[9] Each of these reactions represents a net semihydrogenation and describes a different strategy for selective protection of one alkene in the presence of another alkene.

Herein we report a practical methodology for the regioselective semihydrogenation of dienes that accomplishes two important objectives: (1) a new strategy for temporary alkene protection is developed that we hope will serve as a foundation for further advances, and (2) this strategy is developed to accomplish an otherwise difficult transformation, the regioselective semihydrogenation of the more substituted alkene of isolated and conjugated dienes. This new reaction differs from the ad hoc examples presented earlier because it involves no harsh reaction conditions, uses only commercially available reagents, proceeds sequentially in one flask without need for isolation of intermediates, and has proven effective on a variety of substrates. Given the variety of molecular architectures that can be prepared concurrent with diene formation,[10] such a methodology would be useful in small molecule synthesis. Furthermore, this methodology simultaneously expands the scope of catalytic hydrogenation, a reaction of considerable synthetic value.[1,3,5]

Scheme 1. Previous Reports of Diene Semihydrogenation



The biggest challenge associated with the regioselective hydrogenation of the more substituted alkene of a diene is the inherent diminished reactivity of alkenes toward catalytic hydrogenation as their degree of substitution increases. In order to take advantage of current hydrogenation technologies, the more reactive (less substituted) diene would have to be temporarily protected with a

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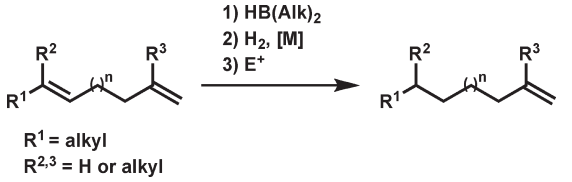
functional group that is both stable to reducing conditions and easily removed following hydrogenation. The ideal protective group would share properties associated with the historically most utilized protective groups, namely, commercial availability and simple, high-yielding protection and deprotection steps. We have found that 9-borabicyclo-[3.3.1]nonane (9-BBN-H) meets these criteria, and we have developed an operationally simple, one-pot reaction sequence that accomplishes the desired transformation in good to excellent yield.

9-BBN-H was selected as an alkene protective group for three principal reasons: (1) monohydroboration of differentially substituted terminal dienes is exceptionally regioselective for the terminal alkene when bulky dialkylboranes are used, leaving the more highly substituted alkene intact,[11] (2) trialkylboranes are hydrogenated under heterogeneous catalysis only at elevated temperatures and pressures,[12] and (3) trialkylboranes can be cleaved at elevated temperatures[13a] or in the presence of certain electrophiles,[13b] revealing the original alkene and producing an oxidized borane. This suggests a three-step hydroboration, hydrogenation, oxidation sequence to accomplish the desired regioselective transformation (Scheme 2).

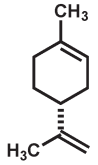
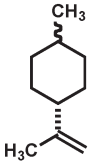
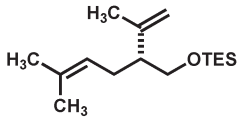
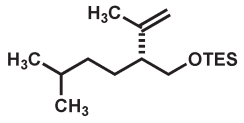
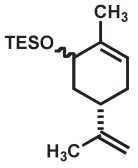
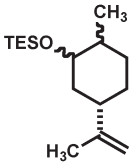
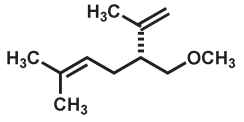
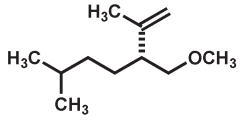
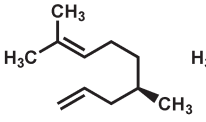
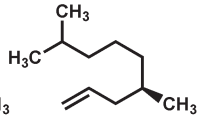
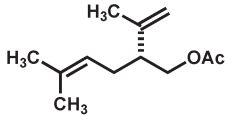
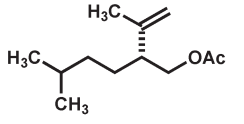
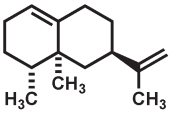
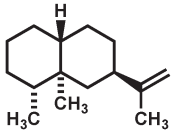
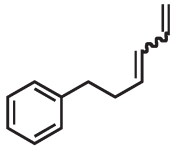
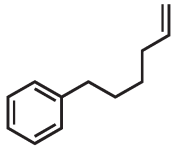
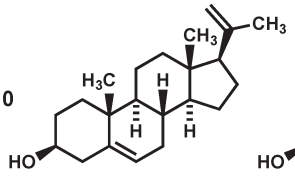
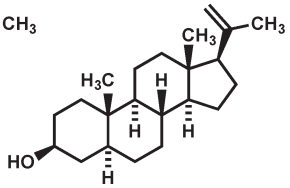
Scheme 2. General Strategy for Diene Semihydrogenation



Since the first two steps of this sequence occur without production of stoichiometic byproduct, we envisioned a one-pot transformation involving sequential addition of 9-BBN-H, followed by hydrogen and catalytic Pd/C,[14] and finally an electrophile. We evaluated a number of commercially available electrophiles[15] and selected the powerful electrophile 2-methyl-2-nitrosopropane[16] (MNP) because it oxidized the intermediate trialkylboranes quantitatively and within minutes to reveal the initial alkene. If ethanolamine is added following the final oxidation step, boron-ethanolamine complexes precipitate out of solution.[17] Thus, purification frequently requires no more than filtration through a plug of silica gel to remove Pd/C and insoluble boronates, the only reaction byproduct. This one-pot procedure leads to the regioselective semihydrogenation of a variety of dienes (Table 1).

Regioselectivity is high; generally only one product alkene regioisomer is observed by NMR. Synthetically useful yields are obtained for a variety of substrates including cyclic and acyclic terminal dienes, dienes with various substitution patterns, and strained internal dienes. As no significant byproducts are observed, we attribute the lower yields obtained in entries 3 and 9 to

Table 1. Substrates and Their Regioselective Semihydrogenation Products

Entry	Substrate	Product	Yield[a]	Entry	Substrate	Product	Yield[a]
1			90 %	6			70 %
2			88 %	7			81 %
3			55 %	8			60 %
4			89 %	9			57 %
5			64 %	10			66 %

[a] Yields are isolated and based on the average of two runs. Diastereomer ratios were not determined.

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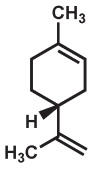
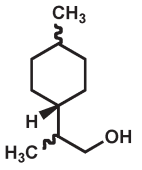
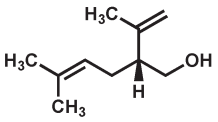
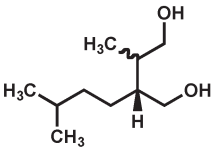
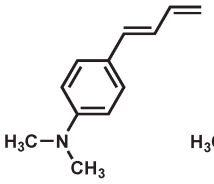
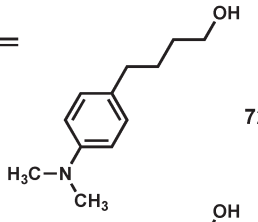
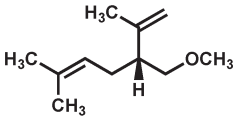
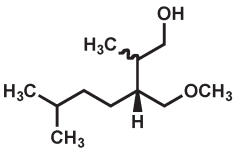
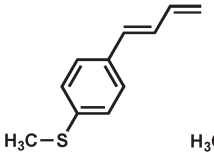
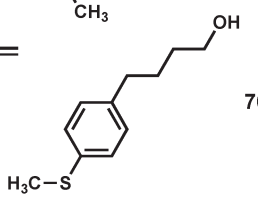
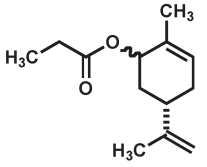
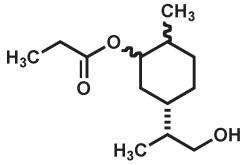
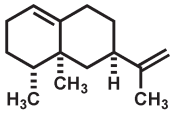
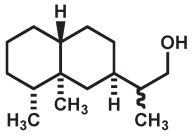
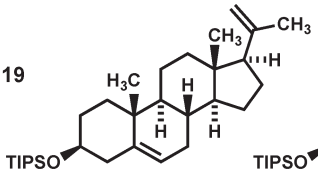
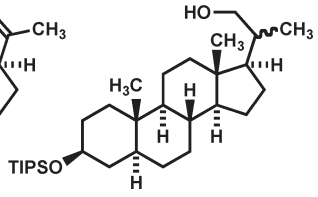
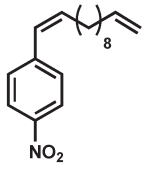
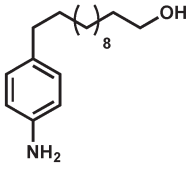
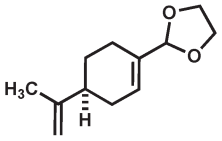
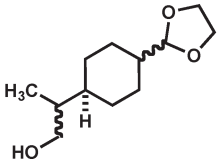
Table 2. Substrates and their Regioselective Semihydrogenation−Oxidation Products

Entry	Substrate	Product	Yield	Entry	Substrate	Product	Yield
11			74 %	16			61 %
12			72 %	17			81 %
13			76 %	18			68 %
14			95 %	19			88 %
15			76 %	20			82 %

the challenges associated with isolating products of high volatility. Importantly, a conjugated terminal diene (entry 9) was semihydrogenated without constitutional isomerization of the remaining olefin, which is usually observed when such reductions are attempted with homogeneous[1] and hetereogeneous[5] catalysts. As expected, the regioselectivity observed in entry 5 is identical to that observed for the corresponding semihydrogenations described in Scheme 1 even though both alkenes are disubstituted and is likely explained by the enhanced reactivity of the strained bridging alkene toward hydroboration. Notably, of the three strategies presented to semihydrogenate dicyclopentadiene, ours provides the highest overall isolated yield.

The trialkylborane generated in this one-pot sequence is a versatile synthetic intermediate. MNP-mediated elimination leads to a net semihydrogenation, as described in Table 1; however, replacing MNP with a hydrogen peroxide-mediated oxidation instead yields product alcohols following regioselective semihydrogenation of the substrates (Table 2). Notably, the products in Table 2 indicate that this methodology is tolerant of certain nonoxygenated functional groups that are known to be stable to dialkylboranes, including anilines (entry 12) and thioethers (entry 13). Yields of the regioselective semihydrogenation−oxidation sequence were generally higher than those observed in Table 1. We attribute these higher product yields to their increased polarity, which diminishes their volatility and facilitates isolation. As expected, nitro groups are reduced to amines during hydrogenation (entry 15). More valuable transformations of the intermediate trialkylboranes, such as cross-coupling, can be envisioned, and we are actively investigating such possibilities.

We anticipate this methodology will be incompatible with functional groups that are known to be reduced in the presence of alkyl boranes, including aldehydes, tertiary amides, isocyanates, and sulfoxides,[18] and for crowded dienes that are reluctant to undergo hydroboration for steric reasons. Indeed, we have attempted to apply our strategy to some of these substrates and have observed undesired reduction of the starting material or sluggish hydroboration (Figure 1). However, competitive reduction of carbonyls can be avoided by using standard acetal protecting group strategies (see Table 2, entry 20), and functional groups that are simply deprotonated by 9-BBN-H (for instance alcohols, Table 1, entry 10 and Table 2, entry 16) are compatible if an additional 1 equiv of 9-BBN-H is used, provided the site of hydroboration is remote from the site of deprotonation.

In summary, we have developed a one-pot, regioselective semihydrogenation and semihydrogenation−oxidation of dienes that proceeds in good to excellent yield on a variety of substrates. We are currently investigating a number of related substrates to expand its scope, including regioselective hydrogenations of internal dienes, polyenes, and enynes.

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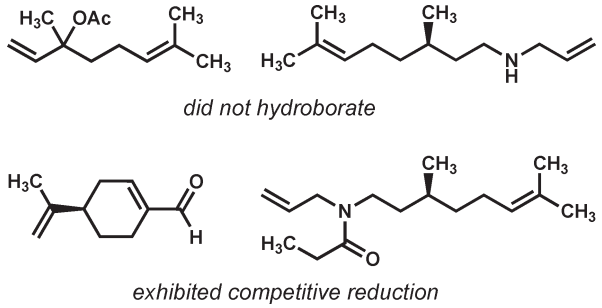

Figure 1. Unsuccessful substrates.

EXPERIMENTAL SECTION

Compound numbers correspond to table entry numbers. Suffix "a" refers to substrates, and suffix "b" refers to products. MNP[19] and compounds **3a**,[20] **7a**,[21] **10a**,[22] and **20a**[23] were prepared according to literature methods.

General Wittig Procedure. A flask was charged with THF (250 mL) and Wittig salt (40.8 mmol), cooled to −78 °C, and *n*-BuLi (2.5 M in hexanes, 16.3 mL, 40.8 mmol) was added dropwise, followed by stirring for 30 min. Aldehyde (37.2 mmol) in THF (15 mL) was added dropwise, and the cooling bath was allowed to expire. The reaction mixture was stirred for 4−16 h. Most of the THF was removed, and the remaining red syrup was diluted with Et_2O (250 mL). The solids were filtered and washed with Et_2O. Concentration of the filtrate yielded crude diene.

General Protection Procedure. A flask was charged with Et_2O (30 mL) and MeCN (20 mL) and cooled to −20 °C, and silyl triflate and pyridine were added. The flask was cooled to −40 °C, charged with alcohol, and stirred for 2 h. The solution was then poured over $NaHCO_3$ (aq), extracted with pentane, washed with water, dried ($MgSO_4$) and concentrated to give products, which were used without further purification.

Triethyl((5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enyloxy)silane (2a). General protection procedure with TESOTf (5.0 mL, 22 mmol), pyridine (2.1 mL, 26 mmol), and (−)-carveol (3.2 mL, 20 mmol) afforded a colorless oil (5.17 g, 97%). R_f = 0.75 (1:9 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 2954, 2877, 1064, 1002, 887, 724 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.56 (br s, 0.6 H), 5.48 (br s, 0.4 H), 4.72 (t, 2 H), 4.27 (br s, 0.4 H), 4.04 (br s, 0.6 H), 1.50−2.51 (m, 11 H), 0.92−1.02 (m, 9 H), 0.50−0.69 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 149.3, 137.2, 135.0, 124.8, 123.6, 109.2, 108.9, 71.7, 69.2, 41.2, 38.9, 37.8, 35.5, 31.3, 31.2, 21.4, 21.1, 20.5, 19.7, 7.1, 7.1, 7.0, 6.6, 5.3, 5.3; HRMS (EI) calcd for $C_{16}H_{30}OSi$: 266.2066; found 266.2072.

(*R*)-Triethyl(5-methyl-2-(prop-1-en-2-yl)hex-4-enyloxy)silane (6a). General protection procedure with TESOTf (3.2 mL, 14 mmol), pyridine (1.3 mL, 17 mmol), and (±)-lavandulol (2.3 mL, 13 mmol) afforded a colorless oil (3.5 g, 99%). R_f = 0.69 (1:9 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 2954, 2912, 2877, 1458, 1415, 1377, 1238, 1101, 1006, 888, 816, 726 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.07 (dddd, J = 7.1, 5.7, 2.8, 1.4 Hz, 1 H), 4.79 (dq, J = 3.0, 1.5 Hz, 1 H), 4.70 (dd, J = 1.3, 0.8 Hz, 1 H), 3.55 (ddd, J = 35.0, 9.9, 6.4 Hz, 2 H), 2.18−2.22 (m, 2 H), 1.98−2.05 (m, 1 H), 1.68 (s, 6 H), 1.60 (s, 3 H), 0.95 (m, 9 H), 0.57 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 132.3, 123.1, 111.8, 65.8, 50.2, 28.8, 26.1, 21.0, 18.2, 7.1, 4.8; HRMS (EI) calcd for $C_{16}H_{32}OSi$: 268.2222; found 268.2226.

Hexa-3,5-dienylbenzene (9a). General Wittig procedure using allyltriphenylphosphonium bromide and dihydrocinnamaldehyde afforded a colorless oil (1.6:1 mixture of geometrical isomers, 1.3 g, 22%). R_f = 0.37 (hexanes); IR (neat) ν_{max} 3085, 3028, 3010, 2941, 1603, 1496, 1453, 1002, 899, 745, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.31 (m, 5 H), 7.17−7.21 (m, 5 H), 6.56−6.63 (m, 1 H), 6.26−6.36 (m, 1 H), 5.71−5.78 (m, 1 H), 5.50 (dd, J = 18.1, 7.6 Hz, 1 H), 5.21 (d, J = 16.8 Hz, 1 H), 5.12 (d, 1 H), 5.08 (s, 1 H), 4.99 (d, J = 9.7 Hz, 3 H), 2.68−2.74 (m, 4 H), 2.53 (q, J = 7.8 Hz, 2 H), 2.40 (dd, J = 15.1, 7.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 137.5, 134.6, 132.4, 131.9, 131.8, 130.0, 128.8, 128.7, 128.7, 126.2, 117.5, 115.5, 36.2, 36.0, 34.7, 29.9; HRMS (EI) calcd for $C_{12}H_{14}$: 158.1096; found 158.1092.

4-(Buta-1,3-dienyl)-*N*,*N*-dimethylaniline (12a). General Wittig procedure using allyltriphenylphosphonium bromide and 4-(dimethylamino)benzaldehyde afforded a translucent yellow oil (2.4:1 mixture of geometrical isomers, 2.19 g, 34%). IR (neat) ν_{max} 2756, 1604, 1518, 1351, 1163, 828, 810 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.25−7.34 (m, 4 H), 6.95−7.04 (m, 1 H), 6.61−6.75 (m, 5 H), 6.47−6.56 (m, 1 H); 6.39 (d, J = 11.5 Hz, 1 H), 6.14 (t, 1 H), 5.34 (d, J = 17.6 Hz, 1 H), 5.25 (d, J = 17.6 Hz, 1 H), 5.18 (d, J = 10 Hz, 1 H), 5.07 (d, J = 10 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 149.9, 138.3; 134.3, 133.6, 131.0, 130.5, 128.1, 128.0, 126.2, 125.9, 125.9, 118.3, 115.3, 112.8, 112.4, 40.74; HRMS (EI) calcd for $C_{12}H_{15}N$: 173.1205; found 173.1199.

(4-(Buta-1,3-dienyl)phenyl)(methyl)sulfane (13a). General Wittig procedure using allyltriphenylphosphonium bromide and 4-(methylthio)benzaldehyde afforded a yellow oil (1.4:1 mixture of geometrical isomers, 2.36 g, 36%). IR (neat) ν_{max} 2955, 2923, 2855, 1459, 1378 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17−7.35 (m, 8 H), 6.70−6.94 (m, 2 H), 6.37−6.56 (m, 3 H), 6.24 (t, 1 H), 5.38 (d, J = 17 Hz, 1 H), 5.32 (d, J = 16.8 Hz, 1 H), 5.23 (d, J = 10.6 Hz, 1 H), 5.16 (d, J = 9.1 Hz, 1 H), 2.48 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.3, 137.2, 134.2, 134.0, 133.1, 132.2, 130.5, 129.7, 129.4, 129.0, 126.8, 126.6, 126.2, 119.6, 117.4, 15.8; HRMS (EI) calcd for $C_{11}H_{12}S$: 176.0660; not detectable due to compound instability.

1-(Dodeca-1,11-dienyl)-4-nitrobenzene (15a). General Wittig procedure using (4-nitrobenzyl)triphenylphosphonium bromide and undecylenic aldehyde afforded a yellow oil (1:1 mixture of geometrical isomers, 2.88 g, 27%). IR (neat) ν_{max} 2925, 1596, 1515, 1357, 908, 856; ^1H NMR (500 MHz, $CDCl_3$) δ 8.12−8.20 (m, 2 H), 7.36−7.46 (m, 2 H), 5.73−5.90 (m, 2 H), 4.97 (d, J = 17.2 Hz, 1 H), 4.92 (d, J = 10.2 Hz, 1 H), 2.2−2.36 (m, 2 H), 1.97−2.07 (m, 2H), 0.80−1.92 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 144.7, 139.3, 137.4, 136.9, 129.6, 127.2, 126.5, 124.2, 123.7, 114.4, 34.0, 34.0, 33.5, 29.9, 29.7, 29.6, 29.6, 29.5, 23.5, 29.4, 29.3, 29.2, 29.2, 29.1, 29.0; HRMS (EI) calcd for $C_{18}H_{25}NO_2$: 287.1885; found 287.1880.

(*S*)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-enyl Propionate (18a). A flask was charged with DCM (50 mL), (−)-carveol (3.8 g, 25 mmol), pyridine (2.97 g, 37.5 mmol), and propionyl chloride (2.54 g, 27.5 mmol). The solution was stirred for 3 h, and then NH_4Cl (aq) (25 mL) was added. The organics were extracted with DCM, washed with $NaHCO_3$ (aq) and brine, and dried ($MgSO_4$). Chromatography (2−20% EtOAc/hexanes) afforded a colorless oil (4.48 g, 86%). IR (neat) ν_{max} 2594, 1731, 1181, 1079, 1023, 916, 886 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.74 (br s, 0.5 H), 5.61 (br s, 0.5 H), 5.47 (br s, 0.5 H), 5.23 (s, 0.5 H), 4.73−4.75 (m, 2 H), 1.45−2.41 (m, 13 H), 1.15−1.19 (dt, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 149.0, 148.5, 133.2, 131.3, 128.0, 126.0, 109.5, 109.4, 73.2, 70.6, 40.5, 36.0 34.2, 34.0, 31.1, 31.0, 28.2, 28.1, 21.1, 20.8, 20.7, 19.0, 9.6, 9.5; HRMS (EI) calcd for $C_{13}H_{20}O_2$: 208.1463; found 208.1461.

((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-10,13-Dimethyl-17-(prop-1-en-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yloxy)triisopropylsilane (19a). General protection procedure with TIPSOTf (4.43 mL, 16.5 mmol), pyridine (1.59 mL, 19.5 mmol), and **10a** (4.72 g, 15 mmol) dissolved in Et_2O (10 mL) afforded a white powder (6.92 g, 98%). IR (neat) ν_{max} 2938, 1097, 1065, 793, 680, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.32 (br s, 1 H), 4.85 (s, 1 H), 4.71 (s, 1 H), 3.52−3.59 (m, 1 H), 2.2−2.3 (m, 2 H), 0.91−2.06 (m, 45 H), 0.58 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 141.9, 121.2, 110.9, 72.7, 57.5, 56.8, 50.6, 43,4, 43.4, 39.0, 37.7, 36.9, 32.6, 32.5, 32.1, 25.7, 24.9, 24.5, 21.4, 19.7, 18.4, 18.3, 12.9, 12.6; HRMS (EI) calcd for $C_{31}H_{54}OSi$ $[M - H]^-$: 469.3866; found 469.3862.

(*S*)-2-(4-(Prop-1-en-2-yl)cyclohex-1-enyl)-1,3-dioxolane (20a). Spectroscopic properties (^1H and ^{13}C NMR) matched those

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previously reported.[23] IR (neat) ν_{max} 2920, 2880, 1644, 1373, 1179, 1081, 944, 886, 822 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (br s, 1 H), 5.13 (s, 1 H), 4.73 (s, 1 H), 4.71 (s, 1 H), 3.88−4.02 (m, 4 H), 1.82−2.22 (m, 6 H), 1.73 (s, 3 H), 1.42−1.52 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 134.9, 127.8, 109.0, 106.4, 65.5, 65.5, 41.3, 30.6, 27.4, 22.6, 20.9; HRMS (EI) calcd for $C_{12}H_{18}O_2$: 194.1307; found 194.1302.

General Hydrogenation Procedure (General Procedure A). A 50 mL Schlenk flask attached to a Firestone valve (Ace Glass, Inc.) was flame-dried and cooled under vacuum (0.01 Torr). The flask was subjected to 3 purge/evacuation cycles with dry Ar and then charged with dry, degassed THF (7 mL). Diene (3.66 mmol) was added, and the solution was cooled to 0 °C. After 10 min, 9-BBN-H (7.33 mL, 3.66 mmol, 0.5 M in THF) was added dropwise via gastight syringe over 30 min. The reaction was stirred for 1 h at 0 °C, then 1 h at 25 °C. Pd/C (150 mg, 4.4 mol % Pd, 10% w/w Pd/C) was then added in one portion. The atmosphere was replaced with H_2 (1 atm) using 7 evacuation/purge cycles, and the resulting black mixture was stirred vigorously. Reaction progress was monitored by disappearance of olefinic protons via ^{1}H NMR. An NMR sample was prepared by removing an aliquot (100 μL), dilution with DCM, filtration through Celite, and concentration. Following consumption of the desired olefin, the atmosphere was replaced with Ar via 7 evacuation/purge cycles. MNP dimer (382 mg, 2.19 mmol) was added in one portion, and the resulting solution was stirred for 45 min. The reaction mixture was diluted with Et_2O, filtered through Celite, rinsed with Et_2O and concentrated. The residue was dissolved in Et_2O (10 mL), cooled to 0 °C, treated with ethanolamine (40 μL, 6.6 mmol), and stirred for 10 min. The resulting white mixture was diluted with pentane, filtered through a plug of silica, rinsed with pentane and concentrated to give crude product. Products **7b** and **8b** were sometimes contaminated with MNP derived byproduct. Dissolving the crude product in Et_2O and washing with NH_4Cl (aq) removed the byproduct. The byproduct has characteristic ^{1}H NMR signals: 1.25 (s), 1.50 (s) and is not observable by TLC.

1-Methyl-4-(prop-1-en-2-yl)cyclohexane (1b). General procedure A and chromatography (pentane) produced a colorless volatile oil (0.45 g, 90%). R_f = 0.62 (hexanes, $KMnO_4$); IR (neat) ν_{max} 2948, 2922, 2851, 1644, 1448, 1376, 885 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (s, 2 H), 4.66 (s, 2 H), 1.18−1.90 (m, 26 H), 0.94 (d, J = 7.1 Hz, 3 H), 0.88 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 150.6, 108.7, 108.2, 45.6, 44.6, 35.8, 32.9, 32.2, 32.2, 32.2, 32.2, 32.0, 30.2, 28.6, 26.8, 23.1, 23.0, 21.7, 21.3, 20.3, 19.0; HRMS (EI) calcd for $C_{10}H_{18}$: 138.1409; found 138.1408.

Triethyl((5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohexyloxy)-silane (2b). General procedure A and chromatography (1−5% EtOAc/hexanes) afforded an inseparable mixture of diastereomers as a colorless oil (0.86 g, 88%). R_f = 0.75 (1:9 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 2954, 2876, 1047, 1003, 886, 723 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65−4.75 (m, 2 H), 3.62−3.9 (m, 1 H), 1.13−2.42 (m, 12 H), 0.87−1.01 (m, 18 H), 0.56−0.63 (q, 6 H), 0.49−0.56 (q, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 149.7, 108.7, 108.3, 73.3, 71.6, 44.8, 41.0, 38.2, 37.4, 35.0, 34.9, 31.8, 31.0, 28.6, 25.0, 21.0, 20.8, 19.0, 11.0, 7.1, 7.1,7.1,7.1, 6.9, 6.6, 5.9, 5.4, 5.3, 5.3, 5.2; HRMS (EI) calcd for $C_{16}H_{32}OSi$: 268.2222; found 268.2217.

(*R*)-4,8-Dimethylnon-1-ene (3b). General procedure A and chromatography (pentane) produced a colorless volatile oil (0.31 g, 55%). R_f = 0.70 (hexanes, $KMnO_4$); IR (neat) ν_{max}, 2955, 2926, 2870, 1463, 1378, 993, 910 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75−5.81 (m, 1 H), 4.96−5.00 (m, 2 H), 2.04−2.06 (m, 1 H), 1.86−1.88 (m, 1 H), 1.49−1.53 (m, 2 H), 1.25−1.31 (m, 3 H), 1.07−1.16 (m, 3 H), 0.86 (d, J = 6.7 Hz, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 115.7, 41.9, 39.7, 37.3, 33.2, 28.4, 25.3, 23.1, 23.0, 19.8; HRMS (EI) calcd for $C_{11}H_{22}$: 154.1722; found 154.1724.

(1*R*,4a*R*,7*R*,8a*S*)-1,8a-Dimethyl-7-(prop-1-en-2-yl)decahydronaphthalene (4b). General procedure A and chromatography (pentane) produced a colorless oil (0.67 g, 89%). R_f = 0.62 (hexanes, $KMnO_4$); IR (neat) ν_{max} 2919, 2854, 1643, 1449, 1379, 885, 545 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 (s, 2 H), 2.11 (t, 1 H), 1.66−1.75 (m, 5 H), 0.83−1.40 (m, 12 H), 0.77 (d, J = 6.7 Hz, 3 H), 0.74 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 108.3, 46.8, 44.5, 43.7, 40.9, 37.3, 32.5, 31.3, 29.4, 29.3, 27.1, 21.2, 15.5, 11.6; HRMS (EI) calcd for $C_{15}H_{26}$: 206.2035; found 206.2033.

1*H*,2*H*-Dicyclopentadiene (5b). General procedure A and chromatography (pentane) produced the title compound as a colorless oil (0.31 g, 64%), whose spectroscopic properties matched those previously reported.[22]

(*R*)-Triethyl(5-methyl-2-(prop-1-en-2-yl)hexyloxy)silane (6b). General procedure A and chromatography (hexanes) produced a colorless oil (0.69 g, 70%). R_f = 0.70 (1:9 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 2955, 2934, 2916, 2876, 1460, 1096, 1005, 888, 814, 725 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (dq, J = 2.9, 1.4 Hz, 1 H), 4.70 (dd, J = 1.5, 0.7 Hz, 1 H), 3.57 (dd, J = 9.9, 6.5 Hz, 1 H), 3.48 (dd, 1 H), 2.15 (m, 1 H), 1.65 (dd, J = 1.3, 0.9 Hz, 3 H), 1.48−1.54 (m, 2 H), 1.21−1.28 (m, 1 H), 1.08−1.14 (m, 2 H), 0.94 (t, J = 7.9 Hz, 9 H), 0.87 (dd, J = 6.6, 3.9 Hz, 6 H), 0.58 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 112.0, 66.4, 50.4, 36.8, 28.50, 27.6, 23.2, 22.7, 20.3, 7.1, 4.8; HRMS (EI) calcd for $C_{16}H_{34}SiO$: 271.2457; found 271.2450.

(*R*)-3-(Methoxymethyl)-2,6-dimethylhept-1-ene (7b). General procedure A and chromatography (1−8% Et_2O/pentane) produced a colorless oil (0.50 g, 81%). R_f = 0.59 (1:9 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 2954, 2925, 2869, 1451, 1366, 1193, 1114, 888 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.82 (dd, J = 2.0, 1.6 Hz 1 H), 4.74 (m, 1 H), 3.27−3.36 (m, 5 H), 2.31 (m, 1 H), 1.66 (s, 3 H), 1.43−1.52 (m, 1 H), 1.38−1.42 (m, 1 H), 1.23−1.31 (m, 1 H), 1.09−1.13 (m, 2 H), 0.87 (dd, J = 6.6, 3.6 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 108.4, 72.0, 55.1, 43.7, 32.76, 24.5, 23.9, 19.2, 18.8, 15.3; HRMS (EI) calcd for $C_{11}H_{22}O$: 170.1671; found 170.1672.

(*R*)-5-Methyl-2-(prop-1-en-2-yl)hexyl Acetate (8b). General procedure A and chromatography (1−8% Et_2O/pentane) produced as a colorless oil (0.44 g, 60%). R_f = 0.55 (1:9 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 2956, 2932, 2871, 1742, 1767, 1365, 1226, 1035, 892 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.82 (dd, J = 3.3, 1.7 Hz, 1 H), 4.72−4.76 (m, 1 H), 4.02 (d, J = 7.1 Hz, 2 H), 2.35 (dtd, J = 9.3, 7.1, 5.3 Hz, 1 H), 2.02 (s, 3 H), 1.66 (s, 3 H), 1.51 (dp, J = 13.3, 6.7 Hz, 3 H), 1.30−1.41 (m, 2 H), 1.09−1.15 (m, 2 H), 0.87 (dd, J = 6.6, 3.2 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 145.0, 113.1, 66.7, 46.6, 36.5, 28.3, 27.6, 23.0, 22.6, 21.2, 19.4; HRMS (EI) calcd for $C_{12}H_{22}O_2$: 198.1620; found 198.1617.

Hex-5-enylbenzene (9b). General procedure A and chromatography (hexanes) produced a colorless oil (0.33 g, 57%). R_f = 0.40 (hexanes, $KMnO_4$); IR (neat) ν_{max} 3077, 3060, 3028, 2929, 2857, 1640, 1496, 1453, 909, 745, 697, 541 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 2 H), 7.10 (m, 3 H), 5.73 (m, 1 H), 4.89 (m, 2 H), 2.54 (t, J = 7.7 Hz, 2 H), 2.01 (dd, J = 14.3, 7.2 Hz, 2 H), 1.55 (m, 2 H), 1.37 (dt, J = 17.7, 7.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 139.2, 128.7, 128.6, 125.9, 114.7, 36.2, 33.9, 31.3, 28.9; HRMS (EI) calcd for $C_{12}H_{16}$: 160.1252; found 160.1251.

(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*R*)-10,13-Dimethyl-17-(prop-1-en-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (10b). The general procedure was modified as follows: 2 equiv of 9-BBN-H was used, 20 mol % Pd/C was used, and 2 equiv of MNP was used. Instead of filtration after the addition of ethanolamine, the white slurry was concentrated in the presence of silica gel, and chromatography (20% EtOAc/hexanes) afforded a white solid (0.76 g, 66%). R_f = 0.40 (3:7 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3654 (br), 2978, 2898, 1063, 721 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.85 (br s, 1 H), 4.71 (br s, 1 H), 3.58 (m, 1 H), 0.82−2.05 (m, 22 H), 1.74 (s, 3 H), 0.81 (s, 3 H), 0.58 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 110.8, 71.4, 57.5, 56.4, 54.6, 45.1, 43.5, 39.1, 38.3, 37.2, 36.0, 35.7, 32.4, 32.2, 31.6, 28.9, 25.6, 24.8, 24.3, 22.2, 21.4, 13.1, 12.5; HRMS (EI) calcd for $C_{22}H_{36}O$: 316.2766; found 316.2764.

General Regioselective Semihydrogenation−Oxidation Procedure (General Procedure B). General Procedure A should be followed until immediately after purging the hydrogen atmosphere with Ar, at which point the procedures diverge: NaOH (7 mL, 10.5 mmol, 1.5 M in H_2O) was added, the reaction cooled to 0 °C, and H_2O_2 (3.5 mL, 30 mmol, 30% in H_2O) was added dropwise over the course of 10 min. The reaction was then stirred for 30 min, diluted with Et_2O (10 mL), and filtered through Celite. The pad was rinsed with Et_2O and the filtrate extracted with Et_2O (3×), washed with brine, dried ($MgSO_4$), and concentrated to give crude product.

2-(4-Methylcyclohexyl)propan-1-ol (11b). General procedure B and chromatography (5−25% EtOAc/hexanes) produced a colorless oil (0.42 g, 74%). R_f = 0.18 (1:4 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3327, 2915, 1447, 1375, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.51−3.61 (m, 1 H), 3.35−3.41 (m, 1 H), 2.35 (br s, 1 H), 0.90−1.75 (m, 10 H), 0.80−0.90 (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.4, 66.4, 40.9, 39.2, 38.7, 38.3, 35.8, 35.7, 33.1, 31.7, 31.5, 31.0, 29.1, 28.7, 26.1, 24.5, 22.9, 19.3, 14.2, 13.6; HRMS (EI) calcd for $C_{10}H_{20}O$ $[M + NH_4]^+$: 174.1858; found 174.1854.

4-(4-(Dimethylamino)phenyl)butan-1-ol (12b). General procedure B and chromatography (5−25% EtOAc/hexanes) produced a colorless oil (0.51 g, 72%). R_f = 0.23 (1:4 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3297, 2930, 1519, 1341, 1058, 908, 728 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, J = 8.5 Hz, 2 H), 6.70 (d, J = 8.8 Hz, 2 H), 3.63 (t, 2 H), 2.94 (s, 6 H), 2.60 (t, 2 H), 2.35 (br s, 1 H), 1.58−1.72 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 131.1, 129.3, 113.5, 63.0, 41.3, 34.9, 32.6, 28.1; HRMS (EI) calcd for $C_{12}H_{19}NO$: 193.1467; found 193.1471.

4-(4-(Methylthio)phenyl)butan-1-ol (13b). General procedure B and chromatography (5−25% EtOAc/hexanes) produced a colorless oil (0.55 g, 76%). R_f = 0.25 (1:4 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3283, 2932, 1494, 1437, 1056, 804, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J = 8.5 Hz, 2 H), 7.11 (d, J = 8.3 Hz, 2 H), 3.65 (t, 2 H), 2.61 (t, 2 H), 2.47 (s, 3 H), 1.57−1.71 (m, 4 H), 1.54 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 135.4, 129.2, 127.4, 63.0, 35.3, 32.5, 27.8, 16.6; HRMS (EI) calcd for $C_{11}H_{16}OS$: 196.0922; found 196.0925.

2-((2*R*,4a*R*,8*R*,8a*S*)-8,8a-Dimethyldecahydronaphthalen-2-yl)propan-1-ol (14b). General procedure B and chromatography (5−25% EtOAc/hexanes) produced a colorless oil (0.78 g, 95%). R_f = 0.23 (1:4 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3289, 2916, 2854, 1447, 1381, 1026, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.59−3.63 (m, 1 H), 3.41−3.49 (m, 1 H), 0.61−1.68 (m, 26 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.7, 66.5, 46.9, 46.9, 43.7, 43.7, 43.6, 41.5, 41.2, 41.2, 37.1, 36.9, 34.5, 34.2, 31.3, 31.1, 31.1, 29.3, 29.2, 29.2, 29.2, 28.9, 26.9, 15.4, 15.4, 13.9, 13.4, 11.6, 11.6; HRMS (EI) calcd for $C_{15}H_{28}O$: 224.2140; found 224.2140.

12-(4-Nitrophenyl)dodecan-1-ol (15b). General procedure B and chromatography (20−60% EtOAc/hexanes) produced a white solid (0.77 g, 76%). R_f = 0.28 (2:3 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3313, 2917, 2849, 1518, 1061, 814, 720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.96 (dd, J = 8.3 Hz, 2 H), 6.62 (dd, J = 8.5 Hz, 2 H), 3.78 (br s, 1H), 3.61−3.66 (m, 2 H), 3.53 (br s, 2 H), 2.49 (t, 2H), 1.72−1.78 (m, 2 H), 1.45−1.66 (m, 4 H), 1.22−1.37 (m, 14 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 133.4, 129.4, 115.5, 72.0, 63.2, 43.5, 35.3, 34.3, 33.0, 32.0, 31.3, 29.9, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 26.0, 22.3; HRMS (EI) calcd for $C_{18}H_{31}NO$: 277.2406; found 277.2408.

(*R*)-2-Isopentyl-3-methylbutane-1,4-diol (16b). General procedure B was modified as follows: 2 equiv of 9-BBN-H was used, and 20 mol % Pd/C was used. Chromatography (20−70% EtOAc/hexanes) produced a colorless oil (0.39 g, 61%). R_f = 0.22 (2:3 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3298, 2925, 1710, 1375, 1240, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.78−4.47 (br s, 2 H), 3.45−3.73 (m, 4 H), 1.09−1.90 (m, 7 H), 0.84−0.98 (m, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.4, 64.8, 63.1, 62.2, 44.5, 44.2, 38.3, 37.3, 37.2, 37.1, 28.6, 28.5, 27.0 26.1, 23.0, 22.9, 22.8, 22.7, 15.4, 12.8; HRMS (EI) calcd for $C_{10}H_{22}O_2$ $[M + H]^+$: 175.1698; found 175.1698.

(*R*)-3-(Methoxymethyl)-2,6-dimethylheptan-1-ol (17b). General procedure B and chromatography (5−30% EtOAc/hexanes) produced a colorless oil (0.56, 81%). R_f = 0.20 (1:4 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3290, 2924, 1466, 1104, 1034, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.34−3.64 (m, 3 H), 3.33 (s, 3 H), 3.19−3.32 (m, 2 H), 1.07−1.88 (m, 7 H), 0.81−0.98 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.8, 73.6, 72.4, 66.8, 65.3, 59.0, 58.9, 41.9, 41.5, 38.2, 37.8, 37.3, 37.1, 34.9, 28.6, 28.5, 27.6, 27.3, 27.0, 25.4, 23.0, 22.9, 22.9, 22.8, 22.7, 15.4, 12.2; HRMS (EI) calcd for $C_{11}H_{24}O_2$ $[M + H]^+$: 189.1855; found 189.1856.

(*S*)-2-Methyl-5-(prop-1-en-2-yl)cyclohexyl Propionate (18b). General procedure B and chromatography (7−45% EtOAc/hexanes) produced a colorless oil (0.57 g, 68%). R_f = 0.15 (1:4 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3315, 2929, 1717, 1196, 1011, 908, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.97 (br s, 0.38 H), 4.75−4.83 (m, 0.24 H), 4.63−4.7 (m, 0.12 H), 4.30−4.41 (m, 0.26 H), 3.46−3.57 (m, 1 H), 3.33−3.46 (m, 1 H), 2.2−2.34 (m, 2 H), 1.94−2.18 (br s, 1H), 1.15−1.9 (m, 8 H), 1.04−1.13 (m, 3 H), 0.76−1.04 (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 174.6, 174.6, 174.3, 174.2, 78.8, 78.6,78.6, 75.5, 75.4, 75.2, 74.8, 73.7, 73.6, 66.4, 66.2, 66.2, 66.1, 66.1, 66.0, 65.9, 40.5, 40.4, 40.3, 40.3, 40.2, 38.1, 38.0, 37.9, 37.7, 37.5, 37.5, 36.4, 35.5, 35.5, 35.1, 34.8, 33.9, 33.3, 33.2, 33.0, 32.7, 31.3, 31.3, 30.5, 30.5, 30.2, 30.1, 30.0, 29.4, 29.2, 28.3, 28.2, 28.2, 28.2, 28.1, 27.8, 27.8, 27.7, 23.8, 21.6, 18.4, 18.4, 18.3, 17.3, 14.4, 13.7, 13.7, 13.6, 13.4, 13.2, 11.8, 11.8, 9.6, 9.6, 9.5, 9.5, 9.4, 9.4; HRMS (EI) calcd for $C_{13}H_{24}O_3$ $[M+H]^+$: 229.1804; found 229.1808.

2-((3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*R*)-10,13-Dimethyl-3-(triisopropylsilyloxy)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)propan-1-ol (19b). General procedure B and chromatography (5−25% EtOAc/hexanes) produced an inseparable mixture of diastereomers as a colorless oil (1.58 g, 88%). R_f = 0.22 (1:4 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3293, 2924, 1055, 905, 815, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.61 (m, 2 H), 3.33 (dd, J = 7.0 Hz, 1 H), 1.91−1.97 (m, 1 H), 1.07−1.88 (m, 19 H), 1.0−1.07 (m, 28 H), 0.79 (s, 3 H), 0.66 (s, 3 H), 0.56−0.63 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.3, 68.2, 56.5, 54.7, 52.8, 45.3, 42.9, 40.2, 39.1, 39.0, 37.5, 35.8, 35.7, 32.4, 32.4, 29.0, 28.0, 24.6, 21.5, 18.4, 18.4, 17.0, 12.6, 12.4; HRMS (EI) calcd for $C_{31}H_{58}O_2Si$ $[M + H]^+$: 491.4284; found 491.4266.

2-(4-(1,3-Dioxolan-2-yl)cyclohexyl)propan-1-ol (20b). General procedure B and chromatography (7−60% EtOAc/hexanes) produced an inseparable mixture of diastereomers as a colorless oil (0.64 g, 82%). R_f = 0.25 (1:2 EtOAc/hexanes, $KMnO_4$); IR (neat) ν_{max} 3421, 2923, 2874, 1738, 1451, 1027, 937, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.81 (d, J = 5.9 Hz, 0.26 H), 4.58 (s, J = 5.1 Hz, 0.76 H), 3.81−3.96 (m, 4 H), 3.57−3.67 (m, 1 H), 3.44−3.50 (m, 1 H), 0.95 (m, 11 H), 0.66−0.87 (s, 3 H), 0.56−0.63 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.8, 106.2, 66.6, 66.5, 65.1, 65.1, 42.0, 41.0, 39.4, 39.3, 37.5, 37.2, 30.2, 28.0, 27.6, 27.5, 26.9, 25.8, 24.8, 24.6, 14.6, 13.7; HRMS (EI) calcd for $C_{12}H_{22}O_3$ $[M - H]^-$: 213.1491; found 213.1489.

■ ASSOCIATED CONTENT

Supporting Information. IR, ^1H NMR, ^{13}C NMR, and mass spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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