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Allylsamarium Bromide-Mediated Cascade Cyclization of Homoallylic Esters. Synthesis of 2-(2-Hydroxyalkyl)cyclopropanols and 2-(2-Hydroxyethyl)bicyclo[2.1.1]hexan-1-ols

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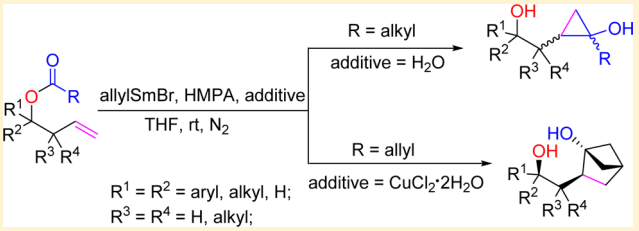
Supporting Information

ABSTRACT: In continuation of our previous study on the intramolecular reductive coupling of simple homoallylic esters promoted by allylSmBr/HMPA/H_2O, which afforded a facile synthesis of 2-(2-hydroxyalkyl)cyclopropanols, here we report the reductive cascade cyclization of but-3-enyl but-3-enoates mediated by allylSmBr/HMPA/$CuCl_2$·$2H_2O$, in which the two C═C bonds were successively coupled to allow the construction of the structurally interesting bridged bicyclic tertiary alcohols. Thus, the 2-(2-hydroxyethyl)bicyclo[2.1.1]-hexan-1-ols were prepared in moderate to good yields with excellent diastereoselectivity.



INTRODUCTION

1,4-Diols are widely used for the preparation of important heterocycles such as γ-lactones, pyrroles, tetrahydrofurans, and related natural products.[1] While a large number of methods have been published for the synthesis of 1,2-, 1,3-, and 1,5-diols, only a handful of methods are available for the synthesis of 1,4-diols.[2]

2-(2-Hydroxyalkyl)cyclopropanols are 1,4-diols with a cyclopropanol motif, which exists in a number of pharmaceutical phorbol derivatives,[3] and have also been utilized to assemble multisubstituted tetrahydrofurans[4a,b] and in other transformation.[4c] They could be prepared by Kulinkovich hydroxycyclopropanation of alkene with an ester in the presence of $Ti(O^iPr)_4$ and Grignard reagents.[5] On the other hand, 2-(2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ols are 1,4-diols with a pentacyclic alcohol motif, which is a component of, or used for, the synthesis of a number of natural products or pharmaceuticals.[6] The assembly of 1,4-diols with the pentacyclic alcohol subunit[7] was achieved via SmI_2/HMPA-promoted intramolecular coupling of unactivated olefinic ketones followed by treatment with carbonyl electrophiles, but no bridged structure was reported in the initial work.

In this paper, we report the allylSmBr-promoted intramolecular reductive coupling of the aliphatic esters of homoallylic alcohols in the presence of appropriate additives. The reaction afforded a facile and diastereoselective synthesis of 2-(2-hydroxyalkyl)cyclopropanols[8] and 2-(2-hydroxyethyl)-bicyclo[2.1.1]hexan-1-ols from readily available materials.

Reductive coupling reactions promoted by SmI_2[9] have played a unique role in C−C bond formation and have been employed as the key step in natural product synthesis.[10] One of the most important SmI_2-promoted coupling reactions is the coupling of a carbonyl with an alkene that typically proceeds through initial reduction of an aldehyde or ketone.[11] Active carboxylic acid derivatives such as acid chlorides[12] could also be transformed into a ketyl-like intermediate (acyl radical) by treatment with samarium reagent. Activated amides[13a] and thioesters[13b,c] underwent addition to activated alkenes via the acyl-type radical intermediate. Although the reduction of unactivated carboxylic acid derivatives, such as esters and amides, by SmI_2 have been known for some time,[14] reports concerning the reductive coupling of unactivated carboxylic acid derivatives with alkenes have only recently been developed by the Procter group who expanded the work to a number of lactone-alkenes and related coupling reactions with SmI_2/H_2O as the reducing agent.[15,16] Mechanistic studies by the Procter group have shown that the key for the reduction or reductive coupling of esters is to trap the ketyl radicals that were formed by electron transfer from Sm(II) to the ester carbonyl, findings consistent with a fast reversible first electron transfer.[17] However, the reductive coupling between aliphatic acyclic esters and alkenes promoted by Sm(II) still remains a challenge.

AllylSmBr, known as a C-nucleophilic reagent used for the allylation reaction[18] has been recognized as an effective SET reagent.[19a,b] We found the addition of HMPA could prohibit its nucleophilicity and at the same time enhance the reducing ability significantly.[19c] It is our hypothesis that the application

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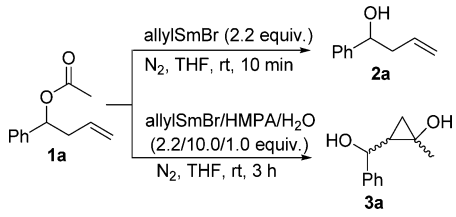
of allylSmBr as a SET reagent is worth further study because it may exhibit unique advantages in comparison to SmI_2 or related reagents.

RESULTS AND DISCUSSION

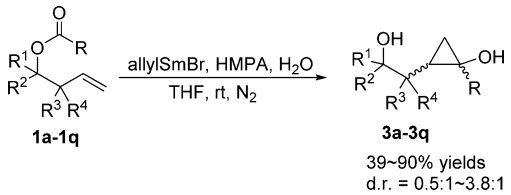
During the preliminary studies in our previous work,[8] homoallylic alcohol acetate **1a** was employed as the model substrate in our initial attempt to investigate the reductive coupling between an acyclic ester group and an alkene moiety. Without any additive, the use of 2.2 equiv of allylSmBr afforded 1-phenylbut-3-en-1-ol **2a** in 86% yield (Scheme 1).

Scheme 1. Reaction of 1a with AllylSmBr without or with Additive



When fresh anhydrous HMPA was used as the additive (10 equiv),[20] a complex mixture resulted. Fortunately, the accidental use of undistilled HMPA as the additive afforded the desired product **3a** in 38% yield. We thus deduced that the presence of water should facilitate the reductive ester−alkene coupling reaction despite the strong moisture sensitivity of allylSmBr. By carefully optimizing the conditions, the reaction could afford the desired **3a** in 73% yield with the molar ratio of the reagent allylSmBr/HMPA/H_2O being 2.2/10.0/1.0 (Scheme 1). A number of variously substituted 2-(2-hydroxyalkyl)cyclopropanols were also prepared (Scheme 2) in this way.[8]

Scheme 2. Preparation of 3 with AllylSmBr/HMPA/H_2O

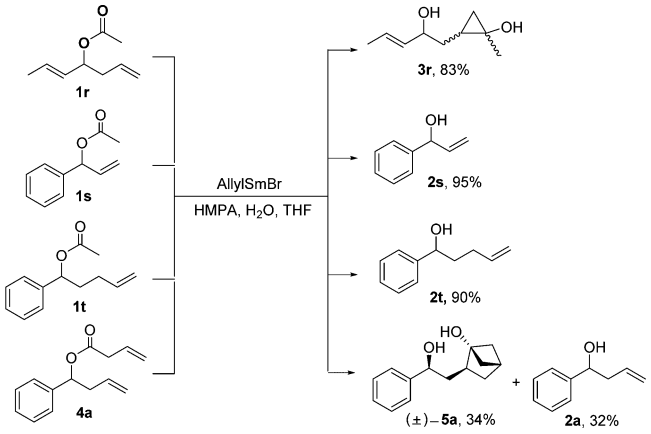


To further expand the scope of the reaction and explore the use of allylSmBr in the preparation of structurally novel compounds that may otherwise be difficult to access, we examined the reductive cascade coupling of alternative substrates with varying the tether length between the ester group and the C=C bond (Scheme 3).

Substrate **1r** with the incorporation of an additional allylic C=C bond afforded **3r** in good yield and left the allylic C=C bond untact. The reactions of allylic ester **1s** and substrate **1t** resulted in deprotection of the acetyl by simple reduction.[21] During these investigations, we observed that the use of the homoallylic ester **4a** produced bicyclohexanols of the type **5a**. The structure of **5a**[22] was confirmed unambiguously by X-ray diffraction analysis, NMR, and HRMS characterization (Figure 1).

To further develop the protocol, a number of conditions were screened to improve the yield of **5a**. We anticipated that

Scheme 3. Reactions of the Substrates with Different Positions of the C=C Bond



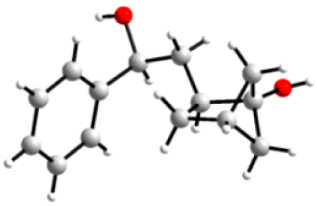


Figure 1. X-ray crystal structure of **5a**.

identifying appropriate conditions to increase the yield would enable us to develop the reaction into a useful synthetic tool for the construction of a variety of 2-(2-hydroxyethyl)-bicyclo[2.1.1]hexan-1-ols.

Excess Sm powder (4.76 equiv) and allylBr (3.3 equiv) were used to ensure more efficient transformation. Increase of the amount of H_2O to 1.6 equiv led to improvement of the isolated yield to 46% (Table 1, entry 1), but no reaction occurred with excess H_2O (entry 2). Room temperature was found suitable (entries 3 and 4). A recent report showed that addition of diethyl phosphate $(EtO)_2P(O)H$ to allylSmBr could promote reductive deoxygenation.[23] Unfortunately, only a trace amount of **5a** was produced with this additive (entry 5). With both HMPA and $(EtO)_2P(O)H$ as the additives, the HPLC yield increased to 46% (entry 6). Because HMPA was shown to be required, all subsequent conditions were examined in its presence unless otherwise specified.

Other proton sources such as MeOH and PhOH afforded even lower yields (entries 7 and 8). We then turned to a basic proton source,[14c] but no major improvement was observed with saturated aq $NaHCO_3$ (entry 9). A literature survey prompted us to attempt ferric salt as the additive.[7] However, neither anhydrous $FeCl_3$ nor $FeCl_3·6H_2O$ afforded good results (entries 10 and 12). LiCl[24] was reported to positively influence the SET ability of Sm(II) and was examined as well. The addition of LiCl or LiCl/H_2O both failed to provide any improvement (entry 11 and 13). Fortunately, when 1.6 equiv of $CuCl_2·2H_2O$ was used as the additive, a 78% yield of the desired product was obtained (entry 14). For comparison, the reductive cyclization of **4a** using SmI_2/HMPA/H_2O and $SmBr_2$/HMPA/H_2O were also attempted. However, in both cases, no desired **5a** was obtained and **4a** was recovered almost quantitatively. Therefore, the use of HMPA (16 equiv) and $CuCl_2·2H_2O$ (1.6 equiv) as the additives was established as the optimal conditions. A number of 2-(2-hydroxyethyl)-

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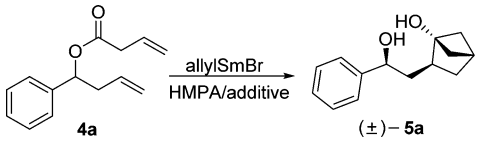
Table 1. Optimization of the Intramolecular Ester−Alkene Coupling Reaction of 4a Mediated by AllylSmBr/Additives



4a (±)−**5a**

entry	additive (equiv)	temp	yield of **4a**[b]
1	H_2O (1.6)	rt	60 (46)[c]
2	H_2O (3.0)	rt	–[d]
3	H_2O (1.6)	40 °C	31
4	H_2O (1.6)	0 °C	36
5	$(EtO)_2P(O)H$ (2.0)[e]	rt	trace
6	$(EtO)_2P(O)H$ (2.0)	rt	46
7	MeOH (1.6)	rt	27
8	PhOH (1.6)	rt	12
9	satd $NaHCO_3$ (1.6)	rt	34
10	$FeCl_3$ (1.0)	rt	trace
11	LiCl (12)	rt	trace
12	$FeCl_3·6H_2O$ (0.26)	rt	28
13	$LiCl/H_2O$ (12/1.6)	rt	15
14	$CuCl_2·2H_2O$ (1.6)	rt	78 (62%)[c]

[a]Reaction conditions: **4a** (0.5 mmol), allylBr (3.3 equiv), HMPA (16 equiv unless otherwise specified), Sm powder (4.67 equiv), THF (15 mL), N_2, 10 h. [b]HPLC yields with naphthalene as the internal standard unless otherwise specified. [c]Isolated yield. [d]No reaction. [e]No HMPA was used.

bicyclo[2.1.1]hexan-1-ols were prepared in moderate to good yields as listed in Table 2.

When R^1 is an aryl with R^2, R^3, and R^4 being H, the reaction of but-3-enyl but-3-enoates **4** proceeded smoothly under the optimized conditions and afforded the corresponding 2-(2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ols **5** in good to excellent yields (Table 2, entries 1−10). When a heteroaryl such as 2-furyl was introduced, the desired product was obtained in 25% yield accompanied by a complex mixture (entry 11). When both R^3 and R^4 are methyl instead of H, the reaction afforded the desired product in a moderate yield (45%, entry 12). The same result was obtained for the reaction of **4s** (52% yield, entry 19), where R^2 is a methyl rather than H. In the cases where R^1 is an alkenyl or alkyl, good yields were usually obtained (entries 13−18) except for **4t** (entries 20, 18%). These results showed that the reductive double cyclization was not substantially affected by electronic effects, but steric hindrance did exert a greater influence on the efficiency. It is noteworthy that the cascade double cyclization reaction afforded only one diastereomer as determined by both HPLC and NMR, showing excellent diastereoselectivity.

The role of $CuCl_2·2H_2O$ was also investigated. Because the addition of chloride did not enhance the yields (Table 1, entries 10−13), several studies were conducted to gain further insight into the role of the salt. First, $CuCl_2·2H_2O$ alone was treated by the allylSmBr/HMPA system to ascertain if the reduction of Cu(II) occurred. XPS results showed that Cu(II) was reduced into low-valent copper (Figure 3). The XPS of CuCl/allylSmBr/HMPA/H_2O system and Cu standard sample was also detected for comparison.

As shown in Figure 2, it is apparent that no satellite peaks (ca. 943 eV) appear for both samples a and b, which indicates that Cu(II) was absent. The Cu(II) in sample a should have been reduced into low-valent copper[25] by the allylSmBr/HMPA/THF system during the reaction. Recent work by Flowers[26] has shown that Ni(0) is the likely reactive species in SmI_2/Ni(II) coupling of halides with ketones. Unfortunately, it is difficult in this case to determine whether the low valent copper is Cu(0) or Cu(I). The Cu 2p photoelectron spectra of samples a, b, and c were very similar and also the overlap of Sm MNN (Auger electron spectra) on that of Cu species interferes with the characterization.

Nevertheless, subsequent experiments demonstrated that neither Cu(0) nor Cu(I) in combination with allylSmBr/HMPA/H_2O was more effective. The use of CuCl (1.6 equiv) afforded 46% yield of **5a**, while Cu(0) afforded a comparable yield (58%) to that obtained from the allylSmBr/HMPA/H_2O system (62%). Therefore, it is probable that the coordinated water in $CuCl_2·2H_2O$ plays the main role in improving the efficiency for the cascade reaction of substrates **5**. Although water is a good proton source for many Sm(II)-promoted reactions,[9] the water released in situ during the reduction of $CuCl_2·2H_2O$ into low-valent copper appears to match well with the requirement of a proton source for this reaction. It was fortunate that in our initial attempts, we used excess Sm powder (4.76 equiv) to ensure the complete reductive coupling and there still remained sufficient reducing reagent for the ester-coupling reactions despite the consumption of electrons by 1.6 equiv of Cu(II). It is also worth mentioning that when more than 1.6 equiv of $CuCl_2·2H_2O$ was used, the efficiency of the reaction decreased (the loading of $CuCl_2·2H_2O$ was optimized, see Table 3 and Figure 3). The consumption of more electrons by Cu(II) and the supply of excess water are both detrimental to the cascade coupling reaction.

More comprehensive studies may be required to clarify the role of the respective additives. Meanwhile, a probable single electron transfer (SET) mechanism for the allylSmBr-promoted cascade intramolecular cyclization for the generation of **3** and **5** was proposed in Schemes 4 and 5.

As shown in Scheme 4, ester **1** accepts an electron (e) from allylSmBr to form ketyl **I**, which undertakes a radical addition to the C=C bond and affords radical **II** in high stereoselectivity. The stereochemistry of **II** can be rationalized via the chairlike transition state **T-1** according to the model proposed by Beckwith for the 5-hexenyl radical cyclization.[27a] The more bulkyl substituent such as OSmL (L represents all the ligands around Sm, including HMPA, THF, and Br) and R^1 (R^1 = aryl or alkyl while R^2 = H) adopt pseudoequatorial orientation in **T-1**, and such a conformer will lead to the formation of **II**, where R^1, OSmL, and the newly formed methylene radical are all cis. Subsequent protonation by H_2O[15e] transforms **II** into hemiketal **III**, which then undergoes ring-opening to afford ketone **IV**. A second electron transfer generates carbanion intermediate **V**. Intramolecular nucleophilic addition[7,27b] to the ketone carbonyl of **V** provides both 1,2-trans and 1,2-cis diastereomers depending upon whether the chelation of Sm(III) is available. Therefore, the employment of racemic substrate **1** would finally afford products **3** in two diastereomers. The chelation of Sm(III) does not seem to dominate as much as that of Ti(IV) as in the Kulinkovich reaction,[5d] and the diastereoselectivity of the trans:cis isomers for **3** is only moderate.

When substrate **4** is applied, intermediate **VII** is first generated and stereoselectively affords key intermediate **VIII** via **T-2** (Scheme 5). Protonation transforms **VIII** into hemiketals **IX** and ketones **X**. Instead of undergoing a further SET process as described in Scheme 3 (from **IV** to **V**), **X** preferably undergoes a second radical cyclization to give new

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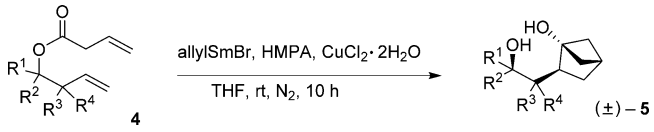
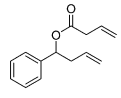
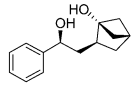
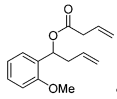
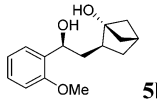
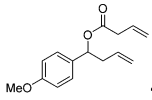
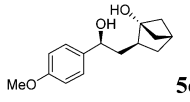
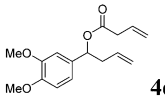
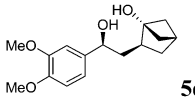
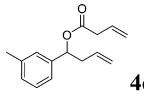
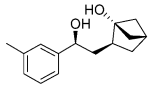
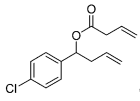
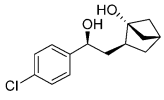
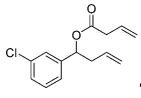
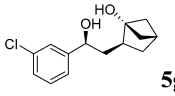
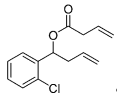
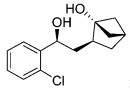
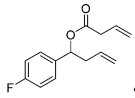
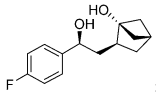
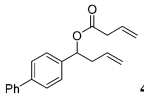
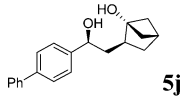
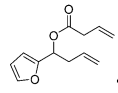
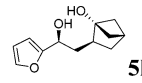
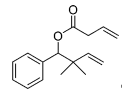
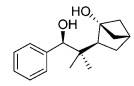
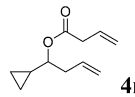
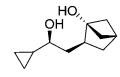
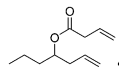
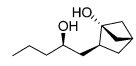
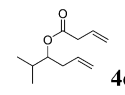
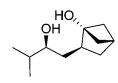
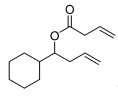
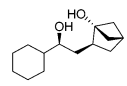
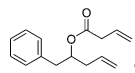
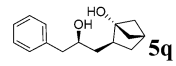
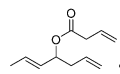
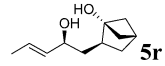
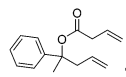
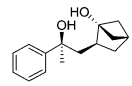
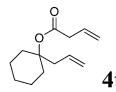
Table 2. Preparation of 2-(2-Hydroxyethyl)bicyclo[2.1.1]hexan-1-ols Mediated by AllylSmBr/HMPA/$CuCl_2$·$2H_2O$



Entry	Substrate **1**	Product **5**	Yield (%)[b]
1	 **4a**	 **5a**	62
2	 **4b**	 **5b**	92
3	 **4c**	 **5c**	88
4	 **4d**	 **5d**	70
5	 **4e**	 **5e**	79
6	 **4f**	 **5f**	71
7	 **4g**	 **5g**	60
8	 **4h**	 **5h**	66
9	 **4i**	 **5i**	76
10	 **4j**	 **5j**	68

Entry	Substrate **1**	Product **5**	Yield (%)[b]
11	 **4k**	 **5k**	25
12	 **4l**	 **5l**	45
13	 **4m**	 **5m**	71
14	 **4n**	 **5n**	76
15	 **4o**	 **5o**	83
16	 **4p**	 **5p**	68
17	 **4q**	 **5q**	75
18	 **4r**	 **5r**	60
19	 **4s**	 **5s**	52
20	 **4t**	**5t**	18

[a]Reaction conditions: allylBr (3.3 equiv), Sm powder (4.67 equiv), HMPA (16 equiv), $CuCl_2$·$2H_2O$ (1.6 equiv), THF (15 mL), N_2, 10 h. [b]Isolated yield.

radical **XI**, which then abstracts an electron from Sm(II) to transform into carbanion **XII**. Finally, intramolecular nucleophilic addition[7,27b] onto the carbonyl followed by protonation affords product **5**. The highly stereoselective radical cyclization process (from **VII** to **VIII**) rationalizes the excellent diastereoselectivity for the formation of **5**.

■ CONCLUSIONS

We have achieved the intramolecular unactivated ester−alkene radical cyclization promoted by allylSmBr/HMPA/H_2O or allylSmBr/HMPA/$CuCl_2$·$2H_2O$ at ambient temperature. The cascade coupling provides a facile synthesis of *cis*-2-(2-hydroxyalkyl)cyclopropanols or 2-(2-hydroxyethyl)-bicyclo[2.1.1]hexan-1-ols depending upon the structures of the homoallylic esters. With but-3-enyl but-3-enoates as the substrates, the two C=C bonds were successively coupled, allowing the construction of the structurally interesting bridged bicyclic tertiary alcohols. The mild reaction conditions, readily available starting materials, good yields, and excellent diastereoselectivity make the reaction attractive for the preparation of the corresponding 1,4-diols.

■ EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all the cascade reactions were carried out under a nitrogen atmosphere in oven-dried flasks. THF was distilled from sodium/benzophenone. The homoallyl alcohols and their esters were prepared according to literature

dx.doi.org/10.1021/jo501797w | J. Org. Chem. 2015, 80, 52−61

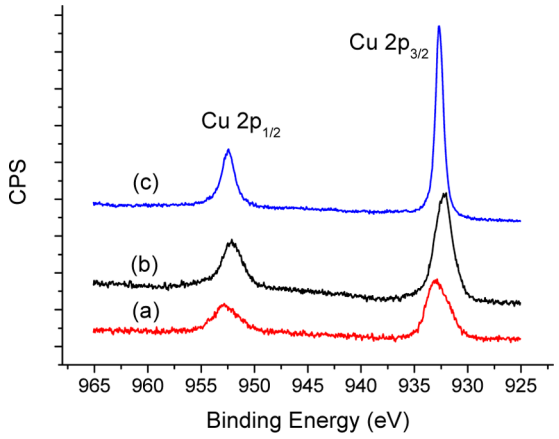


Figure 2. Cu 2p photoelectron spectra: (a) $CuCl_2·2H_2O$/allylSmBr/HMPA/THF system; (b) CuCl/allylSmBr/HMPA/H_2O/THF system; (c) Cu standard sample.

Table 3. Yields of 5a by Using Different Loadings of $CuCl_2·2H_2O$ as the Additive

$CuCl_2·2H_2O$ (equiv)	HPLC yield of **5a** (%)[a]
0.8	39
1.0	45
1.2	53
1.4	65
1.6	78
1.8	48

[a]HPLC yields were determined using naphthalene as the internal standard.

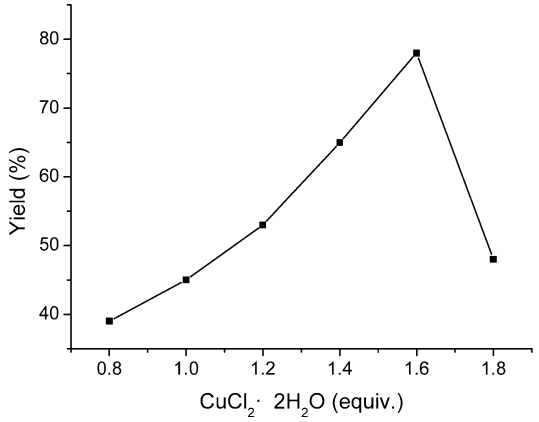
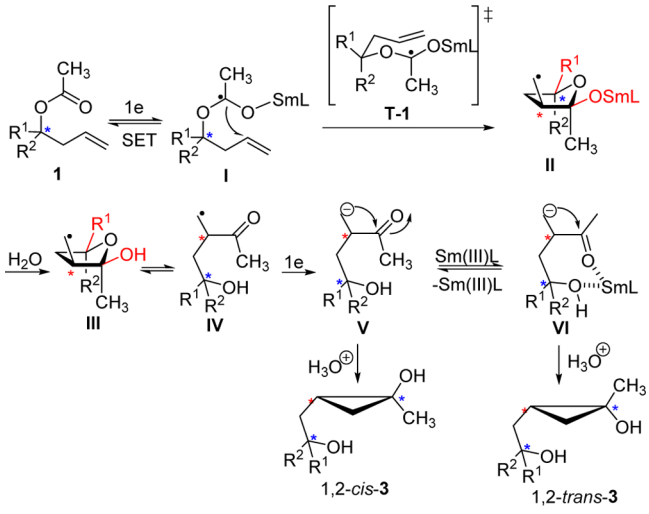


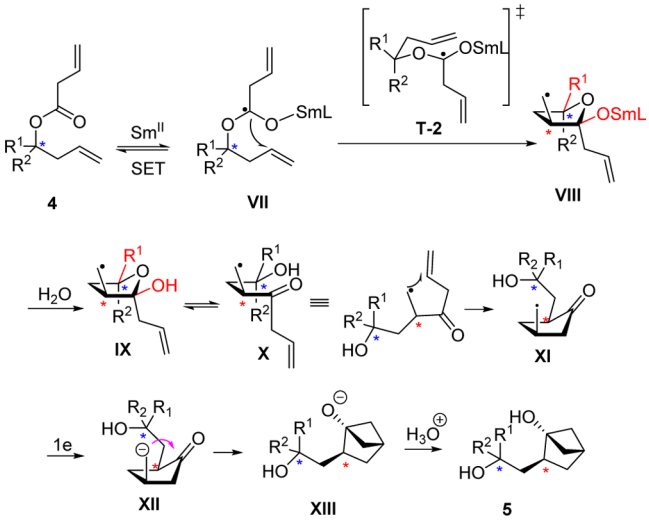
Figure 3. Yields of **5a** vs the loading of $CuCl_2·2H_2O$.

reports.[28] The synthesis of substrates **1a**, **1d**, **1g**, and **1n** have been reported.[28a] Compounds **1b**, **1c**, **1f**, and **1h** are known compounds as reported in the literature.[28b] Compound **1j** is also known.[28c] All other reagents were received from commercial sources and utilized without further purification, if not stated otherwise. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ on a 400 MHz or 600 MHz instrument with TMS as internal standard. Chemical shifts (δ) are 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. The columns were hand packed with silica gel 60 (160−200 mesh). Unknown products were additionally confirmed by high-resolution mass spectra (HRMS) using a TOF-MS instrument with an ESI

Scheme 4. Proposed Mechanism for the Formation of 3



Scheme 5. Proposed Mechanism for the Formation of 5



source. HPLC yields of **4a** were detected by using naphthalene as internal standard. HPLC conditions: C18 column; CH_3CN/H_2O = 40:60; flow rate = 0.8 mL/min; retention time 6.8 min). X-ray photoelectron spectra (XPS) detection of Cu 2p spectra were recorded by using an electron spectrometer. An X-ray source of 250 W power and Al K_α radiation ($h\nu$ = 1486.6 eV) were used. All spectra were calibrated by using the C 1s line at 284.6 eV as a reference.

General Procedure for the Synthesis of the But-3-enyl But-3-enoates.[28e−g] To a solution of the homoallyl alcohol (10 mmol) in CH_2Cl_2 (50 mL) were added Ac_2O (30 mmol) and pyridine (50 mmol) sequentially. The reaction mixture was stirred at 34−37 °C until the reaction was complete (monitored by TLC). The reaction was quenched by the addition of aq HCl (10%). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (300−400 mesh) using petroleum/EtOAc (15/1, v:v) as the eluent to afford compounds **1**.

*1-(3,4-Dimethoxyphenyl)but-3-en-1-yl Acetate (**1e**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83−6.72 (m, 3H), 5.68−5.59 (m, 2H), 5.01−4.94 (m, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 2.60−2.43 (m, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 148.8, 148.7, 133.4, 132.5, 119.1, 117.8, 110.8, 109.8, 75.0, 55.8, 55.7, 40.5, 21.1. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{18}O_4Na$ $[M + Na]^+$: 273.1097; found: 273.1099.

*Hept-1-en-4-yl Acetate (**1i**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77−5.66 (m, 1H), 5.05−5.00 (m, 2H), 4.91−4.86 (m, 1H), 2.27−

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2.24 (m, 2H), 1.99 (s, 3H), 1.53−1.46 (m, 2H), 1.36−1.25 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 133.8, 117.5, 73.0, 38.6, 35.7, 21.1, 18.5, 13.8. HRMS (ESI) m/z: calcd for $C_9H_{16}O_2Na$ $[M + Na]^+$: 179.1043; found: 179.1048.

*1-Cyclopropylbut-3-en-1-yl Acetate (**1k**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80−5.70 (m, 1H), 5.06−4.98 (m, 2H), 4.27−4.21 (m, 1H), 2.43−2.33 (m, 2H), 2.00 (s, 3H), 0.98−0.92 (m, 1H), 0.54−0.40 (m, 2H), 0.38−0.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 133.8, 117.3, 77.7, 39.2, 21.2, 14.8, 3.2, 3.1. HRMS (ESI) m/z: calcd for $C_9H_{14}O_2Na$ $[M + Na]^+$: 177.0886; found: 177.0882.

*1-Allylcyclohexyl Acetate (**1l**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77−5.67 (m, 1H), 5.04−5.00 (m, 2H), 2.62−2.61 (m, 2H), 2.17−2.13 (m, 2H), 1.97−1.96 (m, 3H), 1.57−1.43 (m, 5H), 1.37−1.30 (m, 2H), 1.27−1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 133.0, 118.0, 83.2, 41.9, 34.4, 25.5, 22.2, 21.8, 21.7. HRMS (ESI) m/z: calcd for $C_{11}H_{18}O_2Na$ $[M + Na]^+$: 205.1199; found: 205.1206.

*2,2-Dimethyl-1-phenylbut-3-en-1-yl Acetate (**1m**).* Oil. ^{1}HNMR (600 MHz, $CDCl_3$) δ 7.35−7.29 (m, 5H), 5.98−5.93 (m, 1H), 5.66 (s, 1H), 5.09−4.99 (m, 2H), 2.10 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 144.0, 138.0, 128.0, 127.7, 127.6, 113.1, 81.7, 41.1, 24.1, 22.6, 21.1. HRMS (ESI) m/z: calcd for $C_{14}H_{18}O_2Na$ $[M + Na]^+$: 241.1199; found: 241.1192.

*1-Phenylbut-3-en-1-yl Propionate (**1o**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42−7.31 (m, 5H), 5.92−5.90 (m, 1H), 5.81−5.74 (m, 1H), 5.16−5.10 (m, 2H), 2.74−2.61 (m, 2H), 2.44−2.36 (m, 2H), 1.19 (t, J = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 140.4, 133.5, 128.5, 127.9, 126.5, 118.0, 74.9, 40.9, 27.8, 9.1. HRMS (ESI) m/z: calcd for $C_{13}H_{16}O_2Na$ $[M + Na]^+$: 227.1043; found: 227.1046.

*1-(p-Tolyl)but-3-en-1-yl Isobutyrate (**1p**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.20 (m, 4H), 5.87−5.84 (m, 1H), 5.82−5.75 (m, 1H), 5.16−5.10 (m, 2H), 2.73−2.68 (m, 1H), 2.65−2.59 (m, 2H), 2.39 (s, 3H), 1.23 (dd, J = 20.7, 7.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1, 137.5, 137.4, 133.6, 129.1, 126.4, 117.9, 74.6, 41.0, 34.2, 21.2, 19.1, 18.9. HRMS (ESI) m/z: calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$: 255.1356; found: 255.1358.

*2-Phenylpent-4-en-2-yl Acetate (**1q**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.25 (m, 5H), 5.69−5.58 (m, 1H), 5.09−5.05 (m, 2H), 2.88−2.73 (m, 2H), 2.07 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 144.7, 132.9, 128.2, 127.0, 124.6, 118.7, 83.1, 46.4, 25.0, 22.2. HRMS (ESI) m/z: calcd for $C_{13}H_{16}O_2Na$ $[M + Na]^+$: 227.1043; found: 227.1039.

*(E)-Hepta-1,5-dien-4-yl Acetate (**1r**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.76−5.69 (m, 2H), 5.45−5.41(m, 1H), 5.27−5.23 (m, 1H), 5.09−5.05 (m, 2H), 2.39−2.33 (m, 2H), 2.03 (s, 3H), 1.69 (d, J = 6.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 133.4, 129.3, 129.0, 117.6, 73.9, 39.0, 21.2, 17.7. HRMS (ESI) m/z: calcd for $C_9H_{14}O_2Na$ $[M + Na]^+$: 177.0886; found: 177.0889.

General Procedure for the Cascade Synthesis of Diol 3.[29] To a two-necked flask containing samarium powder (2.5 mmol) were added THF (18 mL) and allyl bromide (2.2 mmol) under nitrogen. The mixture was stirred at rt for 1 h (the color would turn purple). HMPA (2 mL) and H_2O (1 mmol) were then added in sequence via a syringe. A solution of substrate **1** (1 mmol) in THF (5 mL) was subsequently added. The color would fade in 3 h (monitored by TLC). The reaction mixture was quenched with aq sodium−potassium tartrate and extracted with diethyl ether (3 × 20 mL). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (300−400 mesh) using petroleum/EtOAc (5/1, v:v) as the eluent to afford the corresponding products **3**.

General Procedure for the Synthesis of the But-3-enyl But-3-enoates.[30] To a solution of homoallylic alcohol (7.9 mmol) in Et_3N (2.4 g, 23.6 mmol) at 0 °C was added crotonyl chloride (1.57g, 15 mmol). When a yellow precipitate appeared, the reaction mixture was allowed to warm to room temperature and stirred for 3 h before being quenched with 6 N HCl solution (150 mL) and extracted with ether. The organic layer was washed with water, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography on silica gel (150−200 mesh) using petroleum/EtOAc (15/1, v:v) as the eluent to afford the corresponding esters **4**.

*1-Phenylbut-3-en-1-yl But-3-enoate (**4a**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.31 (m, 5H), 6.02−5.86 (m, 2H), 5.79−5.69 (m, 1H), 5.22−5.08 (m, 4H), 3.17−3.15 (m, 2H), 2.74−2.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 140.0, 133.3, 130.2, 128.5, 128.0, 126.5, 118.6, 118.2, 75.4, 40.8, 39.3. HRMS (ESI) m/z: calcd for $C_{14}H_{16}O_2Na$ $[M + Na]^+$: 239.1043; found: 239.1045.

*1-(2-Methoxyphenyl)but-3-en-1-yl But-3-enoate (**4b**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.24 (m, 2H), 6.98−6.87 (m, 2H), 6.30−6.27 (m, 1H), 6.02−5.73 (m, 2H), 5.21−5.03 (m, 4H), 3.85 (s, 3H), 3.16−3.14 (m, 2H), 2.65−2.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 156.1, 133.8, 130.4, 128.7, 128.6, 126.3, 120.5, 118.4, 117.5, 110.6, 69.9, 55.5, 39.7, 39.4. HRMS (ESI) m/z: calcd for $C_{15}H_{18}O_3Na$ $[M + Na]^+$: 269.1148; found: 269.1147.

*1-(4-Methoxyphenyl)but-3-en-1-yl But-3-enoate (**4c**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.29 (m, 2H), 6.92−6.90 (m, 2H), 5.98−5.91 (m, 1H), 5.86−5.81 (m, 1H), 5.76−5.69 (m, 1H), 5.19−5.16 (m, 2H), 5.13−5.07 (m, 2H), 3.82 (s, 3H), 3.14−3.12 (m, 2H), 2.72−2.67 (m, 1H), 2.61−2.56 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 159.3, 133.4, 132.1, 130.3, 128.0, 118.5, 118.0, 113.8, 75.1, 55.2, 40.6, 39.4. HRMS (ESI) m/z: calcd for $C_{15}H_{18}O_3Na$ $[M + Na]^+$: 269.1148; found: 269.1147.

*1-(3,4-Dimethoxyphenyl)but-3-en-1-yl But-3-enoate (**4d**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91−6.82 (m, 3H), 5.95−5.66 (m, 3H), 5.16−5.03 (m, 4H), 3.88 (s, 3H), 3.85 (s, 3H), 3.14−3.06 (m, 2H), 2.68−2.53 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 148.9, 148.8, 133.4, 132.5, 130.3, 119.1, 118.5, 118.0, 110.9, 109.9, 75.2, 55.9, 55.8, 40.6, 39.3. HRMS (ESI) m/z: calcd for $C_{16}H_{20}O_4Na$ $[M + Na]^+$: 299.1254; found: 299.1263.

*1-(m-Tolyl)but-3-en-1-yl But-3-enoate (**4e**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31−7.29 (m, 1H), 7.25−7.22 (m, 2H), 7.17−7.15 (m, 1H), 6.04−5.98 (m, 1H), 5.96−5.89 (m, 1H), 5.83−5.76 (m, 1H), 5.26−5.21 (m, 2H), 5.18−5.12 (m, 2H), 3.22−3.15 (m, 2H), 2.78−2.71 (m, 1H), 2.68−2.62 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 140.1, 138.0, 133.5, 130.4, 128.8, 128.4, 127.3, 123.6, 118.5, 118.0, 75.4, 40.9, 39.3, 21.5. HRMS (ESI) m/z: calcd for $C_{15}H_{18}O_2Na$ $[M + Na]^+$: 253.1199; found: 253.1200.

*1-(4-Chlorophenyl)but-3-en-1-yl But-3-enoate (**4f**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.26 (m, 4H), 5.96−5.63 (m, 3H), 5.19−5.05 (m, 4H), 3.13−3.11 (m, 2H), 2.66−2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 138.5, 133.8, 132.8, 130.0, 128.6, 128.0, 118.7, 118.5, 74.7, 40.6, 39.3. HRMS (ESI) m/z: calcd for $C_{14}H_{15}ClO_2Na$ $[M + Na]^+$: 273.0653; found: 273.0657.

*1-(3-Chlorophenyl)but-3-en-1-yl But-3-enoate (**4g**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.22 (m, 4H), 5.98−5.91 (m, 1H), 5.82−5.80 (m, 1H), 5.74−5.67 (m, 1H), 5.21−5.09 (m, 4H), 3.19−3.12 (m, 2H), 2.68−2.55 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 142.1, 134.4, 132.7, 130.0, 129.8, 128.2, 126.6, 124.7, 118.8, 118.6, 74.6, 40.7, 39.2. HRMS (ESI) m/z: calcd for $C_{14}H_{15}ClO_2Na$ $[M + Na]^+$: 273.0653; found: 273.0656.

*1-(2-Chlorophenyl)but-3-en-1-yl But-3-enoate (**4h**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44−7.43(m, 1H), 7.37−7.35 (m, 1H), 7.30−7.27 (m, 1H), 7.24−7.21 (m, 1H), 6.30−6.28 (m, 1H), 6.01−5.94 (m, 1H), 5.84−5.77 (m, 1H), 5.22−5.19 (m, 2H), 5.14−5.09 (m, 2H), 3.19−3.17 (m, 2H), 2.70−2.58 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 138.0, 132.9, 132.1, 130.1, 129.6, 128.9, 127.1, 127.0, 118.7, 118.3, 71.9, 39.6, 39.2. HRMS (ESI) m/z: calcd for $C_{14}H_{15}ClO_2Na$ $[M + Na]^+$: 273.0653; found: 273.0657.

*1-(4-Fluorophenyl)but-3-en-1-yl But-3-enoate (**4i**).* Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.32 (m, 2H), 7.06−7.03 (m, 2H), 5.97−5.91 (m, 1H), 5.87−5.82 (m, 1H), 5.74−5.67 (m, 1H), 5.19−5.16 (m, 2H), 5.11−5.07 (m, 2H), 3.15−3.12 (m, 2H), 2.70−2.65 (m, 1H), 2.60−2.54 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 162.4 (d, J = 244.9 Hz), 135.8 (d, J = 3.2 Hz), 133.0, 130.1, 128.4 (d, J = 8.1 Hz), 118.6, 118.4, 115.3 (d, J = 21.4 Hz), 74.7, 40.7, 39.3. HRMS (ESI) m/z: calcd for $C_{14}H_{15}FO_2Na$ $[M + Na]^+$: 257.0948; found: 257.0946.

*1-([1,1′-Biphenyl]-4-yl)but-3-en-1-yl But-3-enoate (**4j**).* Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.65 (m, 4H), 7.53−7.49 (m, 4H), 7.44−7.40 (m, 1H), 6.09−5.97 (m, 2H), 5.88−5.78 (m, 1H), 5.28−5.16 (m, 4H), 3.24−3.21 (m, 2H), 2.81−2.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 141.0, 140.8, 139.0, 133.3, 130.3, 128.9,

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127.5, 127.3, 127.2, 127.1, 118.7, 118.3, 75.3, 40.8, 39.4. HRMS (ESI) m/z: calcd for $C_{20}H_{20}O_2Na$ $[M + Na]^+$: 315.1356; found: 315.1360.

*1-(Furan-2-yl)but-3-en-1-yl But-3-enoate (**4k**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.40−7.39 (m, 1H), 6.35−6.34 (m, 2H), 5.95−5.90 (m, 2H), 5.74−5.69 (m, 1H), 5.18−5.12 (m, 3H), 5.09−5.07 (m, 1H), 3.12−3.10 (m, 2H), 2.77−2.72 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 152.0, 142.6, 132.7, 130.1, 118.6, 118.3, 110.2, 108.8, 68.0, 39.1, 36.9. HRMS (ESI) m/z: calcd for $C_{12}H_{14}O_3Na$ $[M + Na]^+$: 229.0835; found: 229.0834.

*2,2-Dimethyl-1-phenylbut-3-en-1-yl But-3-enoate (**4l**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.35−7.29 (m, 5H), 6.03−5.93 (m, 2H), 5.72−5.68 (m, 1H), 5.23−5.21 (m, 2H), 5.10−5.00 (m, 2H), 3.22−3.15 (m, 2H), 1.13−1.09 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 143.9, 137.8, 130.3, 128.0, 127.6, 120.8, 118.6, 113.2, 81.9, 41.2, 39.5, 24.1, 22.6. HRMS (ESI) m/z: calcd for $C_{16}H_{20}O_2Na$ $[M + Na]^+$: 267.1356; found: 267.1356.

*1-Cyclopropylbut-3-en-1-yl But-3-enoate (**4m**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 5.96−5.89 (m, 1H), 5.82−5.75 (m, 1H), 5.18−5.15 (m, 2H), 5.10−5.04 (m, 2H), 4.33−4.29 (m, 1H), 3.12−3.05 (m, 2H), 2.48−2.38 (m, 2H), 1.03−0.97 (m, 1H), 0.58−0.53 (m, 1H), 0.50−0.46 (m, 1H), 0.42−0.38 (m, 1H), 0.28−0.24 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 133.7, 130.5, 118.3, 117.5, 76.9, 39.4, 39.2, 14.8, 3.3, 3.1. HRMS (ESI) m/z: calcd for $C_{11}H_{16}O_2Na$ $[M + Na]^+$: 203.1043; found: 203.1044.

*Hept-1-en-4-yl But-3-enoate (**4n**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 5.91−5.84 (m, 1H), 5.73−5.66 (m, 1H), 5.12−5.09 (m, 2H), 5.03−4.99 (m, 2H), 4.94−4.89 (m, 1H), 3.03−3.01 (m, 2H), 2.30−2.22 (m, 2H), 1.54−1.44 (m, 2H), 1.35−1.23 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 133.6, 130.5, 118.2, 117.5, 73.2, 39.3, 38.6, 35.7, 18.5, 13.8. HRMS (ESI) m/z: calcd for $C_{11}H_{18}O_2Na$ $[M + Na]^+$: 205.1199; found: 205.1198.

*2-Methylhex-5-en-3-yl But-3-enoate (**4o**).* Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.98−5.87 (m, 1H), 5.79−5.69 (m, 1H), 5.19−5.14 (m, 2H), 5.09−5.02 (m, 2H), 4.82−4.77 (m, 1H), 3.09−3.08 (m, 2H), 2.37−2.26 (m, 2H), 1.89−1.85 (m, 1H), 0.92 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 134.1, 130.5, 118.3, 117.4, 76.7, 39.4, 36.0, 31.0, 18.6, 17.5. HRMS (ESI) m/z: calcd for $C_{11}H_{18}O_2Na$ $[M + Na]^+$: 205.1199; found: 205.1197.

*1-Cyclohexylbut-3-en-1-yl But-3-enoate (**4p**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 5.96−5.89 (m, 1H), 5.77−5.70 (m, 1H), 5.18−5.15 (m, 2H), 5.08−5.02 (m, 2H), 4.81−4.78 (m, 1H), 3.12−3.04 (m, 2H), 2.38−2.34 (m, 1H), 2.30−2.25 (m, 1H), 1.75−1.73 (m, 3H), 1.68−1.65 (m, 2H), 1.55−1.49 (m, 1H), 1.26−1.11 (m, 3H), 1.05−0.98 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 134.1, 130.6, 118.3, 117.4, 77.1, 40.7, 39.4, 35.9, 29.0, 28.0, 26.3, 26.0, 25.9. HRMS (ESI) m/z: calcd for $C_{14}H_{22}O_2Na$ $[M + Na]^+$: 245.1512; found: 245.1511.

*1-Phenylpent-4-en-2-yl But-3-enoate (**4q**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.34−7.31 (m, 2H), 7.27−7.23 (m, 3H), 5.92−5.87 (m, 1H), 5.86−5.80 (m, 1H), 5.22−5.20 (m, 1H), 5.19−5.17 (m, 2H), 5.15−5.12 (m, 2H), 3.10−3.03 (m, 2H), 2.96−2.88 (m, 2H), 2.43−2.39 (m, 1H), 2.37−2.33 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 137.4, 133.5, 130.3, 129.5, 128.4, 126.6, 118.5, 118.1, 74.1, 39.9, 39.4, 37.9. HRMS (ESI) m/z: calcd for $C_{15}H_{18}O_2Na$ $[M + Na]^+$: 253.1199; found: 253.1197.

*(E)-Hepta-1,5-dien-4-yl But-3-enoate (**4r**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 5.85−5.79 (m, 1H), 5.67−5.60 (m, 2H), 5.37−5.33 (m, 1H), 5.21−5.17 (m, 1H), 5.07−5.04 (m, 2H), 5.00−4.96 (m, 2H), 2.98−2.97 (m, 2H), 2.30−2.26 (m, 2H), 1.61−1.60 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 133.3, 130.4, 129.2, 128.9, 118.1, 117.6, 73.9, 39.2, 39.0, 17.5. HRMS (ESI) m/z: calcd for $C_{11}H_{16}O_2Na$ $[M + Na]^+$: 203.1043; found: 203.1044.

*2-Phenylpent-4-en-2-yl But-3-enoate (**4s**).* Oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.39−7.36 (m, 4H), 7.31−7.28 (m, 1H), 6.01−5.90 (m, 1H), 5.69−5.62 (m, 1H), 5.23−5.21 (m, 2H), 5.11−5.09 (m, 2H), 3.15−3.14 (m, 2H), 2.90−2.87 (m, 1H), 2.83−2.79 (m, 1H), 1.87 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 144.6, 132.8, 130.6, 128.3, 127.1, 124.6, 118.7, 118.4, 83.5, 46.4, 40.3, 25.0. HRMS (ESI) m/z: calcd for $C_{15}H_{18}O_2Na$ $[M + Na]^+$: 253.1199; found: 253.1204.

*1-Allylcyclohexyl But-3-enoate (**4t**).* Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.92−5.63 (m, 2H), 5.12−4.97 (m, 4H), 2.99−2.97 (m, 2H), 2.61−2.59 (m, 2H), 2.17−2.14 (m, 2H), 1.56−1.52 (m, 1H), 1.47−1.41 (m, 4H), 1.34−1.27 (m, 2H), 1.23−1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 132.8, 130.9, 118.0, 117.9, 83.5, 42.0, 40.4, 34.4, 25.4, 21.7. HRMS (ESI) m/z: calcd for $C_{13}H_{20}O_2Na$ $[M + Na]^+$: 231.1356; found: 231.1345.

General Procedure for the Reductive Cascade Double Cyclization of But-3-enyl But-3-enoates 4 To Synthesize the Bridged Bicyclic Tertiary Alcohols 5. To a two-necked flask containing samarium powder (0.7 g, 4.67 mmol) were added THF (30 mL) and allyl bromide (0.4 g, 3.3 mmol) under nitrogen. A small crystal of I_2 was added to trigger the reaction. The mixture was stirred at rt for 1 h (the color would turn deep purple). HMPA (3 mL, 16 mmol) and $CuCl_2{\cdot}2H_2O$ (0.27 g, 1.6 mmol) were then added in sequence. A solution of but-3-enyl but-3-enoate **4** (1 mmol) in THF (5 mL) was subsequently added. The mixture was stirred at rt for 10 h. The reaction mixture was quenched with aq sodium−potassium tartrate and extracted with diethyl ether (3 × 20 mL). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (150−200 mesh) using petroleum/EtOAc (8/1, v:v) as the eluent to afford the corresponding alcohols **5**.

*2-(2-Hydroxy-2-phenylethyl)bicyclo[2.1.1]hexan-1-ol (**5a**).* White solid (135 mg, 62% yield), mp 103−105 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.31 (m, 4H), 7.27−7.24 (m, 1H), 5.77 (b, s, 1H), 4.73−4.70 (m, 1H), 4.24 (b, s, 1H), 2.09−2.00 (m, 3H), 1.95−1.86 (m, 1H), 1.77−1.72 (m, 1H), 1.59−1.51 (m, 2H), 1.50−1.44 (m, 1H), 1.41 (s, 1H), 1.12−1.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 128.4, 127.4, 125.7, 80.3, 75.3, 46.4, 43.6, 40.9, 40.0, 38.2, 27.9. HRMS (ESI) m/z: calcd for $C_{14}H_{18}O_2Na$ $[M + Na]^+$: 241.1199; found: 241.1203.

*2-(2-Hydroxy-2-(2-methoxyphenyl)ethyl)bicyclo[2.1.1]hexan-1-ol (**5b**).* White solid (228 mg, 92% yield), mp 97−98 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.43−7.41 (m, 1H), 7.29−7.26 (m, 1H), 7.00−6.98 (m, 1H), 6.90 (d, J = 8.2 Hz, 1H), 5.84 (b, s, 1H), 5.06 (dd, J = 10.2, 1.7 Hz, 1H), 3.88 (s, 3H), 2.14−2.06 (m, 3H), 1.96−1.83 (m, 3H), 1.69−1.67 (m, 1H), 1.59−1.56 (m, 1H), 1.53−1.51 (m, 1H), 1.47−1.46 (s, 1H), 1.18−1.16 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.1, 132.6, 128.4, 126.3, 120.9, 110.4, 80.5, 70.9, 55.4, 46.4, 41.0, 40.9, 40.1, 38.3, 27.9. HRMS (ESI) m/z: calcd for $C_{15}H_{20}O_3Na$ $[M + Na]^+$: 271.1305; found: 271.1310.

*2-(2-Hydroxy-2-(4-methoxyphenyl)ethyl)bicyclo[2.1.1]hexan-1-ol (**5c**).* White solid (219 mg, 88% yield), mp 103−105 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 5.74 (b, s, 1H), 4.72 (dd, J = 10.4, 1.7 Hz, 1H), 3.89 (b, s, 1H), 3.82 (s, 3H), 2.12−2.05 (m, 3H), 1.97−1.91 (m, 1H), 1.75−1.73 (m, 1H), 1.64−1.62 (m, 1H), 1.58−1.56 (m, 1H), 1.51−1.49 (m, 1H), 1.45−1.44 (m, 1H), 1.14−1.12 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 137.3, 126.9, 113.8, 80.4, 75.1, 55.3, 46.4, 43.5, 41.0, 40.0, 38.3, 27.9. HRMS (ESI) m/z: calcd for $C_{15}H_{20}O_3Na$ $[M + Na]^+$: 271.1305; found: 271.1301.

*2-(2-(3,4-Dimethoxyphenyl)-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5d**).* White solid (195 mg, 70% yield), mp 98−100 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.84−6.81 (m, 1H), 6.78−6.76 (m, 1H), 4.63−4.61 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.03−1.97 (m, 3H), 1.91−1.82 (m, 1H), 1.72−1.68 (m, 1H), 1.55−1.50 (m, 2H), 1.45−1.41 (m, 1H), 1.37 (s, 1H), 1.10−1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.2, 138.0, 117.8, 110.9, 108.8, 80.2, 75.0, 55.92, 55.86, 46.4, 43.7, 40.9, 40.1, 38.1, 27.9. HRMS (ESI) m/z: calcd for $C_{16}H_{22}O_4Na$ $[M + Na]^+$: 301.1410; found: 301.1408.

*2-(2-Hydroxy-2-(m-tolyl)ethyl)bicyclo[2.1.1]hexan-1-ol (**5e**).* White solid (184 mg, 79% yield), mp 78−80 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27−7.24 (m, 1H), 7.22 (s, 1H), 7.19−7.18 (m, 1H), 7.12−7.11 (m, 1H), 5.45 (b, s, 1H), 4.77−4.75 (m, 1H), 3.56 (b, s, 1H), 2.38 (s, 3H), 2.14−2.06 (m, 3H), 1.99−1.93 (m, 1H), 1.80−1.77 (m, 1H), 1.68−1.66 (m, 1H), 1.60−1.57 (m, 1H), 1.54−1.52 (m, 1H), 1.47−1.46 (m, 1H), 1.17−1.15 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.0, 138.2, 128.4,128.3, 126.3, 122.7, 80.5, 75.7, 46.5, 43.5, 41.1, 40.1, 38.4, 27.8, 21.5. HRMS (ESI) m/z: calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$: 255.1356; found: 255.1365.

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*2-(2-(4-Chlorophenyl)-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5f**).* White solid (179 mg, 71% yield), mp 98−100 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.28 (m, 4H), 4.72−4.70 (m, 1H), 2.10−2.03 (m, 3H), 1.91−1.85 (m, 1H), 1.75−1.72 (m, 1H), 1.61−1.59 (m, 1H), 1.58−1.49 (m, 2H), 1.43−1.42 (m, 1H), 1.14−1.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 133.0, 128.5, 127.0, 80.3, 74.6, 46.5, 43.7, 41.0, 39.9, 38.2, 27.9. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{17}ClO_2Na$ $[M + Na]^+$: 275.0809; found: 275.0814.

*2-(2-(3-Chlorophenyl)-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5g**).* White solid (152 mg, 60% yield), mp 91−93 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39−7.34 (m, 3H), 7.30−7.26 (m, 1H), 5.76 (b, s, 1H), 4.76 (dd, *J* = 10.5, 1.8 Hz, 1H), 4.18 (b, s, 1H), 2.14−2.11 (m, 1H), 2.09−2.04 (m, 2H), 1.97−1.91 (m, 1H), 1.79−1.76 (m, 1H), 1.63−1.61 (m, 1H), 1.58−1.55 (m, 1H), 1.51−1.49 (m, 1H), 1.44−1.43 (m, 1H), 1.15−1.13 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.1, 128.5, 127.5, 125.7, 80.4, 75.5, 46.4, 43.6, 41.0, 40.1, 38.3, 27.9. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{17}ClO_2Na$ $[M + Na]^+$: 275.0809; found: 275.0816.

*2-(2-(2-Chlorophenyl)-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5h**).* White solid (167 mg, 66% yield), mp 120−121 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59−7.57(m, 1H), 7.28−7.23 (m, 2H), 7.17−7.14 (m, 1H), 5.95 (b, s, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.98 (b, s, 1H), 2.14−2.11 (m, 1H), 2.05−2.02 (m, 2H), 1.85−1.82 (m, 1H), 1.71−1.65 (m, 1H), 1.53−1.49 (m, 2H), 1.46−1.44 (m, 1H), 1.36−1.35 (m, 1H), 1.13−1.12 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.5, 131.4, 129.2, 128.2, 127.1, 126.8, 80.2, 71.4, 46.3, 41.7, 40.9, 39.9, 37.9, 27.9. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{17}ClO_2Na$ $[M + Na]^+$: 275.0809; found: 275.0810.

*2-(2-(4-Fluorophenyl)-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5i**).* White solid (180 mg, 76% yield), mp 94−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.02−6.98 (m, 2H), 5.65 (b, s, 1H), 4.71−4.68 (m, 1H), 4.60 (b, s, 1H), 2.10−2.00 (m, 3H), 1.91−1.83 (m, 1H), 1.73−1.69 (m, 1H), 1.57−1.52 (m, 2H), 1.48−1.44 (m, 1H), 1.40 (s, 1H), 1.12−1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J_{C-F} = 243.4 Hz, 1C), 141.0 (d, J_{C-F} = 3.1 Hz, 1C), 127.2 (d, J_{C-F} = 8.0 Hz, 1C), 115.1 (d, J_{C-F} = 21.2 Hz, 1C), 80.3, 74.6, 46.5, 43.7, 41.0, 39.9, 38.1, 27.9. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{17}FO_2Na$ $[M + Na]^+$: 259.1105; found: 259.1108.

*2-(2-([1,1′-Biphenyl]-3-yl)-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5j**).* White solid (200 mg, 68% yield), mp 99−102 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61−7.58 (m, 4H), 7.47−7.45 (m, 4H), 7.39−7.36 (m, 1H), 5.49 (b, s, 1H), 4.83 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.02 (b, s, 1H), 2.19−2.16 (m, 1H), 2.11−2.07 (m, 2H), 2.03−1.97 (m, 1H), 1.85−1.82 (m, 1H), 1.68−1.66 (m, 1H), 1.62−1.59 (m, 1H), 1.56−1.53 (m, 1H), 1.49−1.48 (m, 1H), 1.19−1.17 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.1, 140.8, 140.5, 128.8, 127.3, 127.2, 127.1, 126.1, 80.5, 75.3, 46.5, 43.6, 41.1, 40.1, 38.3, 27.9. HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{22}O_2Na$ $[M + Na]^+$: 317.1512; found: 317.1515.

*2-(2-(Furan-2-yl)-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5k**).* White solid (52 mg, 25% yield), mp 75−78 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.36 (m, 1H), 6.34−6.33 (m, 1H), 6.25−6.24 (m, 1H), 4.79−4.77 (m, 1H), 2.12−2.10 (m, 1H), 2.08−2.02 (m, 3H), 1.97−1.93 (m, 1H), 1.64−1.58 (m, 2H), 1.52−1.49 (m, 1H), 1.46−1.45 (m, 1H), 1.20−1.18 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9, 141.7, 110.2, 105.3, 80.3, 68.4, 46.4, 40.9, 39.4, 39.2, 37.8, 28.0. HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{16}O_3Na$ $[M + Na]^+$: 231.0992; found: 231.0998.

*2-(1-Hydroxy-2-methyl-1-phenylpropan-2-yl)bicyclo[2.1.1]-hexan-1-ol (**5l**).* White solid (111 mg, 45% yield), mp 115−117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29−7.28 (m, 4H), 7.26−7.24 (m, 1H), 4.49 (s, 1H), 2.01 (s, 1H), 1.96−1.94 (m, 1H), 1.84−1.80 (m, 1H), 1.74−1.72 (m, 1H), 1.53−1.50 (m, 1H), 1.46−1.44 (m, 2H), 1.27 (s, 1H), 0.92 (s, 3H), 0.54 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.2, 128.3, 127.6, 127.4, 83.9, 80.4, 51.3, 48.7, 41.6, 41.1, 33.7, 26.5, 25.9, 14.6. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{22}O_2Na$ $[M + Na]^+$: 269.1512; found: 269.1516.

*2-(2-Cyclopropyl-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5m**).* White solid (129 mg, 71% yield), mp 97−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (b, s, 1H), 3.66 (b, s, 1H), 2.94−2.90 (m, 1H), 2.06−1.98 (m, 2H), 1.92−1.88 (m, 1H), 1.77−1.69 (m, 2H), 1.63−1.61 (m, 1H), 1.56−1.52 (m, 1H), 1.46−1.42 (m, 2H), 1.15−1.12 (m, 1H), 0.96−0.90 (m, 1H), 0.52−0.49 (m, 2H), 0.33−0.28 (m, 1H), 0.21−0.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.3, 78.0, 46.4, 40.8, 40.4, 39.7, 38.2, 27.9, 18.5, 3.3, 2.7. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{18}O_2Na$ $[M + Na]^+$: 205.1199; found: 205.1199.

*2-(2-Hydroxypentyl)bicyclo[2.1.1]hexan-1-ol (**5n**).* White solid (140 mg, 76% yield), mp 76−78 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.70−3.66 (m, 1H), 2.08−2.07 (m, 1H), 2.03−1.99 (m, 1H), 1.97−1.94 (m, 1H), 1.64−1.62 (m, 1H), 1.60−1.59 (m, 1H), 1.57−1.53 (m, 2H), 1.51−1.46 (m, 2H), 1.45−1.41 (m, 3H), 1.39−1.34 (m, 1H), 1.14−1.12 (m, 1H), 0.95−0.93 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 80.3, 72.5, 46.5, 40.8, 40.7, 40.5, 39.7, 38.1, 27.9, 18.9, 14.1. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{20}O_2Na$ $[M + Na]^+$: 207.1356; found: 207.1351.

*2-(2-Hydroxy-3-methylbutyl)bicyclo[2.1.1]hexan-1-ol (**5o**).* White solid (153 mg, 83% yield), mp 77−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (s, 1H), 3.64 (b, s, 1H), 3.49−3.44 (m, 1H), 2.07−1.98 (m, 2H), 1.96−1.90 (m, 1H), 1.70−1.66 (m, 1H), 1.63−1.60 (m, 1H), 1.56−1.51 (m, 3H), 1.48−1.44 (m, 1H), 1.42−1.41 (m, 1H), 1.14−1.12 (m, 1H), 0.93−0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.4, 77.7, 46.4, 40.9, 39.8, 38.2, 36.9, 34.4, 27.9, 18.5, 17.6. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{20}O_2Na$ $[M + Na]^+$: 207.1355; found: 207.1358.

*2-(2-Cyclohexyl-2-hydroxyethyl)bicyclo[2.1.1]hexan-1-ol (**5p**).* White solid (153 mg, 68% yield), mp 87−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (b, s, 1H), 3.50−3.46 (m, 1H), 3.21 (b, s, 1H), 2.08−2.01 (m, 2H), 1.96−1.90 (m, 1H), 1.80−1.67 (m, 5H), 1.66−1.58 (m, 3H), 1.57−1.52 (m, 1H), 1.50−1.46 (m, 1H), 1.44−1.43 (m, 1H), 1.38−1.32 (m, 1H), 1.27−1.19 (m, 2H), 1.16−1.13 (m, 2H), 1.11−0.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.4, 46.4, 44.6, 41.0, 39.9, 38.3, 37.3, 29.1, 28.0, 27.8, 26.5, 26.3, 26.2. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{24}O_2^+Na$ $[M + Na]^+$: 247.1669; found: 247.1662.

*2-(2-Hydroxy-3-phenylpropyl)bicyclo[2.1.1]hexan-1-ol (**5q**).* White solid (174 mg, 75% yield), mp 98−101 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.33 (m, 2H), 7.29−7.23 (m, 3H), 5.50 (s, 1H), 3.94−3.91 (m, 1H), 3.19 (s, 1H), 2.86−2.83 (m, 1H), 2.77−2.73 (m, 1H), 2.09 (s, 1H), 2.05−1.96 (m, 2H), 1.75−1.67 (m, 2H), 1.65−1.63 (m, 1H), 1.58−1.55 (m, 1H), 1.49−1.47 (m, 1H), 1.44 (s, 1H), 1.16−1.14 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 129.4, 128.7, 126.7, 80.4, 73.8, 46.4, 44.8, 40.9, 40.2, 39.6, 38.3, 27.9. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{20}O_2^+Na$ $[M + Na]^+$: 255.1356; found: 255.1362.

*(E)-2-(2-Hydroxypent-3-en-1-yl)bicyclo[2.1.1]hexan-1-ol (**5r**).* White solid (109 mg, 60% yield), mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71−5.62 (m, 1H), 5.56−5.50 (m, 1H), 4.15−4.11 (m, 1H), 2.07−1.98 (m, 3H), 1.69−1.66 (m, 4H), 1.63−1.58 (m, 2H), 1.54−1.51 (m, 1H), 1.48−1.44 (m, 1H), 1.43−1.41 (m, 1H), 1.14−1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 126.1, 80.3, 73.7, 46.4, 41.1, 40.9, 39.6, 38.2, 27.9, 17.6. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{18}O_2Na$ $[M + Na]^+$: 205.1199; found: 205.1198.

*2-(2-Hydroxy-2-phenylpropyl)bicyclo[2.1.1]hexan-1-ol (**5s**).* White solid (121 mg, 52% yield), mp 111−113 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52−7.51 (m, 2H), 7.39−7.36 (m, 2H), 7.29−7.27 (m, 1H), 4.97 (b, s, 1H), 3.18 (b, s, 1H), 2.29−2.26 (m, 1H), 2.11−2.10 (m, 1H), 2.09−2.01(m, 2H), 1.84−1.81 (m, 1H), 1.70 (s, 3H), 1.68 (s, 1H), 1.59−1.53 (m, 2H), 1.44−1.43 (m, 1H), 1.18−1.16 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149. 7, 128.3, 126.8, 124.5, 80.5, 75.0, 47.8, 46.5, 40.9, 38.6, 35.9, 28.0, 27.7. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$: 255.1356; found: 255.1359.

*2-((1-Hydroxycyclohexyl)methyl)bicyclo[2.1.1]hexan-1-ol (**5t**).* White solid (38 mg, 18% yield), mp 113−115 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.42 (s, 1H), 2.62 (s, 1H), 2.17−2.16 (m, 1H), 2.10−2.09 (m, 1H), 2.05−2.02 (m, 1H), 1.77−1.72 (m, 2H), 1.69−1.68 (m, 2H), 1.67−1.65 (m, 1H), 1.60−1.57 (m, 2H), 1.56−1.54 (m, 4H), 1.52−1.49 (m, 3H), 1.42−1.41 (m, 1H), 1.34−1.28 (s, 1H), 1.15−1.14 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 80.5, 72.2, 46.4, 40.7, 40.3, 38.6, 35.4, 34. 6, 28.0, 25.7, 22.6, 22.2. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{22}O_2$ Na $[M + Na]^+$: 233.1512; found: 233.1518.

Preparation of the $CuCl_2$·$2H_2O$/allylSmBr/HMPA/THF System. To a two-necked flask containing samarium powder (0.7 g, 4.67 mmol) were added THF (30 mL) and allyl bromide (0.4 g, 3.3 mmol)

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under nitrogen. A small crystal of I_2 was added to trigger the reaction. The mixture was stirred at rt for 1 h (the color would turn into deep purple). HMPA (3 mL, 16 mmol) and $CuCl_2 \cdot 2H_2O$ (0.27g, 1.6 equiv) were then added in sequence. The mixture was stirred at rt for 10 h. Rapid filtration of the mixture afforded deep green powder, which was washed by THF (3 × 3 mL) and then Et_2O (3 × 3 mL). The powder was dried under vacuum before submission to the XPS detection.

Preparation of the CuCl/allylSmBr/H_2O/HMPA/THF System. To a two-necked flask containing samarium powder (0.7 g, 4.67 mmol) were added THF (30 mL) and allyl bromide (0.4 g, 3.3 mmol) under nitrogen. A small crystal of I_2 was added to trigger the reaction. The mixture was stirred at rt for 1 h (the color would turn into deep purple). HMPA (3 mL, 16 mmol) and H_2O (30 μL, 1.6 mmol) were then added in sequence via a syringe. CuCl (0.16 g, 1.6 equiv) was then added, and the mixture was stirred at rt for 10 h. Rapid filtration of the mixture afforded deep green powder, which was washed by THF (3 × 3 mL) and then Et_2O (3 × 3 mL). The powder was dried under vacuum before submission to the XPS detection.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra for the new compounds and the crystallographic data of **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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