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Triethylborane-induced radical reactions with gallium- and indium hydrides

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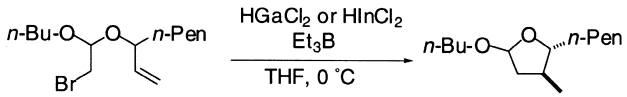
Abstract—A gallium hydride reagent, $HGaCl_2$, was found to act as a radical mediator. Treatment of alkyl halides with the gallium hydride reagent, generated from gallium trichloride and sodium bis(2-methoxyethoxy)aluminum hydride, provided the corresponding reduced products in excellent yields. Radical cyclization of halo acetals was also successful with not only the stoichiometric gallium reagent but also a catalytic amount of gallium trichloride combined with stoichiometric aluminum hydride as a hydride source. An indium hydride reagent, $HInCl_2$, prepared from indium trichloride and diisobutylaluminum hydride also worked as a radical mediator. $HInCl_2$ could reduce aryl iodides and bromides in the presence of Et_3B as a radical initiator.



1. Introduction

Organotin hydrides have played an important role in synthetic radical chemistry because of their excellent reactivity as a radical mediator.[1] However, organotin compounds are toxic[2] and difficult to remove completely from the desired reaction products. Many efforts have been devoted to invent alternatives to organotin reagents.[3,4] Silanes[5] and germanes,[6] group 14 metal hydrides, have been proposed to be alternatives to tributyltin hydride. The phosphorus–hydrogen bond in phosphites, phosphines, and hypophosphorous acid is weak, allowing these reagents to act as hydrogen donor agents and radical chain carriers.[7] Recently, we have reported the $Cp_2Zr(H)Cl$-mediated radical reaction involving homolytic cleavage of the zirconium–hydrogen bond.[8] Here we wish to introduce group 13 metal hydrides, a gallium hydride[9] and an indium hydride[10] reagent, as efficient radical mediators. These reagents show high reactivity and have great ability as an alternative to tin hydride reagents; they display, on the contrary, more ionic reactivity than tin hydride reagents.

2. Results and discussion

2.1. Reduction of alkyl halides with gallium hydride reagent

Gallium trichloride (2.0 mmol) was treated with sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al®, 1.0 mmol) in THF at 0°C for 30 min to prepare dichlorogallane.[11,12] To the mixture, 1-iodododecane (1.0 mmol) and triethylborane (0.20 mmol) as an initiator[13] were sequentially added and the whole mixture was stirred for

Table 1. Radical reduction of alkyl halides

Entry	R–X	Time (h)	Yield (%)
1	1-Iodododecane	4	92
2	1-Bromododecane	5	88[a]
3	1-Bromododecane	5	81[a,b]
4	2-Bromododecane	5	81[b]
5	1-Bromododecane	5	78[a]
6	10-Bromo-1-decanol	5	91[a]
7	*c*-$C_{12}H_{23}$-OC(=S)SMe	6	84
8	3-Bromopropyl benzoate	5	88[a]
9	4-Iodobutyrophenone	9	80
10	1-Bromododecane[c]	9	0[d,e]

Unless otherwise noted, R–X (1.0 mmol), $GaCl_3$ (2.0 mmol), Red-Al® (1.0 mmol), Et_3B (0.20 mmol) and THF (5 mL) were used.
[a] An equimolar amount (1.0 mmol) of Et_3B was employed.
[b] Diisobutylaluminum hydride (2.0 mmol) was used instead of Red-Al®.
[c] Along with an equimolar amount of decanal.
[d] $GaCl_3$ (1.0 mmol), Red-Al® (0.50 mmol), Et_3B (1.0 mmol) were used.
[e] Instead, 1-decanol was obtained in 93% yield.

Keywords: indium hydrides; radical mediator; gallium hydride.

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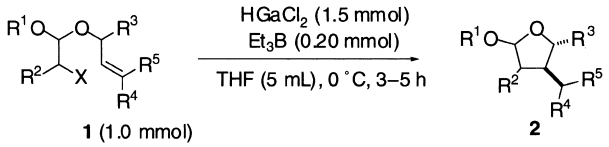
Table 2. Radical cyclization of halo acetals with gallium hydride



Entry	1	X	R^1	R^2	R^3	R^4	R^5	2	Yield (%)[a]
1	**1a**	I	$(CH_2)_3$		H	Me	Me	**2a**	87 (70/30)
2	**1b**	Br	$(CH_2)_3$		H	Me	Me	**2a**	82 (71/29)[b]
3	**1c**	I	$(CH_2)_3$		H	*n*-Pr	H	**2c**	85 (84/16)
4	**1d**	Br	$(CH_2)_3$		H	*n*-Pr	H	**2c**	80 (84/16)[b]
5	**1e**	I	$(CH_2)_3$		*n*-Pen	H	H	**2e**	85 (57/43)
6	**1f**	Br	$(CH_2)_3$		*n*-Pen	H	H	**2e**	80 (56/44)[b]
7	**1g**	I	*n*-Bu	H	H	*n*-Pr	H	**2g**	97 (72/28)
8	**1h**	Br	*n*-Bu	H	H	*n*-Pr	H	**2g**	79 (72/28)[b]
9	**1i**	I	*n*-Bu	H	*n*-Pen	H	H	**2i**	99 (50/50)
10	**1j**	Br	*n*-Bu	H	*n*-Pen	H	H	**2i**	94 (52/48)[b]

[a] Isolated yields. Diastereomer ratios are shown in parentheses.
[b] An equimolar amount (1.0 mmol) of Et_3B was used.

4 h. Dodecane was obtained in 92% yield after aqueous workup and purification. The results of the reduction of various halides were summarized in Table 1.

Alkyl bromides were also reduced to the corresponding hydrocarbons in excellent yields, although a larger amount of triethylborane (1.0 equiv.) was necessary. Without Red-Al® and gallium trichloride, treatment of 1-bromododecane with triethylborane in THF resulted in quantitative recovery of the starting material. A combination of gallium trichloride and 1.0 equiv. of diisobutylaluminum hydride was also effective to form the gallium hydride reagent (entries 3 and 4). Unfortunately, alkyl chlorides and aryl iodides remained almost unchanged. Radical deoxygenation via a dithiocarbonate was successful (entry 7). Interestingly, reduction of a ketone moiety did not take place at all under the reaction conditions (entry 9). When the mixture of an alkyl bromide and an aldehyde was exposed to the reaction conditions, ionic reduction of the aldehyde proceeded exclusively and the alkyl bromide was recovered quantitatively (entry 10). The reaction of a benzylic bromide, 4-bromobenzyl bromide, resulted in recovery of the starting material (89%).[14]

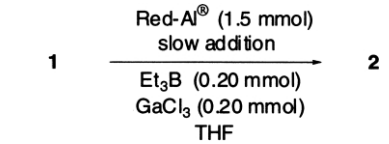
2.2. Radical cyclization with gallium hydride reagent

We turned our attention to the radical cyclization of halo acetals.[15] Substrates shown in Table 2 underwent 5-*exo* reductive cyclization smoothly by the action of the gallium hydride reagent in the presence of triethylborane.

The reaction of **1a** did not proceed in the absence of triethylborane. An addition of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) completely inhibited the reaction. The reaction of halo acetals **1a**, **1c** and **1e** with tributyltin hydride under the similar reaction conditions provided the corresponding products **2a**, **2c** and **2e** in moderate yields with the same diastereoselectivities (**2a**: 60% (69/31), **2c**: 63% (86/14), **2e**: 46% (52/48)) as the reaction with $HGaCl_2$. These results strongly support a radical mechanism for the present reaction. The reaction proceeded less efficiently with chlorogallane (H_2GaCl), which was prepared by mixing $GaCl_3$ and Red-Al® in 1/1 ratio. For example, the reaction of **1g** provided **2g** in 74% yield. Furthermore, treatment of **1f** with H_2GaCl (1.5 mmol) afforded a complex mixture. Red-Al® itself worked far less efficiently compared with $HGaCl_2$. Treatment of **1c** and **1e** with Red-Al® in the presence of triethylborane provided **2c** and **2e** in 23% and <1% yields, respectively. The starting materials **1c** (57%) and **1e** (74%) were recovered.

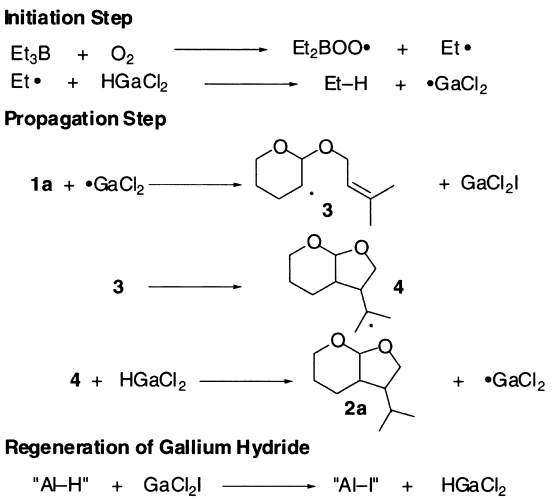
Gallium trichloride is not inexpensive. Therefore, it is of importance to reduce the amount of $GaCl_3$ employed for the reaction. Thus, the catalytic reaction was examined. The cyclization of **1a** was performed with a slow addition (2 h) of Red-Al® (1.5 mmol) to a solution of **1a** (1.0 mmol), $GaCl_3$ (0.20 mmol) and Et_3B (0.20 mmol) in THF. The mixture was stirred for an additional 1 h to yield **2a** in 79% yield (Table 3, entry 1). The slow addition was essential for the success of the catalytic reaction. Treatment of $GaCl_3$ with excess Red-Al® at one time resulted in poor conversion (**2a**, 10%; **1a**, 65% recovered). In this case, the reaction would afford gallane (GaH_3), which would be unstable

Table 3. Radical cyclization of halo acetals with a catalytic amount of gallium trichloride



Entry	Halo acetal	Time (h)[a]	Product	Yield (%)[b]
1	**1a**	2+1	**2a**	79 (70/30)
2[c]	**1a**	2+1	**2a**	36 (68/32)[d]
3	**1c**	2+8	**2c**	64 (88/12)
4	**1e**	2+4	**2e**	95 (59/41)
5[e]	**1b**	2+4	**2a**	6 (69/31)[f]

[a] Red-Al® was added slowly over 2 h and the resulting mixture was stirred additionally for the indicated time.
[b] Isolated yields. Diastereomer ratios are shown in parentheses.
[c] The reaction was performed with 0.10 mmol of $GaCl_3$.
[d] The starting material **1a** was recovered in 40%.
[e] The reaction was carried out with 1.0 mmol of Et_3B.
[f] The starting material **1b** was recovered in 74%.



Scheme 1.

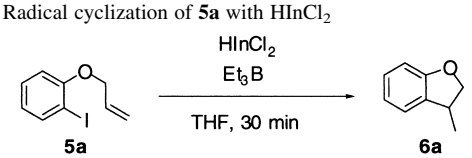
under these reaction conditions.[11c] The fewer amount of $GaCl_3$ was used, the lower yield was obtained (entry 2). This procedure could not be applied to cyclization of a bromo acetal (entry 5).

We assume the catalytic mechanism as shown in Scheme 1, in analogy with the reaction with tributyltin hydride. An ethyl radical, generated from Et_3B by the action of a trace amount of oxygen, abstracts hydrogen homolytically from $HGaCl_2$ to give gallium radical $\bullet GaCl_2$.[16] Halogen abstraction by $\bullet GaCl_2$ from a substrate, **1a** for example, affords $GaCl_2I$ and radical **3**. Ring closure followed by hydride donation from $HGaCl_2$ to the radical **4** provides the product **2a** and regenerates $\bullet GaCl_2$. $GaCl_2I$, formed in the propagation step, is transformed into $HGaCl_2$ with aluminum hydride, and the gallium hydride works again as a hydride source for the carbon-centered radical.

2.3. Radical cyclization with indium hydride reagent

A hexane solution of diisobutylaluminum hydride (DIBAL-H) was added to a THF solution of indium trichloride (1.15 mmol) at 0°C and stirred for 30 min to prepare dichloroindane ($HInCl_2$).[10c,d,g] To a solution of $HInCl_2$ were added **5a** and triethylborane (1.0 M hexane solution, 0.10 mL, 0.10 mmol) as a radical initiator. Stirring for 30 min followed by acidic workup provided reductive 5-*exo*

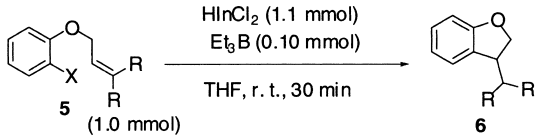
Table 4. Radical cyclization of **5a** with $HInCl_2$



Entry	$HInCl_2$ (equiv.)	Et_3B (equiv.)	Temperature	Yield (%)[a]
1	1.1	0.10	0°C	87
2	1.1	0.10	rt	93 (98)
3	1.2	0.10	rt	(97)
4	1.2	None	0°C	(83)
5	1.2	0.20	0°C	(98)

The substrate **5a** (1.0 mmol) and THF (10 mL) were used.
[a] NMR yields, calculated from integrations of proper protons and an internal standard (Bn_2O), are in parentheses.

Table 5. Radical cyclization of haloaryl ethers



Entry	5	X	R	6	Yield (%)[a]
1	**5b**	I	Me	**6b**	92
2	**5c**	Br	Me	**6b**	71[b]
3	**5d**	Cl	H	**6a**	0[c]

[a] Isolated yields.
[b] Starting material was recovered in 17% yield.
[c] Starting material was completely recovered.

cyclization product **6a** in 87% yield (Table 4, entry 1).[17] The reaction proceeded more smoothly at room temperature (entry 2). For completion of the reaction, 1.1 equiv. of $HInCl_2$ was sufficient (entries 2 and 3). Although spontaneous cleavage of indium–hydrogen bond has been reported, the reaction without triethylborane resulted in a lower yield (entry 4).

We tried to apply this reaction conditions to cyclization of other haloaryl ethers. These results were shown in Table 5. Interestingly, bromoaryl ether **5c** afforded the cyclized product **6c** in moderate yield (entry 2). Unfortunately, the reaction of chloroaryl ether **5d** provided none of the cyclized product and the starting material was recovered (entry 3).

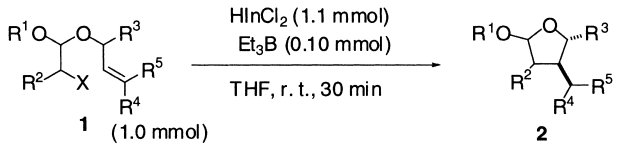
We next attempted to carry out the cyclization reaction of halo acetals[18] by using dichloroindane and triethylborane. Cyclization of various halo acetals is achieved without any further optimization. These results were listed in Table 6. Reactions of iodo acetals **1c** and **1i** provided cyclized products **2c** and **2i**, respectively, in good yields (entries 1 and 2). Moreover, bromo acetals **1b**, **1g** and **1k** could be employed in this reaction (entries 3–5). The cyclization reaction with chloro acetal **1l**, however, did not proceed under the same reaction conditions and the starting material **1l** was recovered (entry 6).

The use of alkynyl acetal **7** as a substrate yielded the ring closing product **8** as a mixture of *E*/*Z* isomers (Scheme 2).

In terms of costs and atom economy, it is naturally desirable to reduce the amount of $InCl_3$ employed. Unfortunately, monochloroindane (H_2InCl) and indane (H_3In)[19] could not endure the reaction conditions and were decomposed immediately. Our next trial was to conduct the reaction with a catalytic amount of $InCl_3$. A hexane solution of DIBAL-H (1.1 mmol) was dropped at a slow speed (1 h) to a mixture of $InCl_3$ (0.20 mmol), **1i** (1.0 mmol) and Et_3B (0.20 mmol) in THF at room temperature. After additional stirring for 1 h, **2i** was obtained in 72% yield (Table 7, entry 1). Slow dropping of DIBAL-H was required to achieve a sufficient yield. This catalytic process could also be applied to cyclization of aryl halides such as **5b** (entry 2). More than 0.1 equiv. of $InCl_3$ was necessary for complete consumption of the starting material.

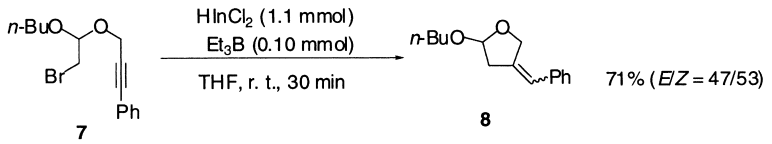
We suppose that the reaction proceeds in a catalytic

Table 6. Radical cyclization of halo acetals



Entry	1	X	R^1	R^2	R^3	R^4	R^5	2	Yield (%)[a]
1	**1c**	I	$(CH_2)_3$		H	*n*-Pr	H	**2c**	70 (84/16)
2	**1i**	I	*n*-Bu	H	*n*-Pen	H	H	**2i**	92 (86/14)
3	**1b**	Br	$(CH_2)_3$		H	Me	Me	**2a**	66 (70/30)
4	**1g**	Br	*n*-Bu	H	H	*n*-Pr	H	**2g**	84 (83/17)
5	**1k**	Br	*n*-Bu	H	Ph	H	H	**2k**	65 (55/45)
6	**1l**	Cl	*n*-Bu	H	H	*n*-Pr	H	**2l**	0

[a] Isolated yields. Diastereomer ratios are shown in parentheses.



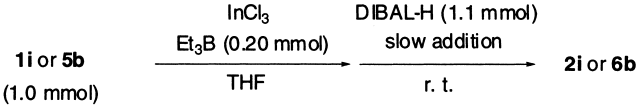
Scheme 2.

mechanism outlined in Scheme 3. An ethyl radical, generated from Et_3B and a trace amount of O_2, reacts with $HInCl_2$ to provide an indium radical ($\bullet InCl_2$). The indium radical abstracts iodine to give $InCl_2I$ and radical **9**, which then cyclizes to radical **10**. Hydride abstraction from $HInCl_2$ by radical **10** provides **2c** and regenerates the indium radical. $HInCl_2$ is regenerated through transmetalation of $InCl_2I$ and DIBAL-H, and then acts again as the hydride source.

2.4. Chemoselective reduction with indium hydride reagent

We tried to investigate the chemoselectivity of the indium hydride reagent (Table 8). When alkyl bromides, which have ester or ketone linkages, were treated with $HInCl_2$, reduction of alkyl bromide moieties proceeded exclusively (entries 1 and 2). On the other hand, ionic reduction of an aldehyde underwent prior to radical reduction of an alkyl bromide (entry 3).

Table 7. Radical cyclization with a catalytic amount of indium trichloride

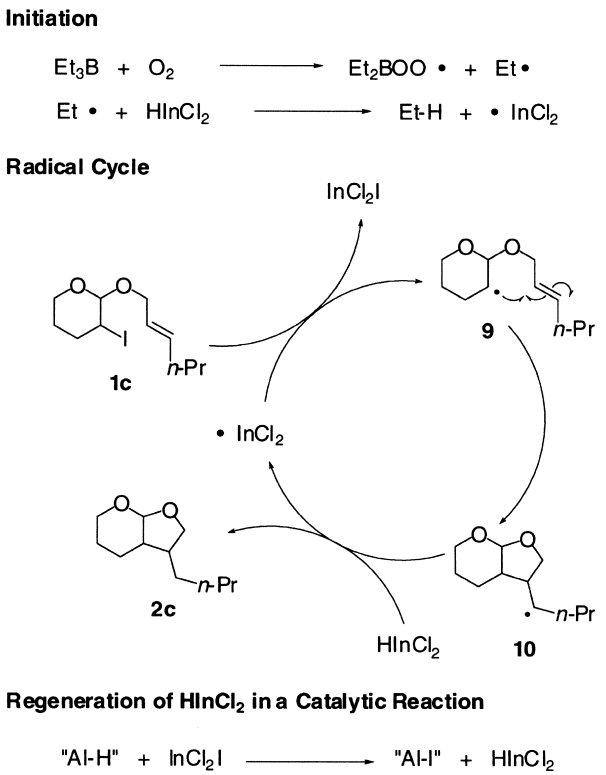


Entry	Substrate	$InCl_3$ (mmol)	Time (h)[a]	Product	Yield (%)[b]
1	**1i**	0.20	1+1	**2i**	72 (57/43)[c]
2	**5b**	0.20	1+1	**6b**	67
3	**5b**	0.15	1+1	**6b**	74
4	**5b**	0.10	1+1	**6b**	64[d]
5	**5b**	0.05	1+3	**6b**	17[e]

[a] DIBAL-H was added slowly over 1 h and the resulting mixture was stirred additionally for the indicated time.
[b] After purification by column chromatography.
[c] Diastereomer ratio is shown in parentheses.
[d] The starting material **5b** was recovered in 8%.
[e] The starting material **5b** was recovered in 57%.

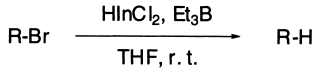
3. Conclusion

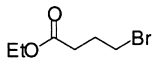
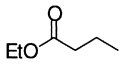
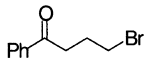
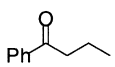
We have disclosed that dichlorogallium hydride and dichloroindium hydride can be used as radical mediators in a radical cyclization reaction. These reagents can be prepared in ease and work effectively under mild conditions. The success of these reactions shows novel reactivities of gallium and indium hydride reagents.



Scheme 3.

Table 8. Chemoselectivity of indium hydride



Entry	Substrate	$HInCl_2$ (mmol)	Product	Yield (%)[a]
1		1.3		99[b]
2		1.0		78
3	n-$C_{12}H_{25}Br$+n-$C_9H_{19}CHO$	1.0	n-$C_{12}H_{25}Br$+n-$C_{10}H_{21}OH$	quant., 88

An alkyl bromide (1.0 mmol) and Et_3B (0.10 mmol) were used, unless otherwise noted.
[a] After purification by column chromatography.
[b] NMR yield, calculated from intergration of proper protons and an inernal standard (Bn_2O).

4. Instrumentation and materials

^{1}NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Gallium trichloride and triethylborane were purchased from Aldrich Chemicals and were diluted to prepare a 1.0 M hexane solution to handle easily. Anhydrous indium trichloride was obtained from Aldrich and was used after removal of water (vide infra). Red-Al® (70 wt% in toluene) was purchased from Nacalai Tesque Inc., and was diluted with toluene to prepare a 2.0 M solution. Diisobutylaluminum hydride was obtained from Aldrich and was used as a 1.0 M hexane solution. These solutions were stored under argon. Halo acetals were prepared according to the literature (Ref. 15).

5. Experimental

The reaction was performed in a reaction flask equipped with a toy balloon that was filled with argon unless otherwise noted. Oxygen, which is necessary to produce an ethyl radical from triethylborane, penetrates the balloon easily. Any further addition of oxygen is not necessary.

5.1. Procedure for reduction of alkyl halides with gallium hydride reagent

Gallium trichloride in hexane (1.0 M solution prepared in advance, 2.0 mL, 2.0 mmol) was placed in a reaction flask under argon and was diluted with 3 mL of THF. Sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al®, 2.0 M toluene solution, 0.50 mL, 1.0 mmol) was then added to the solution at 0°C and the resulting mixture was stirred for 30 min. 1-Iodododecane (296 mg, 1.0 mmol in 2 mL of THF) and triethylborane (1.0 M hexane solution, 0.10 mL, 0.10 mmol) were sequentially added. After being stirred for 4 h at 0°C, the reaction was quenched with 1.0 M hydrochloric acid (20 mL), and the mixture was extracted with hexane (20 mL×3). Combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. Silica gel column purification afforded 156 mg of dodecane in 92% yield. Reduction of bromides was performed with 1.0 mmol of triethylborane.

5.2. Typical procedure for cyclization of halo acetals with gallium hydride

Halo acetal **1a** (296 mg, 1.0 mmol) in 2 mL of THF was added to a solution of the gallium hydride (1.5 mmol) prepared as above, and triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) was added. After being stirred for 5 h at 0°C, the mixture was poured into 1.0 M HCl (20 mL) and was stirred for 15 min. Extraction with hexane/ethyl acetate (10/1=v/v%, 20 mL×3) followed by silica gel column purification afforded **2a** (146 mg) in 86% yield. Diastereomer ratio was determined by the ^{1}H NMR experiment of the product, judging from the integrations of the proper protons.

5.3. Radical cyclization with a catalytic amount of $GaCl_3$

A mixture of gallium trichloride (1.0 M hexane solution, 0.20 mL, 0.20 mmol), **1a** (296 mg, 1.0 mmol), and triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) in THF (5 mL) was placed in a reaction flask. Red-Al® (0.75 mL, 1.5 mmol) was added to the reaction mixture over 2 h with a syringe pump at 0°C. After the slow addition was completed, the whole mixture was stirred for 1 h. Quenching the reaction with hydrochloric acid followed by extraction with hexane/ethyl acetate (10/1=v/v%, 20 mL×3), concentration, and silica gel column purification yielded 134 mg of **2a** (0.79 mmol, 79%) as a colorless oil.

5.4. Typical procedure for triethylborane-induced radical cyclization with indium hydride

Anhydrous indium trichloride (226 mg, 1.2 mmol) was placed in a reaction flask and was heated in vacuo for 2 min. THF (20 mL) was added at room temperature. Cooling the resulting clear solution to −78°C gave a white suspension.

To the suspension, diisobutylaluminum hydride (1.0 M hexane solution, 1.1 mL, 1.1 mmol) was added dropwise, and the mixture was stirred for 30 min at the same temperature. After an addition of **5a** (260 mg, 1.0 mmol in 1.0 mL of THF) and triethylborane (1.0 M THF solution, 0.10 mL, 0.10 mmol), the whole mixture was stirred for 30 min. The reaction was quenched with 1.0 M hydrochloric acid (10 mL). The crude mixture was extracted with hexane/ethyl acetate (10/1=v/v%, 10 mL×3) and the organic layers were dried with anhydrous sodium sulfate. Silica gel column purification afforded **6a** (125 mg, 0.93 mmol, 93%). The diastereomeric ratio of the product was determined with ^{1}H NMR experiment.

5.5. Procedure for radical cyclization with a catalytic amount of indium trichloride

Indium trichloride (44 mg, 0.20 mmol) was dried as above and was dissolved with THF (20 mL) at 25°C. Then, **1i** (354 mg, 1.0 mmol in 1.0 mL of THF) and triethylborane (1.0 M hexane solution, 0.20 mL, 0.20 mmol) were sequentially added. To the mixture, a hexane solution of DIBAL-H (0.10 M, 11 mL, 1.1 mmol) was added over 1 h with a syringe pump and the resulting mixture was stirred for additional 1 h. Quenching with 1.0 M hydrochloric acid (10 mL) and extraction with hexane/ethyl acetate (10/1=v/v%, 10 mL×3) followed by silica gel column chromatography afforded 165 mg of **2i** (57/43 isomeric mixture) in 72% yield.

5.6. Procedure for reduction of alkyl bromides with indium hydride

$HInCl_2$ (1.0 mmol) was prepared in THF (5 mL) as described above. At ambient temperature, 4-bromobutyrophenone (225 mg, 1.0 mmol) and triethylborane (1.0 M hexane solution, 0.10 mL, 0.10 mmol) were added. After being stirred for 1 h, the reaction mixture was quenched with 1.0 M HCl. Extraction with hexane/ethyl acetate (10/1) followed by silica gel column purification afforded butyrophenone (116 mg, 0.78 mmol).

5.7. Characterization data

5.7.1. 3-Bromo-2-(3-methyl-2-propenyloxy)tetrahydropyran (1b). IR (neat) 2930, 2855, 1676, 1441, 1204, 1130, 1072, 1022, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.49–1.60 (m, 1H), 1.69 (s, 3H), 1.76 (s, 3H), 1.88–2.00 (m, 2H), 2.35–2.46 (m, 1H), 3.55–3.62 (m, 1H), 3.90–4.02 (m, 2H), 4.06 (dd, J=7.2, 11.7 Hz, 1H), 4.23 (dd, J=6.6, 11.7 Hz, 1H), 4.64 (d, J=4.5 Hz, 1H), 5.36 (t, J=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.10, 23.40, 25.92, 30.19, 49.64, 62.48, 64.36, 99.90, 119.97, 138.02. Found: C, 48.23; H, 6.64%. Calcd for $C_{10}H_{17}BrO_2$: C, 48.21; H, 6.88%.

5.7.2. 2-[(*E*)-2-Hexenyloxy]-3-iodotetrahydropyran (1c). IR (neat) 2927, 2872, 1464, 1437, 1202, 1123, 1069, 1022, 866, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J=7.2 Hz, 3H), 1.42 (quint., J=7.5 Hz, 2H), 1.51–1.66 (m, 1H), 1.72–1.84 (m, 1H), 1.96–2.09 (m, 3H), 2.33–2.44 (m, 1H), 3.54–3.62 (m, 1H), 4.00 (dd, J=6.9, 11.7 Hz, 2H), 4.11 (dt, J=9.0, 4.5 Hz, 1H), 4.21 (dd, J=5.7, 11.7 Hz, 1H), 4.68 (d, J=5.1 Hz, 1H), 5.56 (dt, J=15.3, 6.6 Hz, 1H), 5.73 (dt, J=15.3, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.71, 22.13, 25.47, 29.46, 32.64, 34.28, 63.26, 68.73, 101.01, 125.29, 135.00. Found: C, 42.76; H, 6.27%. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; H, 6.17%.

5.7.3. 2-Bromoethanal butyl (*E*)-2-hexenyl acetal (1g). IR (neat) 2959, 2874, 1722, 1458, 1379, 1350, 1117, 1043, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=7.5 Hz, 3H), 0.93 (t, J=7.5 Hz, 3H), 1.66–1.47 (m, 2H), 1.53–1.63 (m, 2H), 1.59 (quint., J=7.5 Hz, 2H), 2.03 (dt, J=6.9, 7.5 Hz, 2H), 3.38 (d, J=5.4 Hz, 2H), 3.50 (dt, J=9.0, 6.6 Hz, 1H), 3.62 (dt, J=9.0, 6.6 Hz, 1H), 4.04 (dd, J=6.0, 11.7 Hz, 1H), 4.11 (dd, J=6.0, 11.7 Hz, 1H), 4.70 (t, J=5.4 Hz, 1H), 5.55 (dt, J=15.3, 6.0 Hz, 1H), 5.73 (dt, J=15.3, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.72, 13.87, 19.31, 22.19, 31.77 (2C), 34.34, 66.39, 67.52, 100.62, 125.50, 135.00. Found: C, 51.60; H, 8.04%. Calcd for $C_{12}H_{23}BrO_2$: C, 51.62; H, 8.30%.

5.7.4. 2-Iodoethanal butyl 1-vinylhexyl acetal (1i, 50/50 mixture of diastereomers). IR (neat) 2932, 1458, 1416, 1107, 1022, 926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83–1.02 (m, 6H), 1.21–1.72 (m, 12H), 3.16–3.31 (m, 2H), 3.36–3.66 (m, 2H), 3.86 (q, J=6.9 Hz, 0.50H), 3.99 (q, J=6.9 Hz, 0.50H), 4.61 (dt, J=8.7, 5.1 Hz, 1H), 5.12–5.28 (m, 2H), 5.61–5.84 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 6.18 (0.50C), 6.44 (0.50C), 13.94 (0.50C), 14.10 (0.50C), 19.31 (0.50C), 19.41 (0.50C), 22.61, 24.85 (0.50C), 24.95 (0.50C), 31.59 (0.50C), 31.72, 31.87 (0.50C), 35.28 (0.50C), 35.44 (0.50C), 65.03 (0.50C), 66.59 (0.50C), 78.51 (0.50C), 79.20 (0.50C), 99.00 (0.50C), 100.74 (0.50C), 116.26 (0.50C), 117.55 (0.50C), 138.41 (0.50C), 139.17 (0.50C). Found: C, 47.39; H, 7.82%. Calcd for $C_{14}H_{27}IO_2$: C, 47.46; H, 7.68%.

5.7.5. 2-Bromoethanal butyl 1-phenyl-2-propenyl acetal (1k, 50/50 mixture of diastereomers). IR (neat) 2959, 2874, 1603, 1454, 1421, 1115, 1026, 930, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=7.5 Hz, 1.50H), 0.93 (t, J=7.5 Hz, 1.50H), 1.24–1.47 (m, 2H), 1.47–1.64 (m, 2H), 3.31–3.47 (m, 2H), 3.48–3.58 (m, 2H), 4.64 (t, J=5.4 Hz, 0.50H), 4.88 (t, J=5.4 Hz, 0.50H), 5.07–5.39 (m, 3H), 5.86–6.08 (m, 1H), 7.28–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.91, 13.95, 19.30, 19.36, 31.73, 31.81, 31.97, 32.11, 65.76, 65.93, 79.22, 79.45, 99.22, 99.45, 115.80, 117.30, 126.59, 127.14, 127.60, 127.86, 128.28, 128.41, 137.79, 138.54, 139.76, 140.55. Found: C, 57.30; H, 6.71%. Calcd for $C_{15}H_{21}BrO_2$: C, 57.52; H, 6.76%.

5.7.6. 7-Isopropyl-2,9-dioxabicyclo[4.3.0]nonane (2a, 70/30 mixture of diastereomers). *Faster moving band*, R_f=0.53 *(hexane/ethyl acetate=3/1)*. IR (neat) 2936, 1467, 1402, 1253, 1142, 1114, 1087, 1031, 1000, 950, 898 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78 (d, J=6.6 Hz, 3H), 0.91 (d, J=6.6 Hz, 3H), 1.27–1.43 (m, 1H), 1.50–1.74 (m, 4H), 1.85–1.95 (m, 2H), 3.64–3.79 (m, 3H), 3.92 (dd, J=7.8, 7.8 Hz, 1H), 5.27 (d, J=3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.74, 20.88, 21.65, 23.21, 26.22, 35.67, 48.90, 60.70, 68.99, 102.11. Found: C, 70.40; H, 10.86%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

Slower moving band, R_f=0.47 *(hexane/ethyl acetate=3/1)*. IR (neat) 3510, 2876, 1468, 1387, 1369, 1221, 1149, 1115,

1089, 1061, 1029, 949, 894, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (d, J=6.6 Hz, 3H), 0.93 (d, J=6.9 Hz, 3H), 1.29–1.39 (m, 1H), 1.58–1.75 (m, 2H), 1.75–1.92 (m, 3H), 2.08 (dddd, J=7.2, 8.1, 8.1, 8.7 Hz, 1H), 3.41 (ddd, J=2.4, 11.4, 11.4 Hz, 1H), 3.66 (dd, J=8.1, 8.4 Hz, 1H), 3.86 (ddd, J=3.3, 3.9, 11.4 Hz, 1H), 4.16 (dd, J=8.4, 8.7 Hz, 1H), 4.97 (d, J=3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.37, 20.65, 21.36, 23.43, 29.98, 41.27, 44.31, 64.26, 71.03, 102.50. Found: C, 70.32; H, 10.39%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

5.7.7. 7-Butyl-2,9-dioxabicyclo[4.3.0]nonane (2c, 83/17 mixture of diastereomers). IR (neat) 2928, 2860, 1468, 1252, 1146, 1022 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.9 Hz, 3H), 1.13–1.47 (m, 7H), 1.53–1.76 (m, 3H), 1.80–2.00 (m, 1H), 2.24–2.39 (m, 1H), 3.42 (ddd, J=11.4, 11.4, 1.8 Hz, 0.17H), 3.54 (dd, J=8.4, 8.4 Hz, 0.17H), 3.60–3.69 (m, 1.66H), 3.70–3.80 (m, 0.83H), 3.84–3.93 (m, 0.17H), 3.95 (dd, J=8.1, 8.1 Hz, 0.83H), 4.28 (dd, J=8.4, 8.4 Hz, 0.17H), 5.00 (d, J=3.3 Hz, 0.17H), 5.29 (d, J=3.6 Hz, 0.83H); ^{13}C NMR ($CDCl_3$) for major isomer: δ 14.05, 19.24, 22.91, 23.29, 26.71, 30.49, 36.51, 41.01, 60.92, 70.11, 101.94. For minor isomer: δ 20.79, 22.47, 22.96, 30.49, 30.77, 32.45, 37.83, 44.15, 64.45, 74.26, 102.07. Found: C, 71.43; H, 10.65%. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%.

5.7.8. 7-Methyl-2,9-dioxa-8-pentylbicyclo[4.3.0]nonane (2e, 56/44 mixture of diastereomers). *Faster moving band*, R_f=0.56 *(hexane/ethyl acetate=5/1)*. IR (neat) 3440, 2928, 2870, 1648, 1459, 1402, 1380, 1251, 1146, 1114, 1073, 994, 965, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J=6.9 Hz, 3H), 0.93 (d, J=6.6 Hz, 3H), 1.18–1.70 (m, 12H), 1.86–2.02 (m, 2H), 3.59 (ddt, J=3.6, 11.1, 1.5 Hz, 1H), 3.68–3.79 (m, 2H), 5.25 (d, J=3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.48, 13.90, 20.06, 22.49, 23.16, 25.84, 31.94, 35.02, 39.02, 40.70, 61.00, 82.70, 100.90. Found: C, 73.33; H, 11.58%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

Slower moving band, R_f=0.47 *(hexane/ethyl acetate=5/1)*. IR (neat) 3500, 2926, 1458, 1377, 1340, 1221, 1156, 1128, 1097, 1043, 980, 943, 900, 864, 810, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J=6.6 Hz, 3H), 0.97 (d, J=6.3 Hz, 3H), 1.21–1.40 (m, 6H), 1.46–1.73 (m, 5H), 1.74–1.83 (m, 2H), 1.92 (ddq, J=8.1, 11.9, 6.3 Hz, 1H), 3.36 (ddd, J=2.1, 11.7, 11.7 Hz, 1H), 3.54 (dt, J=8.9, 6.0 Hz, 1H), 3.85 (ddd, J=2.1, 2.1, 11.7 Hz, 1H), 4.92 (d, J=3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 15.11, 20.59, 21.72, 22.52, 26.13, 31.83, 36.09, 37.58, 46.21, 64.45, 87.84, 101.52. Found: C, 73.68; H, 11.35%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

5.7.9. 2-Butoxy-4-butyltetrahydrofuran (2g, 83/17 mixture of diastereomers). IR (neat) 2930, 2862, 1466, 1346, 1097, 1032 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=7.2 Hz, 1.02H), 0.92 (t, J=7.2 Hz, 4.98H), 1.19–1.62 (m, 11H), 1.99–2.09 (m, 0.17H), 2.10–2.30 (m, 1.66H), 2.31–2.45 (m, 0.17H), 3.31–3.40 (m, 0.17H), 3.36 (dt, J=6.6, 9.3 Hz, 0.83H), 3.45 (dd, J=8.1, 8.1 Hz, 1H), 3.52–3.62 (m, 0.17H), 3.67 (dt, J=6.6, 9.3 Hz, 0.83H), 3.93 (dd, J=8.1, 8.1 Hz, 0.83H), 4.04 (dd, J=8.1, 8.1 Hz, 0.17H), 5.06–5.13 (m, 1H); ^{13}C NMR ($CDCl_3$) for major isomer: δ 13.90, 14.05, 19.43, 22.82, 30.91, 31.88, 32.79, 38.62, 39.11, 67.33, 71.76, 104.38. For minor isomer: δ 13.90, 14.05, 19.43, 22.82, 30.69, 31.88, 33.74, 37.00, 39.32, 66.86, 72.48, 103.99. Found: C, 71.69; H, 12.30%. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08%.

5.7.10. 2-Butoxy-4-methyl-5-pentyltetrahydrofuran (2i, 50/50 mixture of diastereomers). IR (neat) 2932, 2862, 1460, 1379, 1344, 1097, 995, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.0 Hz, 3H), 0.92 (t, J=7.2 Hz, 3H), 1.02 (d, J=6.0 Hz, 1.50H), 1.04 (d, J=6.6 Hz, 1.50H), 1.22–1.62 (m, 13H), 1.74 (dtq, J=6.6, 8.1, 9.2 Hz, 0.50H), 2.05 (dd, J=6.6, 11.7 Hz, 0.50H), 2.00–2.18 (m, 0.50H), 2.32 (ddd, J=5.7, 9.2, 13.2 Hz, 0.50H), 3.33 (dt, J=6.5, 9.3 Hz, 0.50H), 3.38 (dt, J=6.6, 9.6 Hz, 0.50H), 3.46–3.56 (m, 1H), 3.68 (dt, J=6.9, 9.3 Hz, 0.50H), 3.69 (dt, J=6.8, 9.6 Hz, 0.50H), 5.00 (d, J=5.1 Hz, 0.50H), 5.07 (dd, J=3.0, 5.7 Hz, 0.50H); ^{13}C NMR ($CDCl_3$) δ 13.75, 13.93, 13.97, 17.09, 17.17, 19.27, 19.33, 22.53, 25.95, 25.99, 31.77, 31.82, 31.90, 31.95, 33.68, 35.84, 36.81, 38.16, 41.31, 41.88, 66.57, 67.26, 83.91, 86.90, 103.24, 103.40. Found: C, 73.40; H, 12.30%. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36%.

5.7.11. 5-Butoxy-3-methyl-2-phenyltetrahydrofuran (2k). *Faster moving band*, R_f=0.43 *(hexane/ethyl acetate=10/1)*. IR (neat) 2959, 2872, 1605, 1454, 1377, 1097, 1015, 754, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J=7.5 Hz, 3H), 1.06 (d, J=6.6 Hz, 3H), 1.31–1.44 (m, 2H), 1.53–1.69 (m, 3H), 1.97–2.09 (m, 1H), 2.51 (ddd, J=5.7, 9.0, 15.0 Hz, 1H), 3.43 (dt, J=9.6, 6.6 Hz, 1H), 3.77 (dt, J=9.6, 6.9 Hz, 1H), 4.49 (d, J=9.3 Hz, 1H), 5.31 (dd, J=3.6, 5.7 Hz, 1H), 7.26–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.01, 16.27, 19.47, 31.93, 41.61, 42.16, 67.80, 85.92, 103.87, 126.41, 127.61, 128.25, 140.60. Found: C, 76.97; H, 9.32%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.

Slower moving band, R_f=0.36 *(hexane/ethyl acetate=10/1)*. IR (neat) 2959, 2872, 1605, 1456, 1379, 1090, 1005, 752, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, J=7.5 Hz, 3H), 1.03 (d, J=6.3 Hz, 3H), 1.37–1.51 (m, 2H), 1.64 (quint., J=7.5 Hz, 2H), 1.78 (dt, J=5.2, 12.3 Hz, 1H), 2.18 (dd, J=6.3, 12.3 Hz, 1H), 2.29–2.42 (m, 1H), 3.44 (dt, J=9.3, 6.6 Hz, 1H), 3.87 (dt, J=9.6, 6.6 Hz, 1H), 4.41 (d, J=9.3 Hz, 1H), 5.16 (d, J=5.2 Hz, 1H), 7.26–7.46 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.08, 15.66, 19.59, 31.97, 40.90, 42.24, 67.33, 89.46, 103.59, 126.75, 127.41, 128.14, 142.01. Found: C, 77.00; H, 9.30%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.

5.7.12. 2-(2-Propenoxy)iodobenzene (5a). IR (neat) 3069, 2939, 1649, 1582, 1472, 1439, 1275, 1248, 1018, 930, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.61 (d, J=4.5 Hz, 2H), 5.32 (dd, J=1.5, 10.8 Hz, 1H), 5.53 (dd, J=1.5, 17.4 Hz, 1H), 6.01–6.13 (m, 1H), 6.72 (t, J=7.5 Hz, 1H), 6.81 (d, J=7.5 Hz, 1H), 7.28 (t, J=7.5 Hz, 1H), 7.78 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 69.50, 86.55, 112.29, 117.42, 122.47, 129.19, 132.34, 139.26, 156.77. Found: C, 41.85; H, 3.39%. Calcd for C_9H_9IO: C, 41.56; H, 3.49%.

5.7.13. 2-(3-Methyl-2-butenoxy)iodobenzene (5b). IR (neat) 2972, 2914, 1676, 1582, 1470, 1275, 1240, 1016, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (s, 3H), 1.80 (s, 3H), 4.59 (d, J=6.6 Hz, 2H), 5.48–5.54 (m, 1H), 6.70 (t, J=

8.1 Hz, 1H), 6.82 (d, *J*=8.1 Hz, 1H), 7.28 (t, *J*=8.1 Hz, 1H), 7.77 (d, *J*=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.42, 25.80, 66.14, 86.81, 112.48, 119.36, 122.23, 129.13, 137.61, 139.22, 157.16. Found: C, 46.11; H, 4.52%. Calcd for $C_{11}H_{13}IO$: C, 45.85; H, 4.55%.

5.7.14. 2-Bromophenyl 3-methyl-2-propenyl ether (5c). IR (neat) 2914, 1585, 1477, 1277, 1242, 1051, 1030, 995, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3H), 1.79 (s, 3H), 4.60 (d, *J*=6.3 Hz, 2H), 5.48–5.56 (m, 1H), 6.82 (dt, *J*=1.5, 7.5 Hz, 1H), 6.90 (dd, *J*=1.5, 7.8 Hz, 1H), 7.24 (dt, *J*=1.5, 7.5 Hz, 1H), 7.53 (dd, *J*=1.5, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.56, 26.01, 66.18, 112.24, 113.58, 119.24, 121.53, 128.06, 133.09, 137.78, 154.89. Found: C, 54.90; H, 5.41%. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43%.

5.7.15. 3-Methyl-2,3-dihydrobenzofuran (6a). IR (neat) 2964, 2872, 1597, 1481, 1462, 1227, 966, 835, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (d, *J*=7.5 Hz, 3H), 3.45–3.58 (m, 1H), 4.04 (t, *J*=7.5 Hz, 1H), 4.65 (t, *J*=8.7 Hz, 1H), 6.78 (d, *J*=7.5 Hz, 1H), 6.85 (t, *J*=7.5 Hz, 1H), 7.10 (t, *J*=7.5 Hz, 1H), 7.13 (d, *J*=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.33, 36.46, 78.35, 109.31, 120.27, 123.63, 127.81, 132.07, 159.49. Found: C, 80.57; H, 7.57%. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51%.

5.7.16. 3-(1-Methylethyl)-2,3-dihydrobenzofuran (6b). IR (neat) 2961, 1595, 1483, 1232, 959, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (d, *J*=6.6 Hz, 3H), 0.94 (d, *J*=6.6 Hz, 3H), 1.89–2.00 (m, 1H), 3.30 (quint., *J*=4.8 Hz, 1H), 4.36 (dd, *J*=4.8, 9.3 Hz, 1H), 4.49 (t, *J*=9.3 Hz, 1H), 6.77 (d, *J*=4.5 Hz, 1H), 6.83 (t, *J*=4.5 Hz, 1H), 7.11 (t, *J*=4.5 Hz, 1H), 7.17 (d, *J*=4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.46, 19.83, 31.71, 48.12, 73.74, 109.19, 119.90, 124.90, 127.96, 129.24, 160.19. Found: C, 81.62; H, 8.64%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

5.7.17. 2-Bromoethanal butyl 3-phenyl-2-propynyl acetal (7). IR (neat) 2959, 2872, 2245, 1724, 1491, 1117, 1043, 758, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J*=7.5 Hz, 3H), 1.35–1.48 (m, 2H), 1.62 (quint., *J*=7.5 Hz, 2H), 3.46 (d, *J*=5.4 Hz, 2H), 3.56–3.67 (m, 1H), 3.67–3.77 (m, 1H), 4.52 (s, 2H), 4.94 (t, *J*=5.4 Hz, 1H), 7.29–7.36 (m, 3H), 7.42–7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.88, 19.29, 31.64, 31.73, 54.73, 67.13, 84.38, 86.48, 100.37, 122.22, 128.15, 128.44, 131.56. Found: C, 58.17; H, 6.05%. Calcd for $C_{15}H_{19}BrO_2$: C, 57.89; H, 6.15%.

5.7.18. 2-Butoxy-3-(phenylmethyliden)tetrahydrofuran (8, *E*/*Z*=47/53). IR (neat) 2932, 2870, 1599, 1491, 1448, 1344, 1184, 1097, 1034, 928, 754, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J*=7.5 Hz, 3H), 1.31–1.42 (m, 2H), 1.49–1.61 (m, 2H), 2.71 (d, *J*=16.5 Hz, 0.53H), 2.83 (d, *J*=17.1 Hz, 0.47H), 2.93 (d, *J*=16.2 Hz, 1H), 3.43 (ddt, *J*=2.4, 13.5, 6.6 Hz, 1H), 3.71 (ddt, *J*=1.8, 9.6, 6.9 Hz, 1H), 4.57 (q, *J*=13.2 Hz, 1H), 4.69 (s, 1H), 5.21 (d, *J*=5.1 Hz, 0.53H), 5.33 (d, *J*=4.2 Hz, 0.47H), 6.39 (d, *J*=16.2 Hz, 1H), 7.13 (d, *J*=7.2 Hz, 1H), 7.16–7.24 (m, 1H), 7.24–7.36 (m, 3H); ^{13}C NMR ($CDCl_3$) for major isomer: δ 13.95, 19.44, 31.77, 37.94, 67.11, 70.81, 104.24, 119.99, 126.31, 127.85, 128.20, 137.28, 138.50. For minor isomer: δ 13.95, 19.44, 31.77, 41.14, 67.03, 67.87, 102.09, 121.41, 126.40, 127.70, 128.32, 137.30, 139.00. Found: C, 71.43; H, 10.65%. Calcd for $C_{15}H_{20}O_2$: C, 71.70; H, 10.94%.

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