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Palladium-catalyzed and samarium-promoted coupling of stereochemically-biased allylic acetates with carbonyl compounds

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ABSTRACT

Stereochemically-biased bicyclic allylic acetates *endo*- and *exo*-**1** were shown as being allyl donors for Pd-catalyzed carbonyl allylation using stoichiometric quantities of samarium diodide. Cyclopentenyl acetate and bicyclic derivatives **1** react with cyclic ketones in the presence of SmI_2 without requirement of palladium catalysis. Use of enantiomerically enriched substrate suggests that the reaction goes through a π-allyl samarium complex. However, this reactivity appears to be restricted to strained cyclopentenyl acetates since other linear and cyclic allylic acetates do not give the carbonyl allylation product.

1. Introduction

Allylation of carbonyl compounds—including its enantioselective version—is recognized as an important and useful carbon–carbon bond formation process.[1] It requires the use of nucleophilic reagents such as allylmetals that are more often prepared from the corresponding allylic halides.

More friendly allylic alcohol derivatives (acetate, alkyl carbonate, phosphate) or allylic alcohols themselves could be used as allylation reagents when activated with palladium(0) catalysts as π-allylpalladium complexes, after these latter being made nucleophilic through an umpolung process. The charge reversal of the allylic moiety can be made by electrochemical means, by reduction with a metal (Zn), a salt ($SnCl_2$, SmI_2), or by transmetalation with an organometal (alkylborane, alkylzinc, allylsilane).[2]

Among these umpolung processes, samarium diodide was used for Pd(0) catalyzed allylation of carbonyl compounds with allylic acetates.[3] Allylic carbonates and phosphates were also investigated as substrates with ketones through mischmetal/SmI_2/$Pd(0)_{cat}$ mediating system.[4] In both reports, the allylic substrates were shown to react preferentially at the least substituted allylic terminus. The mechanism is supposed to involve the reduction of the intermediate π-allylpalladium complex by SmI_2. Such a mechanism has been postulated for the SmI_2-mediated reduction of allylic acetates[5] and synthesis of allylsilanes.[6] Since no enantioselective version of such a reaction has been carried out, we aimed at investigating the SmI_2-mediated, Pd-catalyzed allylation of ketones in order to get some insight into the mechanism and stereochemical outcome of this reaction.

2. Results and discussion

Diastereomeric stereochemically-biased allylic acetates *endo*-**1** and *exo*-**1** have been shown to be useful for gathering information about the mechanism and stereochemical outcome of Pd-catalyzed allylation of nucleophiles performed with allylic acetates.[7] *exo*-**1** was unreactive with either "soft" or "hard" nucleophiles in the presence of palladium(0)/phosphine complexes, whereas only "hard" nucleophiles underwent reaction with *endo*-**1** under the same conditions. We anticipated that these model substrates could give information about the mechanistic features of the SmI_2-induced umpolung of allylpalladium complexes.

As expected, *endo*-acetate **1** reacted with cyclobutanone and cyclohexanone in a Pd(0)-catalyzed, SmI_2-mediated Barbier-type process to give the homoallylic alcohols **2a** and **2b**, in poor isolated yields however, 48% and 38%, respectively. A single-crystal X-ray diffractometry structure of **2b** could be obtained (Scheme 1, Fig. 1).

Surprisingly, reactions of the diastereomeric *exo*-acetate **1** performed under identical conditions (THF, room temperature, 20 h)

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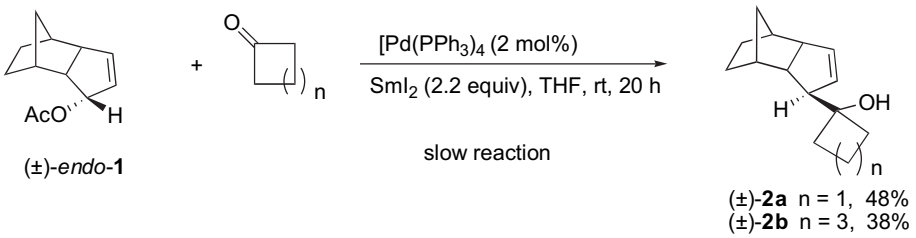


Scheme 1. Pd-catalyzed, samarium-promoted allylation of cyclic ketone by stereochemically-biased allylic acetate *endo*-**1**.

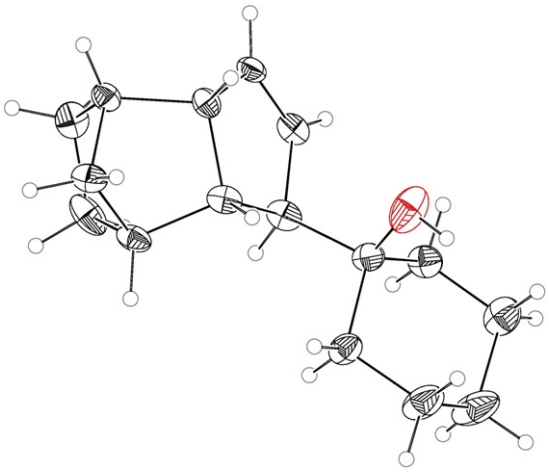


Figure 1. ORTEP drawing of the X-ray crystallographic structure of **2b** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level.

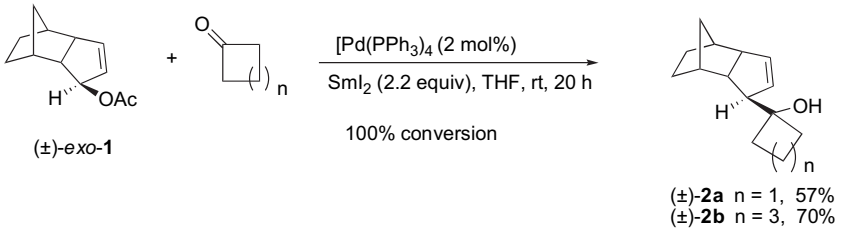
with cyclobutanone and cyclohexanone gave, through quantitative conversion, the *same* products **2a** and **2b**, and in higher yields (57% and 70%, respectively) (Scheme 2).

homoallylic alcohol **2b** in nearly as good a yield (60%) as the one (70%) recorded under palladium catalysis (vide supra).

In both cases, the reduction product **3** was isolated as a side product in low yield, likely resulting from a radical-induced protonation by the THF solvent (Scheme 4).

This behavior was confirmed by reaction of cyclopentenyl acetate with cyclohexanone in the presence of 2.2 equiv SmI_2, which gave the homoallylic alcohol **4** in yields of 52% (without Pd catalyst) and 70% (with Pd) (Scheme 5).

In order to get some insight into the mechanism of the reaction, we aimed at looking further the stereochemistry of the reaction using an enantiomerically enriched allylic substrate. Since we were not able to resolve analytically the enantiomers of **2b**, (by chiral HPLC, even after derivatization of the alcohol into the corresponding acetate or benzyl carbamate), reactions were performed with 4-phenylcyclohexanone as the substrate instead of cyclohexanone. Two diastereomers **5** were obtained in a 3/1 ratio. The major diastereomer **5a** could be separated by silica gel chromatography from the minor **5b** and enantiomers of **5a** distinguished by chiral HPLC. The relative stereochemistry of **5a** could not be established. When enantiomerically enriched *exo*-**1** was reacted with 4-phenylcyclohexanone in the presence of 2.2 equiv SmI_2, two diastereomers **5** were obtained in a 3/1 ratio, and the homo-



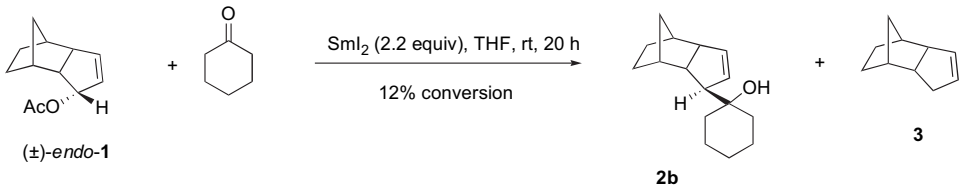
Scheme 2. Pd-catalyzed, samarium-promoted allylation of cyclic ketone by stereochemically-biased allylic acetate *exo*-**1**.

We were then inquiring about any involvement of the palladium complex to promote the reaction, especially for diastereomer *exo*-**1**. Reactions were then performed in the absence of any palladium complex. *endo*-**1** acetate exposed to samarium diodide afforded the product **2b** on reaction with cyclohexanone but in low (12%) conversion (vs 38% in the presence of Pd catalyst) (Scheme 3).

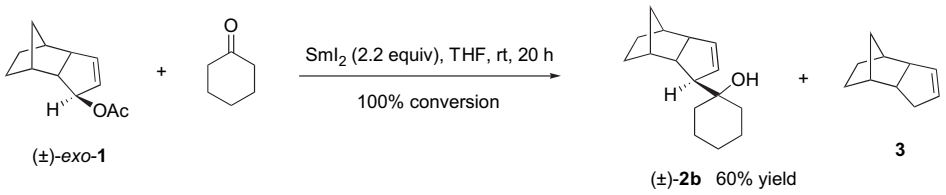
Conversely, reaction of *exo*-acetate **1** with cyclohexanone under Barbier-like conditions proceeded smoothly to provide the allylic alcohol **5a** was obtained in good yield but in racemic form (Scheme 6).

These results indicate that a symmetrical π-allyl radical or a π-allyl samarium species might be involved at some stage of the process, through one or two consecutive one-electron transfer.

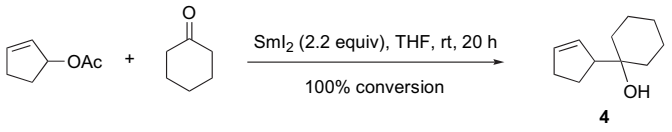
When the reaction of *exo*-**1** was performed in the presence of 1 equiv of *O*-deuterated ethanol and SmI_2 (2 equiv), the deuterated



Scheme 3. Samarium-promoted allylation of cyclic ketone by stereochemically-biased allylic acetate *endo*-**1**.



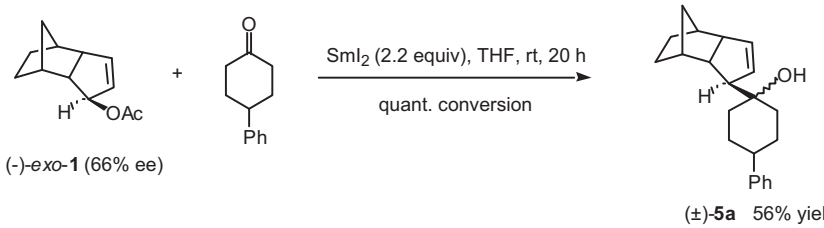
Scheme 4. Samarium-promoted allylation of cyclic ketone by stereochemically-biased allylic acetate *exo*-**1**.



Scheme 5. Samarium-promoted allylation of cyclic ketone by cyclopentenyl acetate.

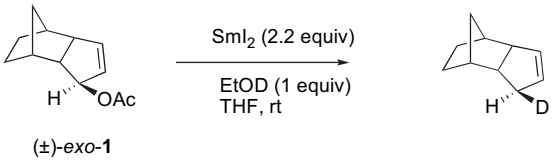
results are better explained by the formation of an allylsamarium intermediate compound resulting of a 2-electron transfer process onto the allylic acetate.

In order to investigate the generalization of the reactivity of samarium-induced coupling of allylic acetates with cyclohexanone under Barbier conditions, we carried out reactions with allyl, cinnamyl, cyclohex-2-enyl, and cyclohept-2-enyl acetates under the same conditions used above for reaction of cyclopent-2-enyl acetate and bicyclic allylic acetates *endo*-**1** and *exo*-**1**. Surprisingly, allylation of cyclohexanone did not take place. Moreover, a competitive reaction between equimolecular amounts of cyclopent-2-enyl and cyclohex-2-enyl acetates with cyclohexanone in the presence of 4.4 equiv of diodosamarium in THF resulted (GLC and ^{1}H NMR monitorings) in full conversion of only cyclopent-2-enyl acetate into the homoallylic product **4**. Our results are in agreement with those early reported by Inanaga for the reduction of allylic acetates with samarium diodide under Pd catalysis since he mentioned that no reaction occurred in the absence of Pd(0).[5] However, he did not investigate the reaction of cyclopentenyl acetate or analogs.



Scheme 6. Samarium-promoted allylation of 4-phenylcyclohexanones by stereochemically-biased allylic acetate (−)-*exo*-**1**.

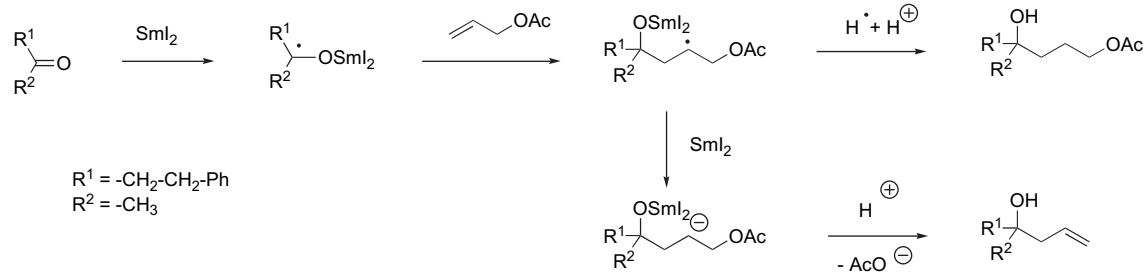
reduction compound was obtained (^{2}H NMR and mass spectrometry), in agreement with the formation of an intermediate allylsamarium species (Scheme 7).



Scheme 7. Samarium-promoted reduction of stereochemically-biased allylic acetate *exo*-**1**.

The SmI_2-mediated coupling of carbonyl compounds with allylic phosphate is documented,[8] and showed to proceed without Pd catalysis. In contrast, only one example of such a coupling has been described with allyl acetate, the SmI_2/HMPA-mediated reaction of allyl acetate with phenethyl methyl ketone to give the corresponding homoallylic alcohol (Scheme 8).[9] For this process, Inanaga suggested a mechanism going through initial ketyl formation, subsequent attack the double bond, followed by β-elimination of the acetoxy group to deliver the homoallylic alcohol.

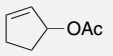
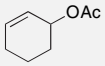
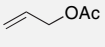
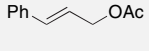
This mechanism does not fit our results since it would lead to optically active products from optically active substrates. Our



Scheme 8. Mechanism of diodosamarium-induced allylation of phenethyl methyl ketone suggested by Inanaga.[9]

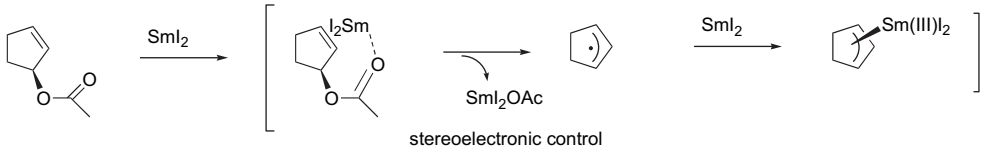
These strained substrates show a two-wave reduction process whereas other substrates show only one 2-electron wave. There appears some correlation between the electrochemical behavior and the reactivity of the investigated substrates. However we are not presently able to offer any rationalization to such a correlation.

Table 1
Reduction potential of allylic acetates measured by cyclic voltammetry[a]

		*endo*-**1**	*exo*-**1**				
Concentration (10^{-3} mmol/L)	8.00	6.35	6.35	7.15	6.30	9.30	5.20
E_1 (mV/ECS)	−0.67	−0.62	−0.68	—	—	—	—
E_2 (mV/ECS)	−0.92	−1.03	−1.05	−1.01	−1.08	−0.99	−1.00

[a] $NBu_4^+BF_4^-$ as electrolyte in THF (0.5 mol/L); scan rate 10 mV/s.

The chemoselectivity of the reaction could be tentatively explained by the requirement of both a steric and stereoelectronic control (Scheme 9). A steric control for the coordination of SmI_2 to the carbonyl of the allylic substrate should explain the more difficult access for samarium species to the acetato group and the lower reactivity of *endo*-**1** compared to the *exo* isomer.



Scheme 9. Consecutive one-electron transfers for the formation of the allylsamarium complex. The first one being under strong stereoelectronic control.

Indeed for several other SmI_2-induced reactions, a coordination of the samarium species to some carbonyl function of the substrate has been shown to be required for the reaction to proceed. Among these are the reduction of the α,β-unsaturated esters,[10] the deoxygenation of α-oxygenated esters.[11] Such coordination appears to be also requisite for the scarce SmI_2-promoted reactions of acetates with ketones that have been reported, i.e., the samarium-mediated Reformatsky coupling reactions with ketones of α-acetoxyesters[12] or 2-pyridinemethyl acetates.[13] In this latter example, 2-pyridinemethyl acetates are active substrates toward ketones while 3 or 4-pyridinemethyl acetates and benzyl acetate are inert. In other hand, we suggest that the success of the SmI_2-mediated allylation of cyclic ketones by allylic acetates depend upon a stereoelectronic control of a SmI_2-*O*-coordinated allylic acetate complex for the first electron transfer. For strained allylic substrates, the requisite conformation allowing a rapid electron transfer would be highly populated whereas it would be poorly populated for linear, cycloheptenyl and cyclooctenyl substrates.

In conclusion, through the use of stereochemically-biased and enantiomeric allylic enriched substrates **1**, we showed that palladium catalysis was not necessarily involved in the samarium diodide mediated coupling reaction of allylic acetates and cyclic ketones. However, this was observed only for a restricted number of strained allylic acetates that were reactive with cyclic ketone under samarium diodide mediation and smooth conditions (THF, room temperature). The conducted experiments would be in favor of the involvement of a π-allyl samarium species as intermediate. Formation of this complex should be under strong stereoelectronic control, via a requisite conformation being readily found in the cyclopent-2-enyl series for the first electron transfer. Further mechanistic studies would be required to provide a better understanding of such a control.

3. Experimental section

3.1. General comments

All reactions were carried out under argon using standard Schlenk and vacuum line techniques. THF was dried over sodium/benzophenone under an argon atmosphere.

Samarium diodide was prepared according to a reported procedure.[14]

^1H and ^{13}C NMR spectra were recorded at 250 and 62.5 MHz, respectively, with a Bruker AC 250 instrument. HRMS data were obtained with a GC/MS Finnigan MAT-95 spectrometer. Flash chromatography was carried out on silica gel (Merck 230–240 mesh; 0.0040–0.0630 mm).

3.1.1. X-ray crystallography. X-ray diffraction data were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[15] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[16] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[17]

The absolute configuration was determined by refining the Flack's parameter using a large of Friedel's pairs.[18]

CCDC 723105 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic Data for 2b.

Empirical formula	$C_{16}H_{24}O$	Cell volume (Å^3)	5315.0(8)
Formula wt, g/mol	232.35	*Z*	16
Temp (K)	100(1)	Density (calcd)	1.161
Wavelength	0.71073	Absorb coeff (mm^{-1})	0.070
Crystal system	tetragonal	Reflections collected	53,312
Space group	$P4_32_12$	Independent reflections	7432 (R_{int}=9.22%)
a (Å)	11.3270(7)	Final *R* indices [$I>2\sigma(I)$]	0.0764
b (Å)	11.3270(7)	Final *wR* indices [$I>2\sigma(I)$]	0.1891
c (Å)	41.426(5)	Flack parameter	0.2(3)

3.1.2. Cyclopent-2-enol. Cerium trichloride heptahydrate (27.3 g, 73.6 mmol) was dissolved in 120 mL of methanol. Then cyclopent-2-enone (6 g, 73 mmol) was introduced. After 5 min of vigorous stirring, 5.6 g (147 mmol) of sodium borohydride were carefully added portionwise and the resulting heterogeneous mixture was stirred for 15 min at room temperature. Water was added dropwise until obtention of a clear solution and then the mixture was

extracted thrice with diethylether. The organic layers were collected, dried over magnesium sulfate and the solvents were removed under vacuum. Cyclopenten-2-ol was obtained as a colorless oil (5.2 g, 85% yield) and was acylated without further purification.

^{1}H NMR ($CDCl_3$, 250 MHz): 1.65 (m, 2H), 2.26 (m, 2H), 2.5 (m, 1H), 4.90 (d, J=5.4 Hz, 1H), 5.86 (dd, J=2.2 and 5.7 Hz, 1H), 6.01 (dd, J=2.2 and 5.7 Hz, 1H).

3.1.3. Cyclopent-2-enyl acetate. Cyclopenten-2-ol (3.31 g, 39.4 mmol) was diluted in 20 mL of diethylether followed by the addition and dissolution of 500 mg (4.1 mmol) of *N*,*N*-dimethylaminopyridine. Then, triethylamine (7 mL, 50 mmol) and acetic anhydride (4.2 mL, 45 mmol) were successively added at 0 °C. The reaction mixture was stirred one night at room temperature. Diethyl ether (20 mL) was added and the mixture washed with a 1 M solution of hydrochloric acid and a saturated solution of sodium hydrogenocarbonate. The organic layer was dried over magnesium sulfate and the solvents were removed under vacuum. The crude product was then distilled under reduced pressure (70 °C/20 mmHg) to afford 3.45 g (70% yield) of a colorless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): 1.7–1.9 (m, 1H), 2.0 (s, 3H), 2.2–2.3 (m, 1H); 2.3–2.4 (m, 1H), 2.4–2.65 (m, 1H), 5.65 (m, 1H), 5.8 (m, 1H), 6.1 (m, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 21.2, 29.7, 31.0, 80.4, 129.2, 137.4, 170.9.

*3.1.4. exo-3a,4,5,6,7,7a-Hexahydro-1H-4,7-methanoindenyl acetate exo-**1**.* ^{1}H NMR ($CDCl_3$, 250 MHz): 1.1–1.6 (m, 6H), 2.05 (s, 3H), 2.35 (m, 2H), 2.45 (m, 1H), 3.15 (m, 1H), 5.6 (m, 1H), 5.8 (ddd, J=6, 2 and 2 Hz, 1H), 6.05 (m, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 21.3, 23.3, 24.7, 39.1, 39.4, 41.5, 50.9, 52.1, 81.2, 129.3, 141.7, 171.2. IR (neat): 2954, 2875, 1735, 1364, 1244, 1042, 1018, 948, 767. HRMS (EI): 192.1143, calcd: 192.1150. GLC the enantiomers are separable over a Chiraldex-b-PM column (15 m), isotherm program at 140 °C, t_1=12.6 min, t_2=13.3 min. $[\alpha]_D^{20}$ −12 ($CHCl_3$, c=1) (66% ee, by chiral GLC analysis).

*3.1.5. endo-3a,4,5,6,7,7a-Hexahydro-1H-4,7-methanoindenyl acetate endo-**1**.* ^{1}H NMR ($CDCl_3$, 250 MHz): 1.1–1.7 (m, 6H), 2.05 (s, 3H), 2.1 (s, 1H), 2.3 (s, 1H), 2.85 (m, 2H), 5.6 (dm, J=9 Hz, 1H), 5.7 (ddd, J=6 and 2 Hz, 1H), 5.9 (ddd, J=5 and 2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 21.0, 23.6, 24.6, 39.3, 40.5, 41.2, 46.3, 51.0, 78.7, 129.6, 137.1, 171.0. IR (neat): 2951, 2875, 1735, 1364, 1263, 1242, 1081, 1047, 1020, 748. HRMS (EI): 192.1143, calcd: 192.1150. GLC the enantiomers are separable over a Chiraldex-b-PM column (15 m), isotherm program at 140 °C, t_1=13.4 min, t_2=17.6 min. $[\alpha]_D^{20}$ +98.6 ($CHCl_3$, c=1.15) (96% ee, by chiral GLC analysis).

3.2. General procedure for the samarium diodide mediated coupling between allylic acetates and electrophiles

Equimolar quantities of allylic acetate (0.5 mmol) and electrophile (0.5 mmol) were diluted in 1 mL of dry THF and were then added to 11 mL (1.1 mmol) of a 0.1 M solution of SmI_2 in THF. The resulting mixture was stirred for 15 h at room temperature. After hydrolysis with a 1 M solution of hydrochloric acid the mixture was extracted thrice with diethylether, the organic layers were dried over magnesium sulfate and the solvents were removed under vacuum. The crude product was then purified by flash chromatography on silica gel (heptane/ethyl acetate: 9/1).

3.2.1. 1-(Cyclopent-2′-enyl)cyclohexan-1-ol. Colorless oil, 58% yield (70% in the presence of a catalytic amount of $Pd(PPh_3)_4$).

^{1}H NMR ($CDCl_3$, 250 MHz): 1.30–1.70 (m, 8H), 1.90 (m, 4H), 2.35 (m, 2H), 2.70 (m, 1H), 5.75 (dq, J=2.2 and 6 Hz, 1H), 5.92 (dq, J=2.2 and 6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 19.4, 21.9, 24.4, 29.4, 32.2, 35.5, 52.1, 130.1, 133.8. IR (neat): 3460, 3052, 2931, 2850, 1447, 1260. HRMS (EI): 166.1352, calcd: 166.1358.

*3.2.2. exo-1-(3′a,4′,5′,6′,7′,7′a-Hexahydro-1′H-4′,7′-methano)indenylcyclobutan-1-ol **2a**.* Yellow oil, 57% yield starting from the *exo*-acetate **1** in the presence of a catalytic amount of $Pd(PPh_3)_4$.

^{1}H NMR ($CDCl_3$, 250 MHz): 1.41–1.59 (m, 6H), 1.63–1.79 (m, 4H), 2.06 (m, 2H), 2.17 (m, 1H), 2.27 (m, 2H), 2.88 (m, 1H), 2.99 (m, 1H), 5.65 (dt, J=2.1 and 5.7 Hz, 1H), 5.89 (dt, J=2 and 5.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 22.7, 22.9, 25.0, 29.4, 29.7, 33.8, 45.4, 52.9, 53.8, 68.0, 76.2, 129.1, 138.2. IR (neat): 3426, 3040, 2949, 2871, 1454, 1363, 1244. HRMS (EI): 204.1310, calcd: 204.1314.

*3.2.3. exo-1-(3′a,4′,5′,6′,7′,7′a-Hexahydro-1′H-4′,7′-methano)indenylcyclohexan-1-ol **2b**.* Colorless crystals, 70% yield starting from the *exo*-acetate **1** in the presence of a catalytic amount of $Pd(PPh_3)_4$.

Mp 85–88 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): 1.2 (m, 6H), 1.3–1.7 (m, 11H), 2.11 (m, 1H), 2.28 (m, 1H), 2.42 (dt, J=3.6 and 9.6 Hz, 1H), 2.55 (q, J=3 Hz, 1H), 2.94 (m, 1H), 5.68 (dt, J=2.3 and 5.9 Hz, 1H), 5.78 (ddt, J=0.8, 2.1 and 5.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 22.0, 23.0, 24.9, 26.0, 35.0, 36.1, 39.2, 41.0, 41.4, 44.8, 52.6, 56.1, 73.2, 129.8, 136.9. IR (neat): 3422, 3043, 2949, 2875, 1451, 1363, 1240. HRMS (EI): 232.1822, calcd: 232.1827.

*3.2.4. exo-1-(3′a,4′,5′,6′,7′,7′a-Hexahydro-1′H-4′,7′-methano)indenyl-4-phenylcyclohexan-1-ol **5a**.* White solid. 56% yield of the major diastereomer.

Mp 76–79 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): 1.39–1.65 (m, 8H), 1.70–1.92 (m, 7H), 2.17 (m, 1H), 2.33 (m, 1H), 2.47 (m, 2H), 2.56 (m, 1H), 2.99 (m, 1H), 5.73 (dt, J=2.1 and 5.7 Hz, 1H), 5.82 (dt, J=2.1 and 5.7 Hz, 1H), 7.21–7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 15.3, 23.0, 25.0, 35.1, 35.9, 39.2, 41.0, 41.4, 44.2, 45.0, 52.6, 57.5, 65.9, 72.6, 125.9, 126.9, 128.3, 129.8, 137.1, 147.4. IR (neat): 3425, 3031, 2976, 2865, 1708, 1363, 1244. HRMS (EI): 308.1804, calcd: 308.2140.

Enantiomers were separated analytically, on Chiralpak IA, hexane/isopropanol 75:25, flow 0.8 mL·min^{-1}, l=225 nm, 293 K, t_1=8.40 min, t_2=9.55 min.

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