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Article

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Additive Tuned Selective Synthesis of Bicyclo[3.3.0]octan-1-ols and Bicyclo[3.1.0]hexan-1-ols Mediated by AllylSmBr

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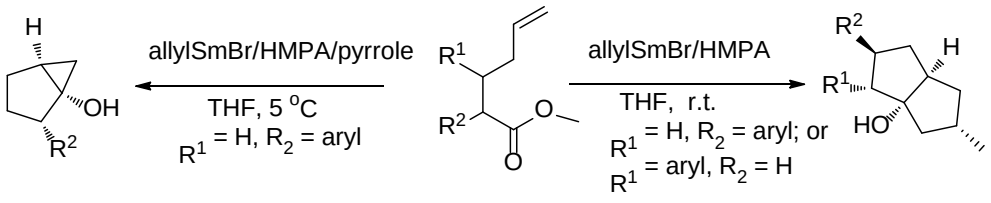


Abstract: The selective construction of bicyclo[3.3.0]octan-1-ols and bicyclo[3.1.0]hexan-1-ols was achieved by using allylSmBr/additive(s) system. By employing HMPA as the only additive, the momoallylation/ketone-alkene coupling occurred preferably and afforded bicyclo[3.3.0]octan-1-ols in good yields with high diastereoselectivities. While the ester-alkene coupling predominated to generate bicyclo[3.1.0]hexan-1-ols in moderate yields with excellent diastereoselectivities in the presence of a proton source, such as pyrrole as the co-additive with HMPA. The tunable reactivity of allylSmBr by additive(s) would make it a versatile reagent in

organic synthesis.

Introduction

Divalent samarium reagents[1] especailly SmI_2 have played important roles in organic and natural products synthesis due to the unique single-electron transfer (SET) property for C-C bond formation reactions. New Applications[2] of the reductive coupling reactions as well as new types of coupling reactions[1c,3] promoted by the divalent samarium reagents continue to emerge.

On the other hand, allylsamarium bromide (allylSmBr) represents a typical divalent organosamarium reagent, which has been well known as an efficient *C*-nucleophilic reagent for the allylation of a variety of compounds.[4] However, the potential of allylSmBr to act as a SET reagent has long been neglected despite the reagent's inclination to revert to the more stable Sm(III) oxidation state. Although a number of additives[1j] have been found to enhance or tune the reactivity of SmI_2 to various extent or even switch the reaction pathways,[5] only in recent years, certain additives were found to be able to switch allylSmBr from a nucleophilic species into a SET reagent. For example, allylSmBr combined with MeOH could achieve the reductive dehalogenation of α-haloketones and α-haloesters.[6] With MeOH or H_2O as additive, a variety of carbonyl compounds could undergo the pinacol coupling promoted by allylSmBr, instead of being transformed into homoallylic alcohols.[7] Furthermore, the unique reductive coupling ability of allylSmBr has been demonstrated by using HMPA/H_2O[8] or HMPA/$CuCl_2.2H_2O$[9] as co-additives, thus the homoallylic esters were transformed into 2-(2-hydroxyalkyl)cyclopropanols and

2-(2-hydroxyethyl)bicycle [2.1.1]hexan-1-ols in moderate to good yields with good to excellent diastereoselectivities. In addition, allylSmBr/HMPA/CH_3SO_3H system has recently been applied in the preparation of oxobicyclo[3.1.0]hexane-1-ols *via* the "ester-alkene" coupling/cyclization cascade of α-allyloxy esters.[10]

The distinctive utility of allylsamarium bromide both as a nucleophilic reagent and a single-electron transfer reagent in one pot has been reported by Zhang's group. Treatment of α-halo, γ-halo-α,β-unsaturated ketones or esters with allylSmBr afforded 1,4-dienes and trienes in good to excellent yields[2] *via* the Grignard reaction followed by reductive removal of the halogen and oxygen at the same time. Alternatively, the nucleophilic addition to the carbonyl compounds followed by deoxygenation by allylSmBr/diethyl phosphate system provided a facile synthesis of terminal olefins.[11]

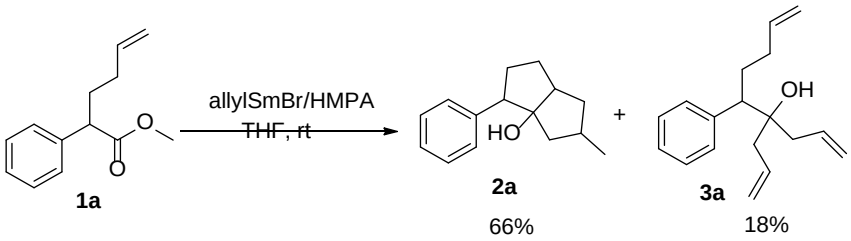
Despite the above reports, the factors that may influence the reactivity of allylSmBr as for its nuclophilicity or reductivity are not well known and further study concerning the applications of the reagent in organic synthesis are still worth exploring.

Results and Discussion

The survey began with 2-phenyl-hex-5-enoate **1a** as the model substrate where an ester group was included for either nucleophilic addition or reductive coupling. Firstly, HMPA was used as the only additive (Table 1, entries 1-4). To the allylSmBr/THF solution prepared *in situ* was added HMPA and **1a** sequentially. The reaction mixture was allowed to stir at rt until the disappearance of **1a**. Unexpectedly **2a** was obtained

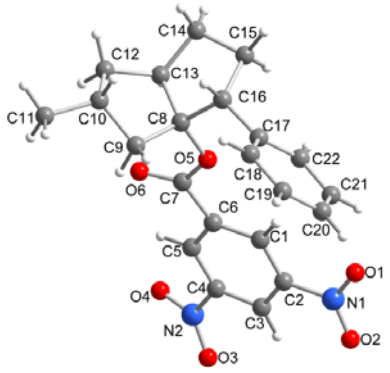
as the major product together with the isolation of the diallylation products **3a** in 18 % yield (Scheme 1).

Scheme 1. Formation of **2a** as the major product with HMPA as the only additive



The structure of **2a** has been characterized by NMR and HRMS determination and also unambiguously ascertained by deriving into its ester of 3,5-dinitrobenzoic acid (**2a′**, 79% yield) followed by single crystal diffraction analysis (Figure 1).[12]

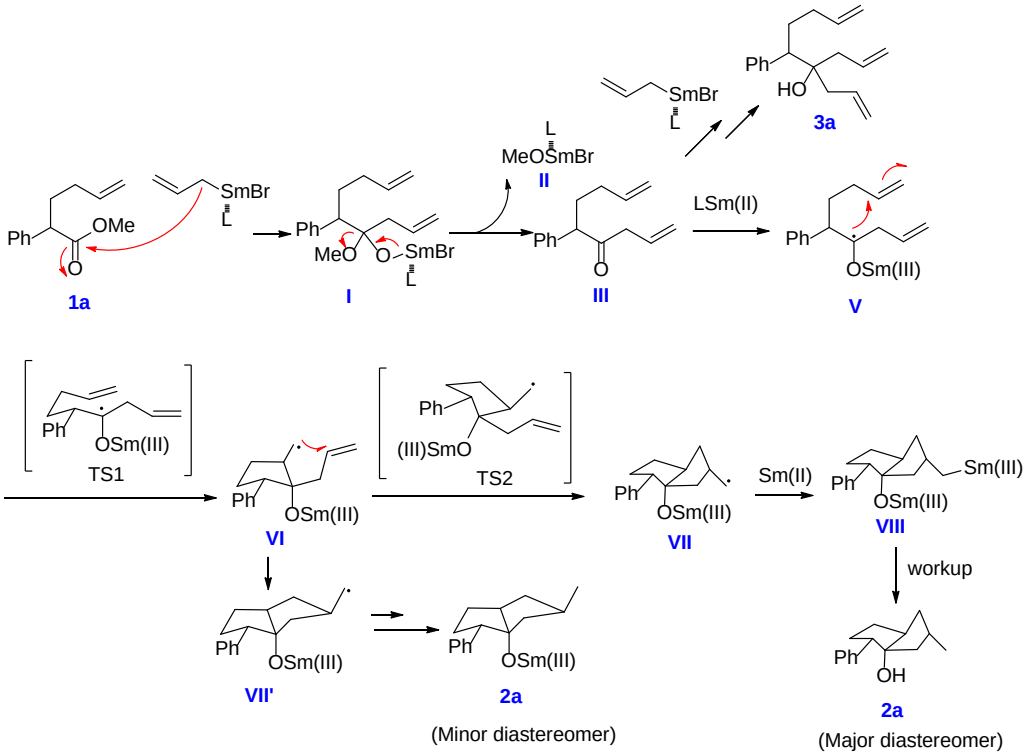
Figure 1. The X-ray crystal structure of **2′a**



The mechanism for the formation of **2a** was then probed. By comparison with the ^{13}C-NMR data of **1a**, three additional carbons were found to have been included in **2a**. It is reasonable to deduce that the three carbons came from allylSmBr. Accordingly, a possible mechanism was proposed in Scheme 2. The allylation of **1a** with the allylSmBr in the presence of HMPA would first generate intermediate **III**. Under the circumstances, a second allylation of **III** by the allylSmBr/HMPA complex

would afford **4a**, or alternatively the allylSmBr/HMPA complex may function as an electron donor to trigger the ketyl-alkene coupling of **III** thus converting the carbonyl into a ketyl (**IV** and **V**). The isolation of **2a** as the major product indicated the ketyl-alkene coupling of intermediate **III** was preferred rather than being further allylated. **V** underwent subsequent cascade radical cyclization *via* the chair-like transition state would afford the predominant diastereomer **2a** with the phenyl, the hydroxyl and the methyl pointing at the same direction. The minor diastereomer of **2a** could be formed form the less preferential transition state with the methyl being anti- to the phenyl and hydroxyl.

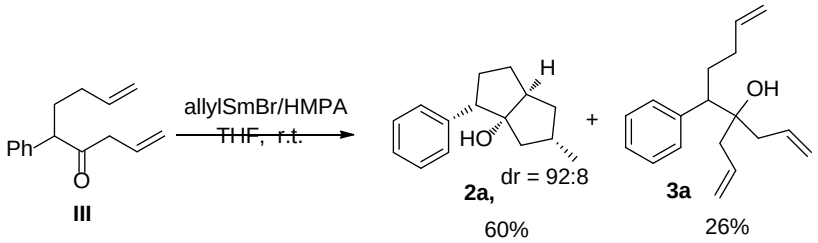
Scheme 2. Proposed mechanism for the formation of **2a**



To further rationalize the mechanism, authentic sample **III** was synthesized[13] and subjected to the allylSmBr/HMPA (2.2 equiv/8.8 equiv) system to examine the ketone-alkene coupling reaction.[14] The isolation of **2a** in 60% yield (Scheme 3)

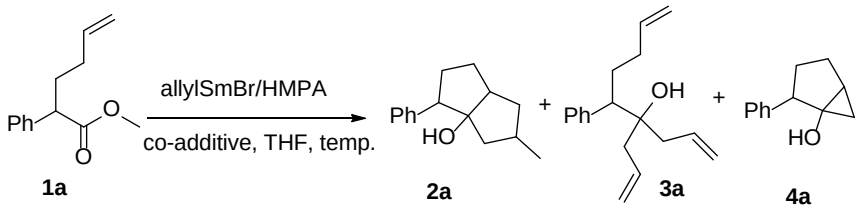
provided a reasonable support to the proposed mechanism.

Scheme 3. Generation of **2a** from **III**

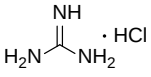


It is interesting to observe the coordination of HMPA has enhanced the SET property of allylSmBr to such an extent that the ketyl-alkene coupling predominated over the second alllylation of intermediate **III**. On the other hand, the reducing power of allylSmBr/HMPA was not strong enough to trigger the "ester-alkene" coupling since the momoallylation occurred prior to the reduction of ester. Based on the elucidation on the formation of **2a**, a variety of conditions were further examined for preparative purposes and also to demonstrate the influences of other additives on the nucleophilicity/reducibility of the reagent (Table 1).

Table 1. Reaction of **1a** with AllylSmBr Under Various Conditions[a]



Entry	allylSmBr (equiv)/ HMPA(equiv)	Co-additive (equiv)	Temp (°C)	Yield of **2a**[b]	Yield of **3a**[b]	Yield of **4a**[b]
1	3.3/16	none	r.t.	66	18	-
2	3.3/16	none	0 °C	70	14	-

3	3.3/16	none	-20	55	26	-
4	4.4/20	none	r.t.	78	Trace	12
5	2.2/8	none	r.t.	35	48	trace
6	3.3/0	none	r.t.	0	94%	trace
7	3.3/16	H_2O (1.6)	r.t.	trace	0	52
8	3.3/16	H_2O (1.6)[c]	r.t	40	0	51
9	3.3/16	H_2O (3.0)	r.t.	trace	0	trace
10	3.3/16	MeOH (1.6)	r.t.	trace	0	37[d]
11	3.3/16	$CuCl_2 \cdot 2H_2O$ (1.6)	r.t.	trace	0	43[d]
12	3.3/16	 (1.6)	r.t.	trace	0	41[d]
13	3.3/16	 (1.6)	r.t.	trace	0	55[d]
14	3.3/16	 (1.6)	5 °C	trace	0	65[d]
15	3.3/16	 (1.6)	-5 °C	trace	0	53[e]

[a]Reaction conditions: **1a** (1 mmol) was added to the mixture of allylSmBr (3.3 eq), HMPA (16 eq) and co-additive (1.6 eq) in dry THF (30 mL). The reaction mixture was stirred at rt for 12 h under N_2 unless otherwise specified. [b]Isolated yield. [c]A mixture of **1a** and H_2O (1.6 eq) was added dropwise to the allylSmBr (3.3 eq)/HMPA (16 eq) mixture. [d]2-Methyl-5-phenylcyclopentanol and other unidentified by-products mixture were observed by crude ^1H NMR. [e]Reaction time: 24 h; Starting **1a** recovered in 21% yield and unidentified by-products were also detected.

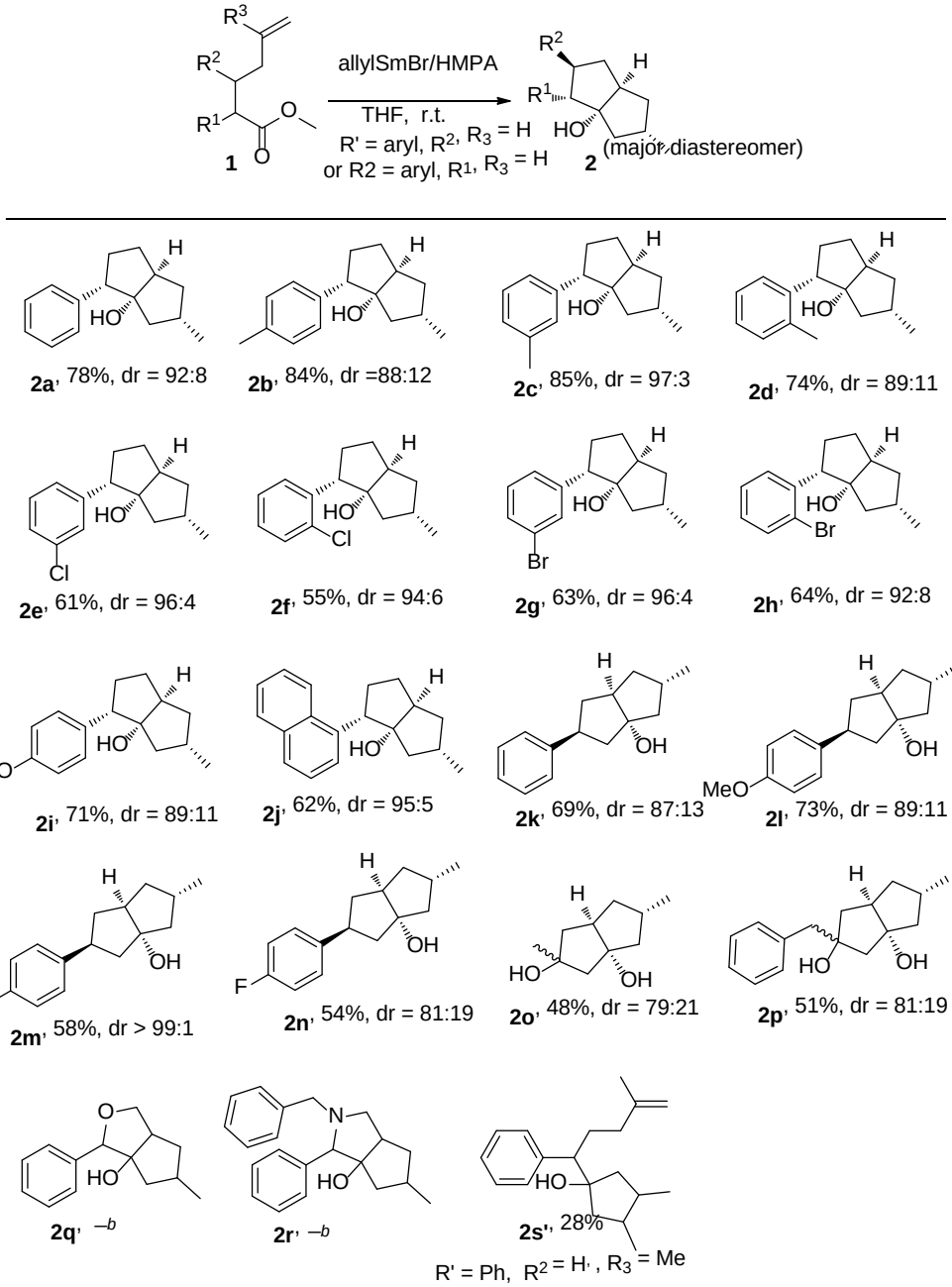
The investigation showed lowering the temperature to 0 °C afforded a slightly better yield of **2a**. However, decrease of the temperature to -20 °C would otherwise be beneficial for the formation of **3a** (Table 1, entries 2 and 3). The employment of excess allylSmBr/HMPA (4.4 equiv/20 equiv) led to improved yield of **2a** (78%, entry 4). On the contrary, decrease in the loading of allylSmBr/HMPA (2.2 equiv/8 equiv) would sharply lower the yield of **2a** while the yield of **3a** was increased (entry 5). The results indicate the divalent samarium species **II** should not be the reductive coupling reagent, and allylSmBr/HMPA was indispensable for the efficient ketone-alkene coupling. Control experiment showed in the absence of HMPA, allylSmBr was strongly nucleophilic and its reaction with **1a** would give the diallylated **3a** almost quantitatively (Table 1, entry 6). Besides, it is interesting to find the coexistence of H_2O (1.6 equiv) would afford **4a** as the major product, following an "ester-alkene" coupling cascade cyclization.[8,9] At the same time, **2a** was only formed in a trace amount (Table 1, entry 7) and **3a** was not observed, indicating the reducing potential of allylSmBr may be further facilitated by the co-existence of the proton source and at the same time its nucleophilicity was further diminished. When a mixture of **1a** and H_2O was added dropwise to the allylSmBr/HMPA, a mixture of **2a** (40%) and **4a** (51%) was obtained and again the formation of **3a** was not observed (entry 8). However, increase the loading of H_2O to 3.0 equiv was destructive and almost no reaction occurred under the conditions (Table 1, entry 9). Other proton sources such as MeOH, $CuCl_2 \cdot 2H_2O$ and guanidine hydrochloride were less effective than H_2O, except pyrrole, which afforded slightly better yield (entry 13). Lowering the

temperature to 5 °C afforded a synthetically useful 65% yield of **4a** (entry 14). Further decrease of the temperature to -5 °C led to sluggish reaction and prolonging the reaction time to 24 h resulted in 53 % yield of the desired **2a**, 21% recovery of the starting materials and other unidentified by-products (entry 15).

According to the above observations, a variety of substrates **1** were tested under the optimized conditions (Talbe 1, entry 14) to explore the synthetic utility of the allylSmBr/HMPA mediated monoallylation/reductive cyclization cascade. As shown in Scheme 4, substrates **1a**-**1p** underwent the reaction smoothly and the desired bicyclo[3.3.0]octan-1-ols **2** were prepared in good to moderate yields. Good to excellent diastereoselectivities were also observed. The halogen such as chloro and bromo is well tolerated despite the strong reducing conditions. *Ortho*-substituion of the aryl ring also showed good reactivity (**2d**, **2f** and **2h**). Generally, when R^1 is an electron-rich aryl, the reaction afforded better yields than their counterparts with withdrawing aryl group. Notably the hydroxyl group could be tolerated (**2o** and **2p**). Thus the allylSmBr/HMPA mediated addition/coupling cascade of hex-5-enoates afforded a facile synthesis of bicyclo[3.3.0]octan-1-ols. However, the attempt to involve an heteroatom such as *O*- or *N*-in the bicyclo[3.3.0]octan-1-ol failed (**2q**, 0%; **2r**, 0%). When substrate **1s**, a more-substituted alkene structure was included, the desired **2s** was not obtained either. On the other hand, an unexpected product **2s′** was isolated in 28% yield. The formation of **2s′** is not clear at the stage, nevertheless the monoallylation and ketone-alkene coupling in a different way undoubtedly occurred. The result indicates a more difficult ketone-alkene coupling when the alkene is more

substituted.

Scheme 4. Preparation of Bicyclo[3.3.0]octan-1-ols[a]



[a]Reaction conditions: a mixture of substrate **1** (1 mmol), allylSmBr (4.0 eq) and HMPA (20 eq) in dry THF (30 mL) was stirred at rt for 12 h under N_2. Isolated yields were reported.

[b]Complicated mixture.

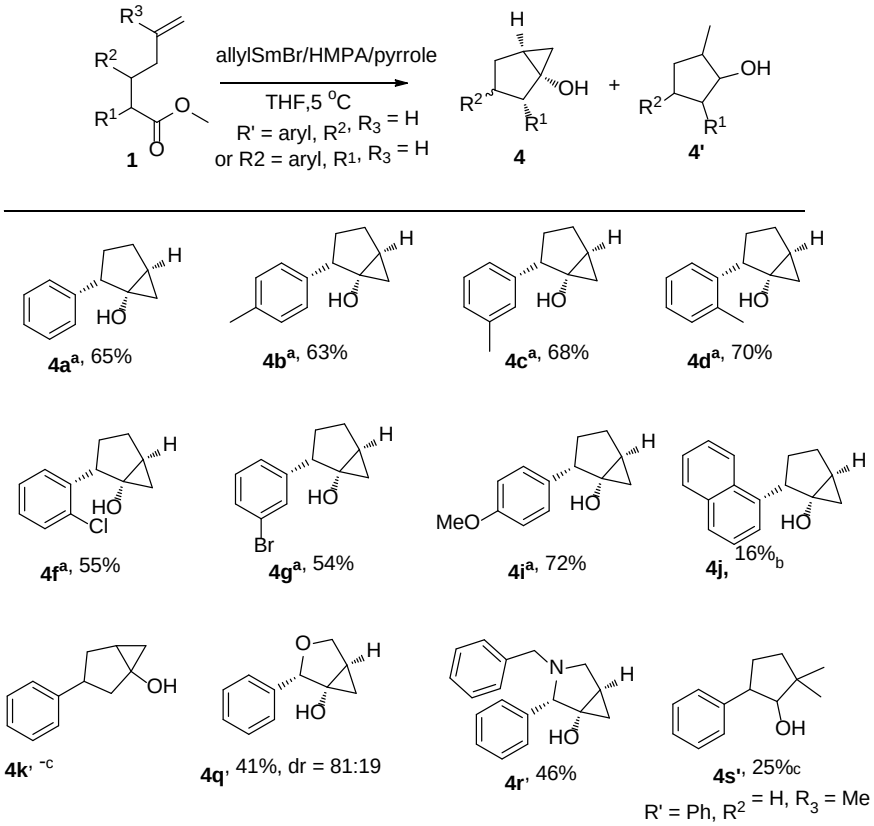
The substrates **1** were then treated with allylSmBr/HMPA/pyrrole at 5 ^{o}C for the preparation of bicyclo[3.1.0]hexan-1-ols **4**. Usually only one diastereomer was observed, showing excellent diastereoselectivity. In view of the analogous mechanism for the formation of bicyclo[3.1.0]hexan-1-ols **4** and oxobicyclo[3.1.0]hexane-1-ols,[9]the stereochemistry of **4** was tentatively designated and the results were listed in Scheme 5.

Substrates with R^1 being an aryl generally afforded the desired **4** in good yields except **1j**, which afforded a mixture of **4j** and **4j′**. Surprisingly, **1k** with R^2 being the phenyl afforded a complicated mixture. Substrate **1q and 1r**, where the β-carbon substituted by an heteroatom, afforded moderate yields of the oxobicyclo[3.1.0]hexane-1-ol **4q** and azabicyclo[3.1.0]hexane-1-ol **4r**. Substrte **1s** afforded complicated mixture, from which the major product was isolated and characterized as **4s′** (25 % yield). The desired ester-alkene coupling did proceed although the desired **4s** was not obtained with additional substitution on the C=C bond.

It is worth mentioning that the switch of reactivity of allylSmBr to generate **4** could be well accounted for by the proton coupled electron transfer (PCET) mechanism.[15] Only in the presence of a coordinating proton source, the reduction of the unactiviated ester is likely and the ester-alkene coupling could occur. Hoz and Flowers recently demonstrated a range of amines have high affinity of Sm(II).[16] It is possible that pyrrole in the presence of the basic HMPA also has high affinity with Sm(II) and therefore afforded relatively better result for the production of **4** than other

proton sources examined.

Scheme 5. Preparation of Bicyclo[3.1.0]hexan-1-ols[a]



[a] Reaction conditions: a mixture of substrate **5** (1 mmol), allylSmBr (3.3 eq), HMPA (16 eq) and H_2O (1.6 eq) in dry THF (30 mL) was stirred at 5 °C for 12 h under N_2. Isolated yields were given. [b]Together with 0.11 g of inseparable mixture of **4j** and **4j′** (**4j: 4j′**. = 1.5:1, determined by ^{1}HNMR). [c]Complicated mixture.

Conclusions

In conclusion, HMPA was found to moderately tuning up the reducing power while tuning down the nucleophilic ability of allylSmBr. With HMPA as the additive, the hex-5-enoates afforded bicyclo[3.3.0]octan-1-ols in moderate to good yields *via* the intermolecular monoallylation/intramolecular ketyl-alkene coupling cascade, which is unprecedented for the Sm(II) reagent. Preparation of the bicyclo[3.3.0]octan-1-ols

with versatile substitution patterns from the readily available hex-5-enoates make the approach advantageous as compared with the alternative methods *via* the Barbier reaction of δ-iodocyclopentanone[17] or ketone/alkene coupling of olefinic cyclopentanones promoted by SmI_2/HMPA.[14a, b] On the other hand, the co-existence of a proton source was found to greatly enhance the reducing power while diminishing the nucleophilicity of allylSmBr at the same time, as was demonstrated by the fact that the hex-5-enoates preferred to undergo the ester-alkene coupling cascade and produced bicyclo[3.1.0]hexan-1-ols as the major products. Synthetically, the latter reaction was less attractive since the Kulinkovich reactions[18] could afford better yields of bicyclo[3.1.0]hexan-1-ols from the same substrates. Further studies concerning further tuning the nucleophilicity and reductivity of the divalent organosamarium reagent is still underway in our lab.

Experimental Section

General Information. Metallic samarium and other solvents were obtained from commercial sources, and used without further purification, if not stated otherwise. THF was distilled from sodium/benzophenone. Unless otherwise noted, all the cascade reactions were carried out under a nitrogen atmosphere in oven-dried flasks. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ on a 400 M Hz or 600 M Hz instrument with TMS as internal standard. Chemical shifts (δ) were reported in parts per million (ppm) downfield from TMS. Data are represented as follows: chemical shift, mutiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (*J*, Hz) and integration. Thin layer

chromatography (TLC) was performed with 0.2 mm thick silica gel plates (GF 254). Visualization was accomplished by UV light or by using phospho molybdate as the chromogenic reagent. The columns were hand packed with silica gel (200–300 mesh). Unknown products were additionally confirmed by high-resolution mass spectra (HRMS) using a TOF-MS instrument with ESI or APCI ionization. Compound **1a**[19] is known compound and was prepared using method A;[20] Compounds **1k**[21] is known compound and was prepared using method B.[22] Compounds **1o**[23] is a known compound and was prepared using method C.[24] Substrate **1q** is a known compound and was prepared according to the literature.[10]

General procedure for the preparation of substrates 1

Substrates 1a-1j were prepared using method A.[20] To a 0 °C solution of $^{i}Pr_2NH$ (1 mL, 6.6 mmol) in THF (30 mL) was added n-BuLi (2.5 M in Et_2O, 2.6 mL, 6.6 mmol) dropwise. The reaction mixture was stirred for 10 minutes, and then cooled to -78 °C. The respective methyl arylacetate (6.0 mmol) in THF (2 mL) was added dropwise, and the reaction mixture was stirred for 30 min. The 4-bromobut-1-ene (0.972 g, 7.2 mmol) was added in THF (2 mL) followed by HMPA (0.6 mL, 3.7 mmol). It was then warmed to room temperature and stirred overnight. The reaction was diluted with 1:1 Et_2O :Hexanes, washed with sat. aq. NH_4Cl and brine, dried ($MgSO_4$), and concentrated *in vacuo*. Purification by column chromatography (20:1 Hex: EtOAc) afforded **1a-1j** and **1s** as pure compounds. **1b-1j** and **1s** are new compounds.

Methyl 2-phenylhex-5-enoate (1a).[19] Oil (1.05 g, 86% yield); ^1H NMR (400 MHz,

$CDCl_3$) δ 7.34–7.23 (m, 5H), 5.83–5.73 (m, 1H), 5.03–4.96 (m, 2H), 3.64 (s, 3H), 3.58 (t, J = 7.6 Hz, 1H), 2.24–2.14 (m, 1H), 2.01 (dd, J = 14.4, 6.8 Hz, 2H), 1.92–1.83 (m, 1H).

Methyl 2-(p-tolyl)hex-5-enoate (1b). Oil (1.22 g, 93% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 5.83–5.70 (m, 1H), 5.02–4.94 (m, 2H), 3.61 (s, 3H), 3.56–3.53 (m, 1H), 2.30 (s, 3H), 2.19–2.12 (m, 1H), 2.01 (dd, J = 9.8, 4.2 Hz, 2H), 1.88–1.82 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 137.4, 136.7, 135.8, 129.2, 127.7, 115.2, 51.7, 50.1, 32.3, 31.3, 20.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1380; Found: 219.1383.

Methyl 2-(m-tolyl)hex-5-enoate (1c). Oil (1.18 g, 90% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20-7.17 (m, 1H), 7.10-7.04 (m, 3H), 5.83–5.70 (m, 1H), 5.02–4.94 (m, 2H), 3.61 (s, 3H), 3.55–3.52 (m, 1H), 2.30 (s, 3H), 2.19–2.12 (m, 1H), 2.01 (dd, J = 9.8, 4.2 Hz, 2H), 1.88–1.82 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 138.8, 138.1, 137.5, 128.5, 128.4, 127.9, 124.9, 115.2, 51.7, 50.6, 32.4, 31.4, 21.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1380; Found: 219.1381.

Methyl 2-(o-tolyl)hex-5-enoate (1d). Oil (1.14 g, 87% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.30 (m, 1H), 7.18–7.11 (m, 3H), 5.87–5.70 (m, 1H), 5.06–4.94 (m, 2H), 3.87 (t, J = 7.0 Hz, 1H), 3.62 (s, 3H), 2.37 (s, 3H), 2.24–2.19 (m, 1H), 2.08–2.02 (m, 2H), 1.85–1.81 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 137.6, 137.4, 135.9, 130.4, 126.8, 126.6, 126.3, 115.2, 51.7, 45.8, 32.0, 31.5, 19.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1380; Found: 219.1382.

Methyl 2-(3-chlorophenyl)hex-5-enoate (1e). Oil (1.29 g, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.24–7.15 (m, 3H), 5.84–5.70 (m, 1H), 5.02–4.96 (m, 2H), 3.65 (s, 3H), 3.55 (t, J = 7.6 Hz, 1H), 2.21–2.11 (m, 1H), 2.03–1.97 (m, 2H), 1.89–1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 140.8, 137.1, 134.4, 129.8, 128.1, 127.4, 126.2, 115.6, 52.0, 50.3, 32.3, 31.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}ClO_2$ 239.0833; Found: 239.0830.

Methyl 2-(2-chlorophenyl)hex-5-enoate (1f). Oil (1.30 g, 91% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.23–7.14 (m, 2H), 5.80–5.74 (m, 1H)), 5.02–4.94 (m, 2H), 4.17 (t, J = 7.5 Hz, 1H), 3.64 (s, 3H), 2.22–2.14 (m, 1H), 2.09–1.98 (m, 2H), 1.89–1.82 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 137.3, 136.7, 133.9, 129.6, 128.6, 128.2, 127.0, 115.3, 52.0, 46.5, 31.8, 31.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}ClO_2$ 239.0833; Found: 239.0834.

Methyl 2-(3-bromophenyl)hex-5-enoate (1g). Oil (1.49 g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.41–7.36 (m, 1H), 7.24–7.15 (m, 2H), 5.81–5.70 (m, 1H), 5.05–4.95 (m, 2H), 3.65 (s, 3H), 3.54 (t, J = 7.6 Hz, 1H), 2.22–2.11 (m, 1H), 2.00 (dd, J = 14.1, 7.1 Hz, 2H), 1.89–1.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 141.1, 137.1, 131.0, 130.4, 130.1, 126.6, 122.6, 115.6, 52.0, 50.3, 32.3, 31.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}BrO_2$ 283.0328; Found: 283.0330.

Methyl 2-(2-bromophenyl)hex-5-enoate (1h). Oil (1.39 g, 82% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.0, 1.2 Hz, 1H), 7.37-7.35 (m, 1H), 7.29–7.26 (m, 1H), 7.12–7.08 (m, 1H), 5.82– 4.75 (m, 1H), 5.06–4.94 (m, 2H), 4.18 (t, J = 7.4 Hz, 1H), 3.66 (s, 3H), 2.19–2.13 (m, 1H), 2.12–2.06 (m, 1H), 2.05–1.98 (m, 1H), 1.89–1.83 (m,

1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 138.5, 137.4, 133.0, 128.7, 128.6, 127.7, 124.7, 115.4, 52.0, 49.2, 32.2, 31.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}BrO_2$ 283.0328; Found: 283.0323.

Methyl 2-(4-methoxyphenyl)hex-5-enoate (1i). Oil (1.22 g, 87% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.18 (m, 2H), 6.85–6.83 (m, 2H), 5.79–5.73 (m, 1H), 5.01–4.95 (m, 2H), 3.75 (s, 3H), 3.62 (s, 3H), 3.52 (t, J = 7.0 Hz, 1H), 2.16–2.11 (m, 1H), 1.99 (dd, J = 14.4, 7.1 Hz, 2H), 1.87-1.85 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 158.6, 137.4, 130.7, 128.7, 115.1, 113.8, 54.9, 51.6, 49.6, 32.3, 31.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_3$ 235.1329; Found: 235.1326.

Methyl 2-(naphthalen-1-yl)hex-5-enoate (1j). Oil (1.28 g, 84% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24–8.22 (m, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.62 (dd, J = 8.3, 7.0 Hz, 2H), 7.56–7.51 (m, 2H), 5.96–5.87 (m, 1H), 5.15–5.09 (m, 2H), 4.56–4.50 (m, 1H), 3.70 (s, 3H), 2.54–2.47 (m, 1H), 2.26–2.17 (m, 2H), 2.16–2.09 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 137.4, 135.2, 133.9, 131.4, 128.8, 127.6, 126.2, 125.5, 125.4, 124.8, 123.0, 115.4, 51.8, 45.7, 32.1, 31.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}O_2$ 255.1380; Found: 255.1381.

Methyl 5-methyl-2-phenylhex-5-enoate (1s). Oil (0.93 g, 71% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.27 (m, 4H), 7.24–7.21 (m, 1H), 4.73 (s, 1H), 4.66 (d, J = 0.7 Hz, 1H), 3.62 (s, 3H), 3.55 (t, J = 7.5 Hz, 1H), 2.26–2.20 (m, 1H), 2.00–1.86 (m, 3H), 1.69 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 144.4, 138.9, 128.5, 127.8, 127.1, 110.6, 51.7, 50.7, 35.3, 31.2, 22.1; HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1380; Found: 219.1381.

Substrates 1k-1n were prepared using method B.[22]

A reaction vessel containing 4Å molecular sieves (1.0 g) was flame-dried under vacuum and placed under N_2. A solution of anhydrous TBAF (0.2 g, 0.77 mmol; 1.0 M in THF) was then added. The respective methyl cinnamate (6 mmol) dissolved DMF (10 mL) was then added. A solution of HMPA (3.31 g, 18.5 mmol) and freshly distilled allylsilane (2.05 g, 18 mmol) in DMF (20 mL) was then added dropwise to the reaction vessel at rt. Coloration occurred immediately. After 10 min, TLC analysis revealed that reaction was complete. After methanolysis of the reaction mixture using 10 mL of 1M HCl in methanol, the reaction mixture was diluted with 200 mL of water. Workup afforded the residue, which was purified by column chromatography to afford the corresponding **1k-1n**. **1l-1n** are new compounds.

Methyl 3-phenylhex-5-enoate (1k).[21] Oil (0.89 g, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.21–7.16 (m, 3H), 5.70–5.60 (m, 1H), 5.03–4.92 (m, 2H), 3.56 (s, 3H), 3.27–3.16 (m, 1H), 2.69 (dd, J = 15.4, 6.7 Hz, 1H), 2.57 (dd, J = 15.4, 8.3 Hz, 1H), 2.42–2.34 (m, 2H).

Methyl 3-(4-methoxyphenyl)hex-5-enoate (1l). Oil (1.12 g, 80% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.68–5.61 (m, 1H), 5.00–4.95 (m, 2H), 3.76 (s, 3H), 3.56 (s, 3H), 3.20–3.13 (m, 1H), 2.66 (dd, J = 15.3, 6.6 Hz, 1H), 2.53 (dd, J = 15.3, 8.5 Hz, 1H), 2.36 (t, J = 7.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 158.1, 136.0, 135.5, 128.2, 116.7, 113.7, 55.0, 51.3, 40.9, 40.64, 40.55; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_3$ 235.1329; Found: 235.1325.

Methyl 3-(4-chlorophenyl)hex-5-enoate (1m). Oil (1.06 g, 74% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25–7.22 (m, 2H), 7.11–7.08 (m, 2H), 5.65–5.55 (m, 1H), 4.99–4.94 (m, 2H), 3.55 (s, 3H), 3.21–3.15 (m, 1H), 2.66 (dd, J = 15.6, 6.4 Hz, 1H), 2.51 (dd, J = 15.6, 8.7 Hz, 1H), 2.34 (t, J = 7.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 141.9, 135.4, 132.1, 128.7, 128.5, 117.1, 51.4, 41.1, 40.4, 40.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}ClO_2$ 239.0833; Found: 239.0838.

Methyl 3-(4-fluorophenyl)hex-5-enoate (1n). Oil (0.95 g, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.11 (m, 2H), 6.99-6.95 (m, 2H), 5.68–5.58 (m, 1H), 5.01–4.96 (m, 2H), 3.57 (s, 3H), 3.28–3.14 (m, 1H), 2.68 (dd, J = 15.4, 6.4 Hz, 1H), 2.53 (dd, J = 15.4, 8.6 Hz, 1H), 2.36 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 161.5 (d, J = 245.4 Hz), 139.2 (d, J = 3.2 Hz), 135.6, 128.8 (d, J = 7.8 Hz), 117.0, 115.2 (d, J = 21.2 Hz), 51.4, 41.0, 40.6, 40.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}FO_2$ 223.1129; Found: 223.1132.

Substrates 1o and 1p were prepared using method C.[24]

To a mixture of ethyl 3-oxobutanoate (or methyl 3-oxo-4-phenylbutanoate) (5.7 mmol) and allyl bromide (2.1 g, 17.2 mmol) in 30 mL of MeOH/0.1 N HCl (1:4) was added indium powder (1.98 g, 17.2 mmol) in one portion. The reaction mixture was stoppered and stirred vigorously at rt for 10 hr. The reaction was then quenched by the addition of 1N HCl and extracted with ether (4 × 10 mL). Drying over Na_2SO_4 and removal of the solvent afforded a residue, which was purified by column chromatography to afford the corresponding **1o** and **1p. 1p** is a new compound.

Ethyl 3-hydroxy-3-methylhex-5-enoate (1o).[23] Oil (0.85g, 87% yield); ^{1}H NMR (600

MHz, $CDCl_3$) δ 5.95–5.73 (m, 1H), 5.12–5.03 (m, 2H), 4.20–4.12 (m, 2H), 3.84 (s, br, 1H), 2.51–2.38 (m, 2H), 2.32–2.26 (m, 2H), 1.28–1.20 (m, 6H).

Methyl 3-benzyl-3-hydroxyhex-5-enoate (1p). Oil (1.09g, 82% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.19 (m, 5H), 5.95–5.88 (m, 1H), 5.19–5.03 (m, 2H), 3.65 (s, br, 1H), 3.63 (s, 3H), 2.84 (q, J = 13.7 Hz, 2H), 2.41 (dd, J = 48.3, 15.9 Hz, 2H), 2.38–2.25 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 136.7, 133.4, 130.5, 127.9, 126.4, 118.6, 72.7, 51.4, 45.6, 44.2, 41.4; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1223; Found: 217.1222.

Substrates 1q was prepared using method D.[25]

To a solution of the methyl 2-hydroxy-2-phenylacetate (9.0 mmol) in ether (50 mL) was added allyl bromide (1.2 mL, 13.5 mmol) and silver oxide (4.2 g, 18.0 mmol) under an atmosphere of nitrogen. The mixture was refluxed for 2 hours and then stirring was continued for 48 hours at room temperature. The silver salts were removed by filtration, washed with ether (50 mL) and the solvent was removed *in vacuo* to give the residue. Purification by chromatography on silica gel (200–300 mesh) using petroleum ether/EtOAc (25/1, v : v) as eluent afforded the pure **1q**.

Methyl 2-(allyloxy)-2-phenylacetate (1q).[10] Oil (1.39 g, 75% Yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48–7.40 (m, 2H), 7.41–7.34 (m, 3H), 5.98–5.94 (m, 1H), 5.31 (dd, J = 17.2, 1.6 Hz, 1H), 5.25 (dd, J = 10.3, 1.3 Hz, 1H), 4.97 (s, 1H), 4.08–4.07 (m, 2H), 3.74–3.71 (m, 3H).

Substrates 1r was prepared using method E.[26]

To a solution of benzylamine (3.4 mL, 31.2 mmol) and NaI (22.8 mg, 0.15 mmol)

in DMSO (20 mL) was added dropwise 3-bromopropene (1.32 mL, 15.24 mmol) via a syringe at 0 °C. After stirring for 18 h at room temperature, to the reaction mixture was added 1M aqueous $NaHCO_3$ (36 mL), and the aqueous layer was extracted with Et_2O (5 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated in vacuo followed by silica gel flash column chromatography (eluent; n-hexane/ethyl acetate = 8/1) to provide N-benzyl-2-propenylamine as yellow oil (1.1 g, 48%).

To a suspension of N-allyl benzylamine (1.1 g, 7.48 mmol) and K_2CO_3 (2.06 g, 14.9 mmol) in CH_3CN (20 mL) was added methyl bromoacetate (0.90 mL, 8.58 mmol) and the resultant solution stirred for 20 h. The reaction mixture was poured into *sat.* $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. Purification by chromatography (pentane:EtOAc 6:1) provided **1r** (1.29 g, 78%) as a colorless oil

Methyl 2-(allyl(benzyl)amino)acetate (1r). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35–7.29 (m, 4H), 7.26–7.22 (m, 1H), 5.91–5.84 (m, 1H), 5.24–5.13 (m, 2H), 3.77 (s, 2H), 3.67 (s, 3H), 3.32 (s, 2H), 3.27 (d, J = 6.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 138.5, 135.4, 128.9, 128.2, 127.0, 117.9, 57.7, 56.8, 53.4, 51.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}NO_2$ 220.1332; Found: 220.1336.

General procedures for the preparation of bicyclo[3.3.0]octan-1-ols 2

An oven-dried two-necked flask (50 mL) containing finely powdered samarium (0.75 g, 5 mmol) was evacuated and backfilled with N_2 for three times. Under a positive pressure of nitrogen, a solution of allylBr (0.38 mL, 4.4 mmol) in dry THF

(30 mL) was added via a syringe, and a grain of iodine was then added. The mixture was allowed to stir at rt for 1 h (the mixture color was deep purple). HMPA (3.4 mL, 16 mmol) was then added followed by addition of a solution of substrate **1** (1 mmol) in dry THF (3 mL) via a syringe. The reaction mixture was stirred at rt until the completion of the reaction (monitored by TLC). The reaction was quenched by a sat. potassium sodium tartrate solution (5 mL). The mixture was extracted by ethyl acetate (3 × 15 mL). The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (200–300 mesh) using petroleum/EtOAc (10/1, v : v) as eluent to afford the corresponding product **2a-2p** and **2s′**. Compound **3** was obtained with the procedure described above except that HMPA was not added.

2-Methyl-4-phenyloctahydropentalen-3a-ol (2a). Oil (0.168 g, 78% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.34 (m, 5H), 2.73 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.40 (q, *J* = 9.0 Hz, 1H), 2.12–2.17 (m, 2H), 2.03 – 2.08 (m, 1H), 1.97 (dd, *J* = 12.6, 5.4 Hz, 1H), 1.84–1.88 (m, 1H), 1.55–1.60 (m, 1H), 1.49–1.52 (m, 1H), 1.10–1.21 (m, 3H), 1.04 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4, 129.2, 128.4, 126.9, 90.4, 56.5, 51.5, 48.6, 40.7, 33.6, 32.7, 31.1, 19.4; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{19}$ 199.1481; Found: 199.1480.

2-Methyl-4-(p-tolyl)octahydropentalen-3a-ol (2b). Oil (0.193 g, 84% yield); major: ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.25–7.19 (m, 4H), 2.76 (dd, *J* = 13.3, 5.4 Hz, 1H), 2.43–2.36 (m, 1H), 2.32 (s, 3H), 2.17–2.09 (m, 2H), 2.08–1.99 (m, 1H), 1.98–1.94 (m, 1H), 1.85–1.81 (m, 1H), 1.60–1.53 (m, 2H), 1.23 (s, br, 1H), 1.21–1.08 (m, 2H), 1.04

(d, J = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.4, 136.1, 129.00, 128.97, 90.1, 56.0, 51.3, 48.5, 40.6, 33.4, 32.6, 31.1, 21.0, 19.3; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{16}H_{21}$ 213.1638; Found: 213.1636.

Minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25–7.19 (m, 4H), 2.88–2.85 (m, 1H), 2.43–2.36 (m, 1H), 2.32 (s, 3H), 2.26–2.22 (m, 1H), 2.17–2.09 (m, 2H), 2.08–1.99 (m, 1H), 1.78–1.68 (m, 2H), 1.43–1.38 (m, 1H), 1.21–1.08 (m, 2H), 1.01 (d, J = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.3, 136.2, 129.1, 128.3, 91.4, 56.6, 54.0, 50.5, 43.9, 37.6, 33.2, 31.3, 19.5, 19.3.

2-Methyl-4-(m-tolyl)octahydropentalen-3a-ol (2c). Oil (0.196 g, 85% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.29 (m, 1H), 7.11 – 7.16 (m, 3H), 2.76 (dd, J = 13.2, 5.4 Hz, 1H), 2.45 (q, J = 9.0, 1H), 2.41 (s, 3H), 2.17 – 2.22 (m, 2H), 2.10 – 2.15 (m, 1H), 2.03 (dd, J = 12.0, 5.4 Hz, 1H), 1.88 – 1.92 (m, 1H), 1.60 – 1.66 (m, 1H), 1.54 – 1.57 (m, 1H), 1.32 (s, br, 1H), 1.16 – 1.24 (m, 2H), 1.10 (d, J = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.3, 137.9, 123.0, 128.3, 127.7, 126.3, 90.3, 56.4, 51.5, 48.6, 40.7, 33.6, 32.8, 31.1, 21.5, 19.4; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{16}H_{21}$ 213.1638; Found: 213.1639.

2-Methyl-4-(o-tolyl)octahydropentalen-3a-ol (2d). Oil (0.17 g, 74% yield); major: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.22–7.10 (m, 3H), 3.12 (dd, J = 12.8, 5.4 Hz, 1H), 2.45–2.36 (m, 4H), 2.22–2.12 (m, 2H), 2.06–1.99 (m, 1H), 1.88–1.79 (m, 2H), 1.59 (dd, J = 21.6, 11.3 Hz, 1H), 1.52 (dd, J = 12.0, 6.0 Hz, 1H), 1.39 (s, 1H), 1.27–1.19 (m, 1H), 1.15 (t, J = 12.1 Hz, 1H), 1.04 (d, J = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.9, 136.8, 130.8, 129.2, 126.4, 125.8, 90.9, 51.4, 50.5, 48.8, 40.8,

33.7, 33.1, 32.8, 20.7, 19.5; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{16}H_{21}$ 213.1638; Found: 213.1636.

Minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.22–7.10 (m, 3H), 3.21 (dd, *J* = 11.7, 5.8 Hz, 1H), 2.45–2.36 (m, 4H), 2.22–2.12 (m, 2H), 2.06–1.99 (m, 1H), 1.74–1.71 (m, 2H), 1.59 (dd, *J* = 21.6, 11.3 Hz, 1H), 1.52 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.36 (s, 1H), 1.27–1.19 (m, 1H), 1.15 (t, *J* = 12.1 Hz, 1H), 1.00 (d, *J* = 6.4 Hz, 3H).

4-(3-Chlorophenyl)-2-methyloctahydropentalen-3a-ol (2e). Oil (0.153 g, 61% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.34 (m, 4H), 2.74 (dd, J = 13.2, 5.4 Hz, 1H), 2.42-2.38 (m, 1H), 2.12 – 2.17 (m, 2H), 2.05 – 2.08 (m, 1H), 1.97 – 2.00 (m, 1H), 1.84 – 1.88 (m, 1H), 1.55 – 1.61 (m, 1H), 1.49 – 1.52 (m, 1H), 1.21 – 1.10 (m, 3H), 1.05 (d, J = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4, 129.2, 128.6, 128.4, 127.9, 126.93, 90.4, 56.5, 51.5, 48.6, 40.7, 33.6, 32.7, 31.1, 19.3; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{18}Cl$ 233.1092; Found: 233.1096.

4-(2-Chlorophenyl)-2-methyloctahydropentalen-3a-ol (2f). Oil (0.138 g, 55% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.34 (m, 4H), 2.73 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.40 (q, *J* = 9.0 Hz, 1H), 2.12 – 2.17 (m, 2H), 2.03 – 2.09 (m, 1H), 1.98 (dd, J = 12.0, 5.4 Hz, 1H), 1.84 – 1.88 (m, 1H), 1.55 – 1.61 (m, 1H), 1.49 – 1.52 (m, 1H), 1.10 – 1.22 (m, 3H), 1.05 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.4, 129.2, 128.4, 126.9, 90.4, 56.5, 51.5, 48.6, 40.7, 33.6, 32.7, 31.1, 19.4; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{18}Cl$ 233.1092; Found: 233.1090.

4-(3-Bromophenyl)-2-methyloctahydropentalen-3a-ol (2g). White solid (0.186 g, 63% yield), mp 48–49ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.35 (m, 4H), 2.74 (dd, *J* =

13.2, 5.4 Hz, 1H), 2.40 (q, *J* = 8.8 Hz, 1H), 1.96 – 2.18 (m, 4H), 1.83 – 1.89 (m, 1H), 1.48 – 1.62 (m, 2H), 1.10 – 1.23 (m, 3H), 1.05 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 129.2, 128.4, 126.9, 90.4, 56.4, 51.5, 48.6, 40.7, 33.6, 32.7, 31.1, 19.3; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{18}Br$ 277.0586; Found: 277.0588.

4-(2-Bromophenyl)-2-methyloctahydropentalen-3a-ol (2h). Oil (0.189 g, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.39 (m, 4H), 2.78 (dd, J = 13.2, 5.4 Hz, 1H), 2.44 (q, *J* = 8.8 Hz, 1H), 2.00 – 2.22 (m, 4H), 1.87 – 1.93 (m, 1H), 1.52 – 1.68 (m, 2H), 1.14 – 1.24 (m, 3H), 1.08 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 129.2, 128.5, 128.44, 128.35, 126.9, 90.4, 56.4, 51.5, 48.6, 40.7, 33.6, 32.7, 31.1, 19.3; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{18}Br$ 277.0586; Found: 277.0589.

4-(4-Methoxyphenyl)-2-methyloctahydropentalen-3a-ol (2i). Oil (0.175 g, 71% yield); major: ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.26 (d, *J* = 8.2 Hz, 3H), 6.92 (d, *J* = 8.2 Hz, 2H), 3.83 (s, 3H), 2.73 (dd, *J* = 13.3, 5.4 Hz, 1H), 2.41 (q, *J* = 9.3 Hz, 1H), 2.18–2.15 (m, 2H), 2.05–1.98 (m, 1H), 1.98–1.92 (m, 1H), 1.85–1.81 (m, 1H), 164–1.52 (m, 2H), 1.22 (s, br, 1H), 1.20–1.08 (m, 2H), 1.04 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 158.6, 131.3, 130.0, 113.8, 90.0, 55.6, 55.2, 51.2, 48.5, 40.6, 33.4, 32.6, 31.2, 19.3; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{16}H_{21}O$ 229.1587; Found: 229.1588.

Minor: ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.26 (d, *J* = 8.2 Hz, 3H), 6.92 (d, *J* = 8.2 Hz, 2H), 3.83 (s, 3H), 2.86 (dd, *J* = 12.9, 5.5 Hz, 1H), 2.41 (q, *J* = 9.3 Hz, 1H), 2.18–2.15

(m, 2H), 2.05–1.98 (m, 1H), 1.98–1.92 (m, 1H), 1.75–1.73 (m, 2H), 1.42–1.38 (m, 1H), 1.20–1.08 (m, 2H), 1.01 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 158.4, 131.3, 129.4, 113.8, 91.3, 56.2, 54.0, 50.5, 43.9, 37.6, 33.42, 33.37, 31.3, 19.5.

2-Methyl-4-(naphthalen-1-yl)octahydropentalen-3a-ol (2j). White solid (0.165 g, 62% yield), mp 97–98°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.55 (m, 4H), 3.75 (dd, *J* = 12.5, 5.5 Hz, 1H), 2.48 – 2.53 (m, 1H), 2.32 – 2.38 (m, 1H), 2.19 – 2.27 (m, 2H), 1.99 (dd, *J* = 12.5, 5.5 Hz, 1H), 1.89 – 1.93 (m, 1H), 1.60 – 1.66 (m, 2H), 1.31 – 1.37 (m, 2H), 1.04 – 1.09 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.2, 132.9, 129.0, 127.2, 126.7, 126.0, 125.4, 125.2, 123.5, 90.4, 51.4, 49.1, 47.9, 40.8, 33.8, 33.1, 32.7, 19.5; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{19}H_{21}$ 249. 1638; Found: 249. 1641.

2-Methyl-5-phenyloctahydropentalen-3a-ol (2k). Oil (0.149 g, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.35 (m, 5H), 3.26 – 3.33 (m, 1H), 2.37 –2.44 (m, 2H), 2.04 – 2.26 (m, 3H), 1.74 – 1.80 (m, 2H), 1.55 – 1.59 (m, 1H), 1.30 – 1.41 (m, 2H), 1.08 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 128.3, 127.0, 126.1, 90.5, 52.4, 50.13, 50.08, 44.4, 42.8, 40.2, 33.3, 19.2; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{19}$ 199.1481; Found: 199.1482.

2-(4-Methoxyphenyl)-5-methyloctahydropentalen-3a-ol (2l). White solid (0.18 g, 73% yield), mp 63–64°C; major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.16 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.27–3.14 (m, 1H), 2.39–2.29 (m, 2H), 2.17 (dd, *J* = 13.0, 5.8 Hz, 1H), 2.11–1.92 (m, 2H), 1.76–1.65 (m, 2H), 1.53–1.50 (m, 1H),

1.32–1.26 (m, 2H), 1.04 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 136.0, 127.7, 113.7, 90.4, 55.2, 52.4, 50.2, 50.1, 43.5, 43.0, 40.1, 37.0, 19.1; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{16}H_{21}O$ 229.1587; Found: 229.1583.

Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.46–3.38 (m, 1H), 2.39–2.29 (m, 2H), 2.17 (dd, *J* = 13.0, 5.8 Hz, 1H), 2.11–1.92 (m, 2H), 1.76–1.65 (m, 2H), 1.53–1.50 (m, 1H), 1.32–1.26 (m, 2H), 1.02 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 136.0, 127.7, 113.7, 91.4, 55.3, 52.4, 50.7, 49.8, 47.0, 43.0, 42.2, 33.2, 19.2.

2-(4-Chlorophenyl)-5-methyloctahydropentalen-3a-ol (2m). Oil (0.146 g, 58% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 7.2 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.23 – 3.27 (m, 1H), 2.35 – 2.42 (m, 2H), 2.21 (dd, *J* = 12.6, 4.8 Hz, 1H), 2.03 – 2.10 (m, 2H), 1.78 (s, br, 1H), 1.72–1.70 (m, 1H), 1.54 – 1.59 (m, 2H), 1.28 – 1.34 (m, 2H), 1.07 (d, *J* = 5.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 131.6, 128.4, 128.3, 90.4, 52.4, 50.1, 50.0, 43.75, 42.8, 40.1, 33.3, 19.1; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{18}Cl$ 233.1092; Found: 233.1093.

2-(4-Fluorophenyl)-5-methyloctahydropentalen-3a-ol (2n). Oil (0.126 g, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.23 (m, 2H), 6.97 – 7.01 (m, 2H), 3.21 – 3.29 (m, 1H), 2.33 – 2.43 (m, 2H), 2.18 – 2.23 (m, 1H), 2.02 – 2.11 (m, 2H), 1.66 – 1.77 (m, 2H), 1.53 – 1.57 (m, 2H), 1.27 – 1.36 (m, 2H), 1.07 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 245.1 Hz), 139.4 (d, *J* = 3.5 Hz), 128 (d, *J* =7.9 Hz), 115.0 (d, *J* = 20.9 Hz), 90.4, 52.4, 50.2, 50.1, 43.6, 42.9, 40.1, 33.3, 19.1; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{15}H_{18}F$ 217.1387; Found: 217.1384.

2,5-Dimethyloctahydropentalene-2,3a-diol (2o). Oil (0.082 g, 48% yield); major: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.31 (s, br, 1H), 2.74 (s, br, 1H), 2.53 (q, J = 9.0 Hz, 1H), 2.14–2.10 (m, 1H), 1.92–1.84 (m, 3H), 1.64–1.62 (m, 1H), 1.57–1.52 (m, 1H), 1.40 (dd, J = 12.6, 5.7 Hz, 1H), 1.35 (s, 3H), 1.31–1.20 (m, 2H), 1.01 (d, J = 6.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 91.3, 81.3, 54.0, 51.3, 49.2, 48.0, 40.0, 32.8, 26.1, 19.0; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{10}H_{17}O$ 153.1274; Found: 153.1275.

Minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.26 (s, br, 1H), 2.95 (s, br, 1H), 2.53 (q, J = 9.0 Hz, 1H), 2.37–2.29 (m, 2H), 2.14–2.10 (m, 1H), 2.02–1.93 (m, 3H), 1.64–1.62 (m, 1H), 1.35 (s, 3H), 1.31–1.20 (m, 2H), 0.98 (d, J = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 92.3, 84.3, 54.8, 54.1, 48.0, 44.0, 37.2, 32.8, 26.7, 19.3.

2-Benzyl-5-methyloctahydropentalene-2,3a-diol (2p). Oil (0.125 g, 51% yield); major: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.18 (m, 5H), 3.06 (s, 1H), 2.89–2.83 (m, 2H), 2.46 (q, J = 9.2 Hz, 1H), 2.05 (s, br, 1H), 2.03–1.98 (m, 1H), 1.97–1.82 (m, 3H), 1.74-1.72 (m, 1H), 1.67–1.47 (m, 1H), 1.41–1.38 (m, 1H), 1.32–1.25 (m, 2H), 1.01 (d, J = 6.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 130.0, 128.3, 126.6, 90.4, 83.3, 52.4, 50.9, 47.8, 47.2, 45.9, 40.0, 32.7, 18.9; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{16}H_{21}O$ 229.1587; Found: 229.1585.

Minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.18 (m, 5H), 3.06 (s, 1H), 2.89–2.83 (m, 2H), 2.34–2.29 (m, 2H), 2.03–1.98 (m, 1H), 1.97–1.82 (m, 3H), 1.72 (t, J = 13.8 Hz, 1H), 1.67–1.47 (m, 1H), 1.41–1.38 (m, 1H), 1.32–1.25 (m, 1H), 1.20–1.16 (m, 1H), 0.97 (d, J = 6.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.4, 130.0, 128.3, 126.6,

91.5, 86.4, 54.4, 52.5, 49.1, 46.4, 46.3, 44.0, 37.4, 19.3.

3,4-Dimethyl-2-(4-methyl-1-phenylpent-4-en-1-yl)cyclopentanol (2s'). Oil (0.075 g, 28% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5H), 4.70 (s, 1H), 4.61 (d, J = 0.7 Hz, 1H), 2.53 (dd, J = 11.0, 3.4 Hz, 1H), 2.15 (dd, J = 13.5, 7.6 Hz, 1H), 2.07–1.91 (m, 6H), 1.80 (d, J = 8.2 Hz, 1H), 1.69 (s, 3H), 1.53 (dd, J = 13.4, 5.6 Hz, 1H), 1.45 (s, br, 1H), 1.17 (dd, J = 13.7, 6.5 Hz, 1H), 0.99 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 141.9, 129.5, 128.3, 126.7, 110.1, 84.3, 56.1, 47.8, 47.2, 37.4, 37.2, 36.1, 28.0, 22.6, 15.62, 15.59; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{19}H_{27}$ 255.2107; Found: 255.2112.

4-Allyl-5-phenylnona-1,8-dien-4-ol (3a). Oil (0.241g, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.22 (m, 5H), 5.86–5.73 (m, 3H), 5.16–5.10 (m, 3H), 5.04–5.01 (m, 1H), 4.91–4.87 (m, 2H), 2.72–2.70 (m, 1H), 2.34–2.31 (m, 2H), 2.18–2.15 (m, 1H), 2.09–2.06 (m, 1H), 1.97–1.84 (m, 3H), 1.72–1.69 (m, 1H), 1.52 (br, s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.6, 138.5, 133.9, 133.8, 129.9, 128.1, 126.6, 118.61, 118.55, 114.6, 75.2, 52.3, 42.1, 41.5, 32.0, 28.1; HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{18}H_{23}$ 239.1794; Found: 239.1797.

Typical procedures for the preparation of the ester 2a′[27]

2-Methyl-4-phenyloctahydropentalen-3a-ol (**2a**) (0.216 g, 1 mmol) is mixed with 3,5-dinitrobenzoyl chloride (0.461g, 2 mmol) in chilled pyridine (0.8 mL, 10 equiv) and allowed to react for 6 h at rt. The reaction mixture was poured into cold water and extracted with Et_2O (3 × 20 mL). The organic phase was dried over anhydrous sodium, and concentrated under reduced pressure. The residue was purified by

chromatography on silica gel (200–300 mesh) using petroleum ether/EtOAc (20/1, v : v) as the eluent to afford **2a′**.

2-Methyl-4-phenyloctahydropentalen-3a-yl 3,5-dinitrobenzoate (2a'). White solid (0.324g, 79% yield), mp 91–92ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.79 (d, J = 2.1 Hz, 2H), 7.48–7.28 (m, 5H), 3.12–2.97 (m, 2H), 2.33–2.11 (m, 4H), 2.11–1.86 (m, 3H), 1.64 (dd, J = 12.0, 5.8 Hz, 1H), 1.42–1.31 (m, 1H), 1.17 (d, J = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 148.4, 138.9, 135.4, 129.1, 128.7, 128.4, 127.1, 121.8, 101.9, 56.7, 49.9, 43.2, 39.7, 33.1, 32.5, 31.0, 18.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{22}N_2O_6Na$ 433.1370; Found: 433.1371.

General procedures for the preparation of bicyclo[3.1.0]hexan-1-ols 4

An oven-dried 50 mL two-necked flask containing finely powdered samarium (0.75 g, 5 mmol) was evacuated and backfilled with N_2 for three times. Under a positive pressure of nitrogen, a solution of allylBr (0.38 mL, 4.4 mmol) in dry THF (30 mL) was added via a syringe, and then added a grain of iodine. The mixture was allowed to stir at room temperature for 1 h (the mixture color was deep purple). HMPA (3.4 mL, 16 mmol) and pyrrole (0.11 mL，1.6 mmol) was then added. The resulting mixture was then cooled to 5 ºC followed by addition of a solution of substrate **1** (1 mmol) in dry THF (3 mL) via a syringe. The reaction mixture was stirred for 10 hr (monitored by TLC) and quenched with a sat. potassium sodium tartrate solution (5 mL). The mixture was extracted by ethyl acetate (3 × 15 mL). The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel

(200–300 mesh) using petroleum/EtOAc (10/1, v : v) as eluent to afford the corresponding product **4**.

2-Phenylbicyclo[3.1.0]hexan-1-ol (4a). Oil (0.113g, 65% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.41 (m, 5H), 3.41 (d, *J* = 7.8 Hz, 1H), 2.21 – 2.27 (m, 1H), 1.97 (s, br, 1H), 1.72 – 1.78 (m, 1H), 1.63 – 1.70 (m, 3H), 1.08 (dd, J = 9.0, 5.4 Hz, 1H), 0.78 (t, *J* = 4.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 129.0, 128.0, 126.7, 67.1, 49.3, 29.9, 25.9, 25.3, 15.3; HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}O$ 175.1117; Found: 175.1118.

2-(p-Tolyl)bicyclo[3.1.0]hexan-1-ol (4b). Oil (0.118 g, 63% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.23 (m, 4H), 3.38 (d, *J* = 8.4 Hz, 1H), 2.38 (s, 3H), 2.20 – 2.27 (m, 1H), 1.95 (s, br, 1H), 1.71 – 1.78 (m, 1H), 1.60 – 1.67 (m, 3H), 1.07 (dd, J = 9.0, 5.4 Hz, 1H), 0.76 (dd, J = 4.8, 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.1, 136.2, 129.7, 127.8, 67.1, 48.9, 30.0, 25.9, 25.2, 21.1, 15.2; HRMS (APCI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}ONa$ 211.1093; Found: 211.1099.

2-(m-Tolyl)bicyclo[3.1.0]hexan-1-ol (4c). Oil (0.128g, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.30 (m, 1H), 7.10 – 7.14 (m, 3H), 3.38 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 3H), 2.20 – 2.30 (m, 1H), 1.98 (s, br, 1H), 1.60 – 1.80 (m, 4H), 1.07 (dd, *J* = 9.2, 5.6 Hz, 1H), 0.76 (dd, J = 4.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.5, 128.7, 128.8, 127.5, 124.8, 67.1, 49.3, 30.0, 26.0, 25.3, 21.6, 15.2; HRMS (APCI-TOF) m/z: $[M + Na - H_2O]^+$ Calcd for $C_{13}H_{14}Na$ 193.0988; Found: 193.0985.

2-(o-Tolyl)bicyclo[3.1.0]hexan-1-ol (4d). Oil (0.132g, 70% yield); ^{1}H NMR (600

MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.28 (m, 3H), 3.71 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H), 2.18 – 2.25 (m, 1H), 2.13 (s, br, 1H), 1.73 – 1.80 (m, 1H), 1.55 – 1.67 (m, 3H), 1.06 (dd, *J* = 9.6, 6.0 Hz, 1H), 0.80 (dd, *J* = 5.4, 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2, 136.8, 130.9, 126.5, 126.3, 126.0, 66.8, 43.7, 29.3, 25.6, 25.5, 20.3, 14.9; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{13}H_{15}$ 171.1168; Found: 171.1163.

2-(2-Chlorophenyl)bicyclo[3.1.0]hexan-1-ol (4f). Oil (0.115g, 55% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.40 (m, 4H), 3.41 (d, *J* = 7.8 Hz, 1H), 2.21 – 2.27 (m, 1H), 2.00 (s, br, 1H), 1.63 – 1.78 (m, 4H), 1.08 (dd, *J* = 6.0, 9.0 Hz, 1H), 0.77 (dd, *J* = 4.2, 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 129.0, 128.0, 126.7, 67.1, 49.3, 29.9, 25.9, 25.3, 15.3; HRMS (APCI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_{12}ClO$ 207.0582; Found: 207.0587.

2-(3-Bromophenyl)bicyclo[3.1.0]hexan-1-ol (4g). Oil (0.132 g, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.41 (m, 4H), 3.41 (d, *J* = 7.6 Hz, 1H), 2.19 – 2.28 (m, 1H), 1.91 (s, br, 1H), 1.63 – 1.77 (m, 4H), 1.07 (dd, *J* = 9.2, 5.6 Hz, 1H), 0.77 (dd J = 4.4, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 128.9, 127.9, 126.7, 67.1, 49.3, 29.9, 25.9, 25.3, 15.3; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{12}H_{12}Br$ 235.0117; Found: 235.0121.

2-(4-Methoxyphenyl)bicyclo[3.1.0]hexan-1-ol (4i). Oil (0.145 g, 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.72 (s, 3H), 3.25 (d, *J* = 7.8 Hz, 1H), 2.07 – 2.13 (m, 1H), 1.86 (s, br, 1H), 1.59 – 1.64 (m, 1H), 1.48 – 1.55 (m, 3H), 1.02 (dd, *J* = 9.0, 5.4 Hz, 1H), 0.71 (dd, *J* = 5.4, 4.8 Hz, 1H); ^{13}C

NMR (150 MHz, $CDCl_3$) δ 158.3, 135.2, 128.9, 114.3, 67.1, 55.3, 48.4, 30.0, 25.9, 25.1, 15.2; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{13}H_{15}O$ 187.1117; Found: 187.1118.

2-(Naphthalen-1-yl)bicyclo[3.1.0]hexan-1-ol (4j). Oil (0.036g, 16% yield); ^1H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.58–7.44 (m, 4H), 4.30 (d, J = 8.1 Hz, 1H), 2.24–2.18 (m, 1H), 1.87–1.79 (m, 1H), 1.73–1.68 (m, 1H), 1.65–1.58 (m, 2H), 1.06 (dd, J = 9.0, 5.5 Hz, 1H), 0.88 (t, J = 6.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 134.2, 132.2, 128.9, 127.0, 126.0, 125.6, 125.5, 123.7, 66.5, 29.6, 25.7, 25.5, 14.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}O$ 225.1274; Found: 225.1273.

2-Phenyl-3-oxabicyclo[3.1.0]hexan-1-ol (4q).[10] Oil (0.072g, 41% yield); major: ^1H NMR (600 MHz, $CDCl_3$) δ 7.43–7.35 (m, 5H), 4.88 (s, 1H), 4.32 (dd, J = 8.5, 3.2 Hz, 1H), 3.71 (d, J = 8.5 Hz, 1H), 2.20 (br, s, 1H), 1.80–1.77 (m, 1H), 1.32 (dd, J = 9.0, 5.3 Hz, 1H), 0.93 (t, J = 5.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.4 (s), 128.7 (s), 128.1 (s), 127.1 (s), 81.8 (s), 69.5 (s), 65.6 (s), 24.3 (s), 17.2 (s);

minor: ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.35 (m, 5H), 4.92 (s, 1H), 4.09 (dd, J = 8.6, 3.0 Hz, 1H), 3.81 (d, J = 8.6 Hz, 1H), 1.70–1.68 (m, 1H), 1.32 (dd, J = 9.0, 5.3 Hz, 1H), 0.89–0.86 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 128.3, 127.8, 126.1, 81.5, 69.3, 66.9, 23.6, 13.2.

3-Benzyl-3-azabicyclo[3.1.0]hexan-1-ol (4r). (0.079g, 46% yield); ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.34 (m, 5H), 3.66 (q, J = 13.1 Hz, 2H), 3.14 (d, J = 8.3 Hz, 1H), 2.79–2.77 (d, J = 8.4 Hz, 1H), 2.67 – 2.63 (m, 2H), 1.46–1.44 (m,1H), 1.17–1.15

(m, 1H), 0.94 (dd, J = 9.0, 4.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 128.7, 128.2, 127.0, 62.1, 59.0, 58.8, 54.5, 29.7, 23.0; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{12}H_{14}N$ 172.1121; Found: 172.1123.

2,2-Dimethyl-5-phenylcyclopentanol (4s'). Oil (0.048g, 25% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.31 (m, 4H), 7.26–7.23 (m, 1H), 3.67 (dd, J = 9.5, 4.5 Hz, 1H), 3.00 (dd, J = 18.4, 9.4 Hz, 1H), 2.21–2.13 (m, 1H), 1.76–1.71 (m, 1H), 1.69–1.65 (m, 2H), 1.60 (d, J = 4.8 Hz, 1H), 1.13 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 128.5, 127.4, 126.3, 87.4, 51.2, 40.9, 37.4, 28.1, 27.7, 21.5; HRMS (APCI-TOF) m/z: $[M + H - H_2O]^+$ Calcd for $C_{13}H_{17}$ 173.1325; Found: 173.1330.

Supporting Information. The copies of ^{1}H and ^{13}C NMR spectra for substrates **1** and products **2-4** (PDF); a copy of thermal ellipsoid plot/ORTEP diagram for crystal structure **2a′.** The Supporting Information is available free of charge on the ACS Publications website.

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