

Efficient Synthesis of Propargylic Ethers under the DBU Conditions and Its Application to Natural Products Synthesis

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Conversion of dibromides carrying *O*-functional groups at adjacent positions to the corresponding propargylic ethers was successfully carried out under the DBU conditions through 2-bromo-1-alkenes as intermediates. The optically active γ-lactone-class natural products, such as (−)-muricatacin (**4**) and (*R*,*R*)-sapinofuranone B (**5**) were synthesized using the propargylic ether intermediate produced by the elimination reaction mentioned above.

In organic synthesis, carbon–carbon bond formation is one of the most important reactions. Although a number of methodologies have been exploited, the critical point is their feasibility towards diverse molecular frameworks, without any special techniques and limitation of functionalities. Among functional groups, which enable carbon–carbon bond formation at desired positions and/or with high chemoselectivity, alkyne-functions have received much attention for such usage as, precursors of (*Z*)- and (*E*)-1-iodo-1-alkenes,[1] 2-iodo-1-alkenes,[2] metalated alkenes,[1f] and alkynes,[3] along with substrates of organometal-conducted coupling reactions.[4] Generally, terminal alkyne derivatives have been produced by elimination reactions of 1,1-dibromo-1-alkenes[5] and 1,2-dibromoalkanes by alkaline metal amides such as LiHMDS and $NaNH_2$,[6] or coupling of aldehydes with phosphonium diazomethanes (Scheme 1).[7]

In closely related investigation, we have developed the DBU-mediated 2-bromo-1-alkene synthesis from 1,2-dibromoalkanes with electron-withdrawing groups at the C-3 position, which strengthens the proton-acidity at the C-2 position.[8] During studies on the scope and limitation of this elimination reaction and efforts towards total synthesis of 12-oxygenated-tremetones,[8a] tuliparin B,[8b] and tanikolide,[8c,8d] we have found that propargylic ethers were produced as minor products, upon using excess amounts of DBU. This observation prompted us to develop a facile propargylic ether synthesis from 1,2-dibromoalkanes. Its ready availability might be applicable as part of multi-step synthesis. We describe herein the elimination reaction of 2,3-dibromoalkoxy derivatives leading to propargylic ethers by utilizing DBU as the base, and its application towards natural products synthesis.[9]

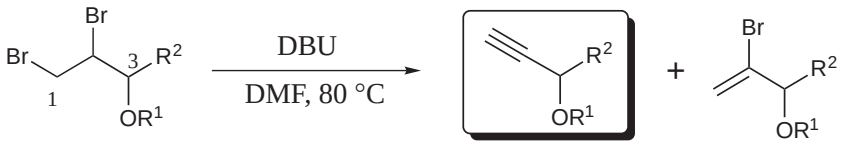
Results and Discussion

To understand the chemistry of the DBU-mediated elimination of 2,3-dibromoalkoxy derivatives leading to the corresponding propargylic ethers, a variety of substrates and reaction conditions were examined, as can be seen in Table 1 and Fig. 1.

Table 1. Elimination Reactions of the 1,2-Dibromoalkanes

Entry	Substrates	DBU /mol amt.	Yields/%	
			Propargylic ethers	2-Bromo-1-alkenes
1[a)]	**1a**	2	**2a** (−)	**3a** (100)
2	**1a**	3	**2a** (trace)	**3a** (46)
3	**1a**	5	**2a** (92)	(−)
4[b)]	**1a**	7[e)]	**2a** (10)	**3a** (83)
5	**1b**	5	**2b** (42)	**3b** (10)
6	**1c**	5	**2c** (68)	(−)
7	**1d**	6	**2d** (92)	(−)
8	**1e**	5	**2e** (71)	**3e** (12)
9[c)]	**1f**	5	**2f** (95)	(−)
10[c)]	**1g**	5	**2g** (−)	**3g** (94)
11	**1h**	5	**2h** (61)	(−)
12	**1i**	5	**2i** (77)	(−)
13	**1j**	5	**2j** (29)	(−)
14	**1k**	5	**2k** (45)	**3k** (30)
15[d)]	**1l**	5	**2l** (72)	(−)

Reaction conditions, see General procedure in experimental part. a) 60 °C, 1.5 h. b) 12 h. c) Racemic compound was used. Relative structure was depicted. d) 23 μmol scale, 85 h. e) NaOPiv was used.



Scheme 1. The DBU-mediated elimination.

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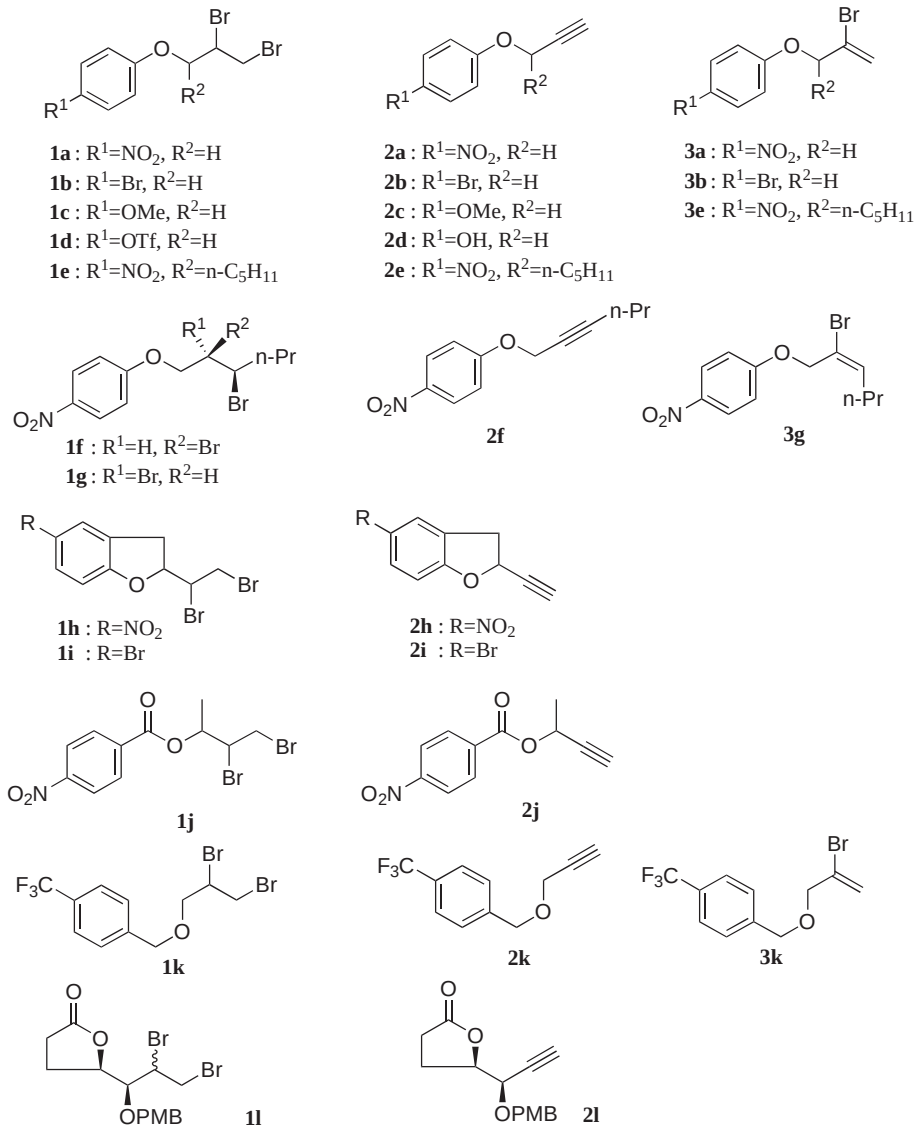
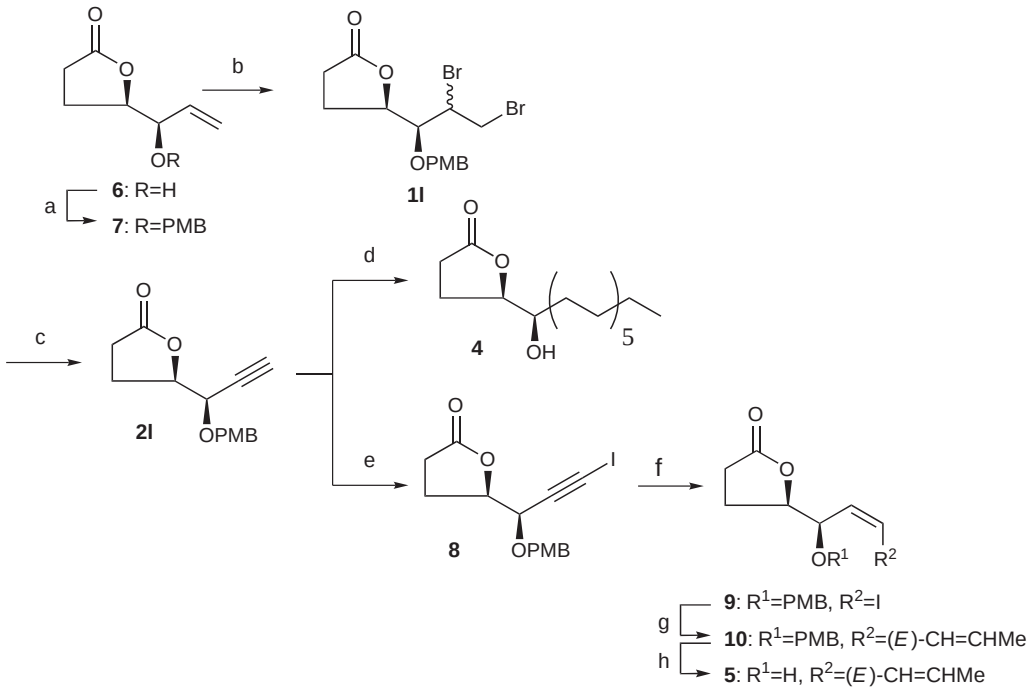


Fig. 1.

Upon using **1a**, which provided the corresponding bromo-olefin **3a** by 2 or 3 molar amounts of DBU, 5 molar amounts of the base provided the alkyne **2a** in 92% yield (Entries 1–3). Dependence of the product yields on the amount of DBU indicated the propargylic ether is produced through the bromo-olefin intermediate. Limitation of NaOPiv as a base was revealed: NaOPiv (7 molar amounts) provided a 1:8 mixture of **2a** and **3a** (Entry 4), while the desired bromo-olefins were produced in high yields by 2 molar amounts of the base.[8a] The ability of NaOPiv to remove the sp^2 protons might be too low to provide the corresponding propargylic ethers. From a comparison of functional groups at the *para*-positions of the aromatic residue, stronger electron-withdrawing property like that of a nitro group, provided the propargylic ethers **2** in higher yields than others (Entries 3, 5, and 6). When a TfO group was used as a functional group on the aromatic residue, propargylic ether **2d** was produced in high yield (Entry 7): removal of the sulfonyl ester might take place after the construction of the triple bond, because the corresponding alkene did not provide **2d** even in the presence of excess DBU. In the presence of an alkyl chain at the C-3 position (**1e**), a decrease of the acidity of protons at C-1 and -2 by an inductive effect of the alkyl chain, caused a relatively low yield of the elimination reaction, and alkene **3e** was obtained. In the case of internal dibromides, *syn*-derivative **1f** afforded **2f** in 95% yield, whereas bromo-olefin **3g** was obtained from the *anti*-derivative **1g** (Entries 9 and 10): these results strongly suggested that this elimination might proceed in a two-step *trans*-elimination manner. In contrast to phenyl substituents, the dihydrobenzofuran residue will be a potent synthetic precursor for several complicated molecules. Similar to the case of **1e** with an alkyl function, the dihydrobenzofuran residue (**1h** and **1i**) afforded the corresponding propargylic ethers in moderate yields (Entries 11 and 12). Introduction of an acyloxy function at the C-3 position (**1j**) provided **2j** in only 29% yield, and no production of the corresponding alkene was monitored. Although the high electron-withdrawing property of the acyl function would be expected to contribute the effective abstraction of protons, the preceding removal of the acyl function interfered with the conversion process to the corresponding propargylic ethers. In the case



Scheme 2. *Reagent and conditions*: a. *p*-methoxybenzyl trichloroacetimidate, $TfOH/Et_2O$ (100%). b. Pyr.-HBr_3/CH_2Cl_2 (100%). c. DBU (5 mol amt.)/DMF, 80 °C (72%). d. i) (*E*)-1-iododec-1-ene, CuI, $PdCl_2(Ph_3P)_2$, Et_3N; ii) H_2, 10% Pd–C, MeOH (97% in 2 steps). e. NIS, $AgNO_3$/acetone (80%). f. NBSH, Et_3N/THF–*i*PrOH (100%). g. $PdCl_2$(dppf), (*E*)-prop-1-enyl(dihydroxyborane), CsF/PhMe (87%). h. DDQ/CH_2Cl_2–H_2O (89%).

of the benzylic substitution, **1k** furnished propargylic ether **2k** in 45% yield, along with the corresponding olefin **3k** in 30% yield, which included a small amount of the 1-bromo isomer. Apparently, insertion of a methylene lowered the electron-withdrawing effect of the aromatic residue. Even in the presence of the γ-lactone moiety (**1l**), the desired elimination reaction proceeded to give **2l** in 72% yield (Entry 15). Different from esters (Entry 13), the lactone ring may be cyclized, even when the ester linkage is cleaved under basic conditions. Therefore, **2l** was obtained in better yield than the case of **1j** carrying the benzoyloxy function.

The relatively facile elimination methodology leading to alkyne derivatives, prompted us to demonstrate its application to natural products synthesis. Along this line, we selected the γ-lactone-class derivatives as the target molecules.

Synthesis of (−)-Muricatacin (4) and (*R*,*R*)-Sapinofuranone B (5). The title compounds might be synthesized by using **2l** as a common intermediate, and the relatively simple structure of (−)-muricatacin (**4**) would be a synthetic model for (*R*,*R*)-sapinofuranone B (**5**). (−)-Muricatacin (**4**) was isolated from seeds of *Annona muricata*, and exhibited cytotoxic activity against certain human tumor cell lines.[10] Total synthesis of this molecule, as well as its analogues, has been reported by several groups.[11] In contrast to other groups, our synthetic strategy using the propargylic ether intermediate, enabled facile derivatization of the alkyl moiety, to contribute to structure–activity relationship studies of biological activity. Indeed, influence of the carbon-chain length of muricatacin on cytotoxicity was studied.[11] A propargylic ether derivative, like **2l**, might be utilized as a common intermediate to provide muricatacin-analogues concerned with the alkyl chain residue.

As mentioned above, intermediate **2l** was produced by the DBU-mediated elimination reaction of **1l**, which can be synthesized from the corresponding olefin derivative **6**[12] by PMB protection and bromination (Scheme 2). The Sonogashira coupling of **2l** with (*E*)-1-iododec-1-ene, followed by hydrogenolysis simultaneously to saturate the triple bond and to remove the protecting group, provided **4**; the optical rotation $[\alpha]_D^{23}$ −21.0 (*c* 0.10, $CHCl_3$) (lit. $[\alpha]_D^{20}$ −16.1,[10] $[\alpha]_D^{23}$ −19.5,[11b] $[\alpha]_D^{20}$ −23.3[11k]) indicated that the synthetic pathway did not affect the continuous stereochemistry.

Based on the muricatacin-synthesis, we attempted a synthesis of (*R*,*R*)-sapinofuranone B (**5**), a phytotoxin isolated from *Saphaeropsis sapinea*.[13] Its enantiomeric substance isolated from *Acremonium strictum* has been synthesized by two groups.[14] Our approach involved conversion of **2l** to the corresponding *cis*-iodovinyl derivative, which was coupled with the appropriate boronic acid under the Suzuki–Miyaura coupling conditions.[15] Thus, **2l** was allowed to react with NIS in the presence of $AgNO_3$ to give iodide **8** in 80% yield, which was reduced under the diimide conditions using NBSH (*o*-nitrophenylsulfonylhydrazide)[16] quantitatively to give the *cis*-iodoolefin **9**. Coupling with (*E*)-1-prop-1-enyl(dihydroxyborane) in the presence of $PdCl_2$(dppf) and CsF successfully furnished the desired product **10** in 87% yield. Finally, deprotection of the PMB group by DDQ provided **5** in 89% yield. Under the full range of spectroscopic data, the synthetic sample was superimposable to the natural (*R*,*R*)-sapinofuranone B (**5**).

In conclusion, despite the heated conditions in the presence of a slight excess DBU, 2,3-dibromoalkoxy derivatives were successfully converted to the corresponding propargylic ethers, through the corresponding alkene intermediates. The effective

elimination reaction required the electron-withdrawing ability of the *O*-functional groups at the C-1 position. Application of this reaction to synthesis of natural molecules, was demonstrated by the synthesis of (−)-muricatacin (**4**) and (*R*,*R*)-sapinofuranone B (**5**). For the relatively simple and reliable procedure, this elimination methodology might be included in reaction candidates applicable to multistep synthesis.

Experimental

General. IR spectra were recorded on a JASCO Model A-202 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on JEOL JNM EX-270 and JEOL JNM GX-400 spectrometers in a deuteriochloroform ($CDCl_3$) solution using tetramethylsilane as an internal standard. High-resolution mass spectra were obtained on a Hitachi M-80 B GC-MS spectrometer operating at the ionization energy of 70 eV or on a JEOL JMS-700 (FAB) spectrometer. Optical rotations were recorded at the sodium D line and at ambient temperatures with a JASCO DIP-360 digital polarimeter. Preparative and analytical TLC were carried out on silica-gel plates (Kieselgel 60 F254, E. Merck AG, Germany) using UV light and/or 5% phosphomolybdic acid in ethanol for detection. Kanto Chemical silica 60N (spherical, neutral, 63–210 μm) was used for column chromatography. Silica-gel column chromatography was used for purification of crude products, unless otherwise stated. DMF (dimethylformamide) dehydrated grade (Kanto Kagaku Ltd.) was used for reactions. Work-up procedure, unless otherwise stated, was performed as follows: a reaction mixture was partitioned between EtOAc or $CHCl_3$ and H_2O. The organic layer was washed with brine, dried (Na_2SO_4), and then evaporated.

General Procedure of the DBU-Mediated Elimination Reaction: 1-Nitro-4-(prop-2-ynyloxy)benzene (2a). To a solution of **1a** (186 mg, 0.5 mmol) in DMF (9.2 mL) was added DBU (381 mg, 2.5 mmol) at 0 °C; the mixture was stirred at 80 °C for 16 h. The reaction mixture was diluted with a 2:1 mixture of hexane and EtOAc, washed with 1 M (1 M = 1 mol L^{-1}) aq HCl, H_2O, and brine. The organic layer was dried (Na_2SO_4), and concentrated in vacuo. A crude product was purified by silica-gel column chromatography to give **2a** (89 mg, 92%). The spectroscopic data was in accordance with commercially available sample.

(5*R*)-5-[(1*R*)-1-(4-Methoxybenzyloxy)prop-2-enyl]-4,5-dihydro-2(3*H*)-furanone (7). To a solution of **6**[12] (506 mg, 3.6 mmol) in Et_2O (25 mL) were added dropwise TfOH (1 μL, 10.7 μmol) and PMBOC(NH)CCl_3 (5.01 g, 18 mmol) over 30 min at 0 °C. After being stirred for 18 h at room temperature and the following work-up, the reaction mixture was chromatographically purified ($CHCl_3$/EtOAc 10/1) to give **7** (934 mg, 100%) as a colorless oil: $[\alpha]_D^{24}$ −50.9 (*c* 1.00, $CHCl_3$); IR (film) 2938, 1776, 1513 cm^{-1}; ^{1}H NMR δ 2.06 (1H, m), 2.18 (1H, m), 2.43 (1H, m), 2.56 (1H, m), 3.81 (3H, s), 3.84 (1H, m), 4.33 (1H, d, J = 11.6 Hz), 4.53 (1H, m), 4.60 (1H, d, J = 11.6 Hz), 5.35–5.42 (2H, m), 5.83 (1H, m), 6.88 (2H, d, J = 8.4 Hz), 7.24 (2H, d, J = 8.4 Hz); ^{13}C NMR δ 23.8, 28.3, 55.3, 70.0, 80.9, 81.4, 113.7(2), 120.4, 129.3(2), 129.7, 133.6, 159.1, 177.2; HRMS m/z 262.1191, calcd. for $C_{15}H_{18}O_4$: M$^+$, 262.1204.

(5*R*)-5-[(1*S*)-2,3-Dibromo-1-(4-methoxybenzyloxy)propyl]-4,5-dihydro-2(3*H*)-furanone (1l). A mixture of **7** (934 mg, 3.6 mmol), pyridine (0.37 mL, 4.6 mmol), and Pyr·HBr_3 (2.28 g, 7.1 mmol) in CH_2Cl_2 (20 mL) was stirred at 0 °C for 12 h. After the addition of sat. aq $Na_2S_2O_3$ and the following work-up, a crude product was chromatographically purified (hexane/EtOAc 5/1) to give **1l** (1.50 g, 100%) as a colorless oil: IR (film) 2937, 1780 cm^{-1}; ^{1}H NMR δ 1.88 (1H, m), 2.34–2.59 (3H, m), 3.72–3.94 (5.7H, m), 4.06 (0.3H, dd, J = 3.9, 11.7 Hz), 4.19 (0.7H, m), 4.43 (0.3H, m), 4.69 (1H, m), 4.81–4.94 (1.7H, m), 5.10 (0.3H, m), 6.90 (2H, d, J = 8.4 Hz), 7.29 (2H, m); ^{13}C NMR δ 24.7, 28.1, 32.5, 50.2, 55.3, 74.2, 78.8, 83.2, 114.0(2), 129.5, 129.9(2), 159.4, 176.1; HRMS m/z 419.9598, calcd. for $C_{15}H_{18}Br_2O_4$: M$^+$, 419.9572.

(5*R*)-5-[(1*R*)-1-(4-Methoxybenzyloxy)prop-2-ynyl]-4,5-dihydro-2(3*H*)-furanone (2l). A mixture of **1l** (9.7 mg, 23 μmol) and DBU (17 μL, 115 μmol) in DMF (1 mL) was stirred at 80 °C for 85 h. After the addition of 2 M aq HCl and the following work-up, a crude product was chromatographically purified (hexane/EtOAc 2/12) to give **2l** (4.3 mg, 72%) as a colorless oil: $[\alpha]_D^{22}$ −112.5 (*c* 1.00, $CHCl_3$); IR (film) 3274, 1774 cm^{-1}; ^{1}H NMR δ 2.24–2.36 (2H, m), 2.44–2.53 (2H, m), 2.65 (1H, m), 3.81 (3H, s), 4.25 (1H, dd, J = 2.8, 4.8 Hz), 4.50 (1H, d, J = 12 Hz), 4.62 (1H, m), 4.78 (1H, d, J = 12 Hz), 6.89 (2H, d, J = 8.8 Hz), 7.28 (2H, d, J = 8.8 Hz); ^{13}C NMR δ 23.7, 28.3, 55.6, 69.9, 70.9, 78.7, 79.8, 100.8, 114.2(2), 129.0, 130.1(2), 159.7, 177.0; HRMS m/z 260.1033, calcd. for $C_{15}H_{16}O_4$: M$^+$, 260.1049.

(−)-Muricatacin (4). To a mixture of (*E*)-1-iododec-1-ene (12 mg, 45 μmol), Et_3N (8 μL, 57 μmol), CuI (0.37 mg, 1.9 μmol), mol), and $PdCl_2(Ph_3P)_2$ (2.0 mg, 3.9 μmol) was added **2l** (10 mg, 38 μmol) in benzene (1.5 mL) were added at 0 °C. After being stirred at room temperature for 19 h and the following work-up, a crude product was chromatographically purified (hexane/EtOAc 2/1) to give a colorless oil. A solution of the product in MeOH (2 mL) in the presence of catalytic 10% Pd–C was stirred for 26 h under a hydrogen atmosphere. After filtration through a Celite pad, the solvent was removed. A crude product was chromatographically purified (hexane/EtOAc 2/1) to give **4** (10.6 mg, 97% in two steps) as colorless plates (hexane–EtOAc): mp 67 °C; $[\alpha]_D^{23}$ −21.0 (*c* 0.10, $CHCl_3$); IR (film) 3445, 2918, 2848, 1741, 1465 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz), 1.20–1.40 (20H, m), 1.53 (2H, m), 1.83 (1H, d, J = 5.9 Hz), 2.07–2.18 (1H, m), 2.21–2.30 (1H, m), 2.57 (1H, dd, J = 17.6, 8.8 Hz), 2.60 (1H, ddd, J = 17.6, 9.8, 4.9 Hz), 3.56 (1H, m), 4.41 (1H, dt, J = 7.3, 4.9 Hz); ^{13}C NMR δ 14.1, 22.7, 24.1, 25.4, 28.7(2), 29.3(2), 29.46, 29.54, 29.61, 29.64, 31.9, 32.9, 73.7, 82.9, 177.1; HRMS m/z 284.2349, calcd. for $C_{17}H_{32}O_3$: M$^+$, 284.2350.

(5*R*)-5-[(1*R*)-1-(4-Methoxybenzyloxy)-3-iodoprop-2-ynyl]-4,5-dihydro-2(3*H*)-furanone (8). A mixture of **2l** (50 mg, 0.19 mmol), NIS (55 mg, 0.23 mmol), and $AgNO_3$ (19.5 mg, 0.115 mmol) in acetone (1 mL) was stirred at 0 °C for 1 h. After work-up, a crude product was chromatographically purified ($CHCl_3$/EtOAc 20/1) to give **8** (59.7 mg, 80%) as a colorless oil: $[\alpha]_D^{24}$ −129.3 (*c* 1.00, $CHCl_3$); IR (film) 1774, 1513 cm^{-1}; ^{1}H NMR δ 2.20–2.35 (2H, m), 2.43–2.66 (2H, m), 3.84 (3H, s), 4.34 (1H, m), 4.48 (1H, m), 4.60 (1H, m), 4.77 (1H, d, J = 11.2 Hz), 6.89 (2H, d, J = 8.4 Hz), 7.24 (2H, m); ^{13}C NMR δ 23.5, 27.9, 55.3, 70.8, 71.0, 79.7, 80.6, 89.4, 113.8(2), 128.6, 129.8(2), 159.4, 176.6; HRMS m/z 387.0118, calcd. for $C_{15}H_{16}IO_4$: M + H, 387.0094.

(5*R*)-5-[(1*R*,2*Z*)-(4-Methoxybenzyloxy)-3-iodoprop-2-enyl]-4,5-dihydro-2(3*H*)-furanone (9). To a solution of **8** (11.2 mg, 29 μmol) in THF–*i*PrOH (1 mL) were added successively NBSH (31.5 mg, 145 μmol) and Et_3N (20 μL, 145 μmol) at 0 °C. After being stirred for 19 h at room temperature and the following work-up, a crude product was chromatographically purified ($CHCl_3$/EtOAc 20/1) to give **9** (11.2 mg, 100%) as a colorless oil: $[\alpha]_D^{21}$ +7.3 (*c* 1.00, $CHCl_3$); IR (film) 2937, 1776, 1513 cm^{-1}; ^{1}H NMR δ 2.03–2.27 (2H, m), 2.42 (1H, m), 2.62 (1H, m), 3.79 (3H, s), 4.13 (1H, m), 4.32 (1H, d, J = 12.0 Hz), 4.57 (2H, m), 6.36

(1H, m), 6.65 (1H, d, $J = 7.6$ Hz), 6.87 (2H, d, $J = 8.4$ Hz), 7.24 (2H, d, $J = 8.4$ Hz); ^{13}C NMR δ 23.7, 28.1, 55.1, 70.3, 80.6, 81.5, 86.6, 113.7(2), 129.2, 129.4(2), 137.7, 159.0, 177.0; HRMS m/z 388.0156, calcd. for $C_{15}H_{17}IO_4$: M^+, 388.0172.

(5*R*)-5-[(1*R*,2*Z*,4*E*)-1-(4-Methoxybenzyloxy)hexa-2,4-dienyl]-4,5-dihydrofuranone (10). To a solution of **9** (18.5 mg, 48 µmol) in PhMe (3 mL) were added successively CsF (14.5 mg, 96 µmol), (*E*)-1-prop-1-enyl(dihydroxyborane) (8.2 mg, 96 µmol) and $PdCl_2$-(dppf) (3.9 mg, 4.8 µmol) at 0 °C. After being stirred at room temperature for 15 h and the following work-up, the reaction mixture was chromatographically purified ($CHCl_3$/EtOAc 10/1) to give **10** (12.5 mg, 87%) as a colorless oil: $[\alpha]_D^{22}$ −48.5 (*c* 1.00, $CHCl_3$); IR (film) 2935, 1776, 1513 cm^{-1}; ^{1}H NMR δ 1.80 (3H, d, $J = 6.8$ Hz), 2.04 (1H, m), 2.19 (1H, m), 2.43 (1H, m), 2.57 (1H, m), 3.81 (3H, s), 4.30 (1H, m), 4.31 (1H, d, $J = 11.2$ Hz), 4.53 (1H, m), 4.59 (1H, d, $J = 11.7$ Hz), 5.26 (1H, m), 5.83 (1H, m), 6.18 (1H, m), 6.31 (1H, t, $J = 11.2$ Hz), 6.87 (2H, m), 7.24 (2H, m); ^{13}C NMR δ 18.4, 24.1, 28.4, 55.3, 69.6, 75.0, 81.8, 113.7(2), 123.1, 126.0, 129.5(2), 129.9, 133.4, 134.7, 159.1, 177.2; HRMS m/z 302.1523, calcd. for $C_{18}H_{22}O_4$: M^+, 302.1517.

(*R*,*R*)-Sapinofuranone B (5). A mixture of **10** (33.7 mg, 0.11 mmol) and DDQ (38.0 mg, 0.17 mmol) in CH_2Cl_2 (2.2 mL)–H_2O (0.2 mL) was stirred at 0 °C for 2.5 h. After work-up, a crude product was chromatographically purified (hexane/EtOAc 2/1) to give **5** (18.1 mg, 89%) as a colorless oil: $[\alpha]_D^{22}$ −12.6 (*c* 0.50, $CHCl_3$) (optical purity: 90% ee); IR: 3421, 1772 cm^{-1}; ^{1}H NMR δ 1.82 (3H, dd, $J = 0.8$, 6.8 Hz), 2.03–2.12 (2H, m), 2.19–2.28 (1H, m), 2.49–2.67 (2H, m), 4.47 (1H, m), 4.58 (1H, m), 5.32 (1H, m), 5.86 (1H, m), 6.20 (1H, t, $J = 11.7$ Hz), 6.36 (1H, m); ^{13}C NMR δ 18.5, 23.8, 28.5, 70.1, 82.8, 123.8, 125.9, 133.88, 133.94, 176.8; HRMS m/z 165.0901, calcd. for $C_{10}H_{13}O_2$: M − OH, 165.09145.

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Supporting Information

Preparation of **1a** and **1c**–**1k**. Spectroscopic data of **2e**, **2f**, **2h**, **2i**, **2k**, **3a**, **3e**, **3g**, and **3k**. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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