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Headline Articles

Radical Cyclization of Allyl 2-Iodophenyl Ether, *N,N*-Diallyl-2-iodoaniline, and 2-Iodoethanal Acetal by Means of Trialkylmanganate(II)

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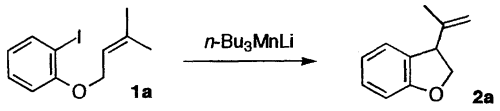
Treatment of allyl 2-halophenyl ethers with tributylmanganate (*n*-Bu_3MnLi or *n*-$Bu_3MnMgBr$) provided dihydrobenzofuran derivatives in good yield. Indoline derivatives are also produced effectively starting from 2-iodoaniline compounds. The reaction could proceed by the following sequences: (1) formation of a radical by treatment of iodophenol or iodoaniline derivatives with tributylmanganate(II), (2) radical cyclization, and (3) recombination of radical and manganese species giving alkylmanganese(II) compound. The reaction proved to proceed in the presence of a catalytic amount of manganese(II) chloride under atmospheric oxygen. The manganese catalyzed radical cyclization could also be applied to 2-iodoethanal acetal, in which case the presence of oxygen was not necessary.

Dialkylcuprates(I)[1] and trialkylzincates[2] have been widely used for organic synthesis. In contrast, much less information is available on the potential utility of trialkylmanganates(II).[3] Herein we report an effective method for the preparation of indoline, dihydrobenzofuran, and 2-alkoxytetrahydrofuran derivatives by means of tributylmanganate(II). Very recently, a synthesis of substituted indolines via anionic cyclization has been reported.[4] In addition, several procedures mediated by free radical,[5] transition metal species,[6] and samarium(II) iodide[7] have also been published on the construction of the heteroatom ring of these molecules. Our new method should provide an alternative route to these important compounds.

(1) Trialkylmanganate(II)-Induced Cyclization of Allyl 2-Iodophenyl Ether and *N,N*-Diallyl-2-iodoaniline.[8]

A THF suspension of manganese(II) chloride was sonicated for 20 min under argon atmosphere. The mixture was cooled to 0 °C, and 3 molar amounts of butyllithium was added. After the mixture was stirred for 20 min, a solution of 2-iodophenyl prenyl (3-methyl-2-butenyl) ether (**1a**) in THF was added. The resulting mixture was stirred for 2 h and then poured into 1 M HCl (1 M=1 mol dm^{-3}). Extractive workup followed by purification afforded 3-isopropenyl-2,3-dihydrobenzofuran (**2a**) in 88% yield (Scheme 1). The use of tributylmanganate(II) (*n*-$Bu_3MnMgBr$), derived from $MnCl_2$ and 3 molar amounts of butylmagnesium bromide, instead of *n*-Bu_3MnLi also provided **2a** in 87% yield. In contrast, *n*-Bu_2Mn, *n*-BuMnCl, Me_3MnLi, or *n*-Bu_2CuLi could not give



Scheme 1.

any cyclized product. Treatment of **1a** with *n*-Bu_2Mn and *n*-BuMnCl resulted in recovery of the starting ether **1a**. The reaction of **1a** with Me_3MnLi provided phenyl prenyl ether quantitatively.[9] *n*-Bu_2CuLi afforded the starting material **1a** (60%) and phenyl prenyl ether (35%). In addition, treatment of **1a** with *n*-BuLi gave phenyl prenyl ether exclusively after aqueous workup.

Representative examples are shown in Table 1. Not only 2-iodophenol derivatives **1** but also 2-iodoaniline derivatives **3** reacted in the same way to provide the corresponding indoline derivatives upon treatment with tributylmanganate(II). Several comments are worth noting.

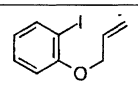
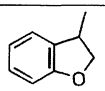
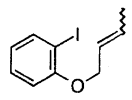
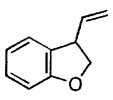
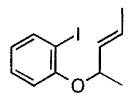
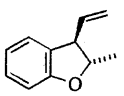
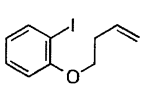
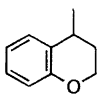
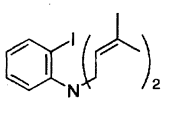
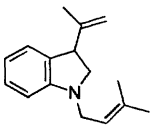
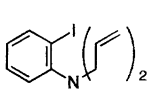
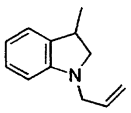
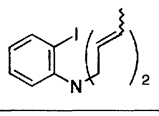
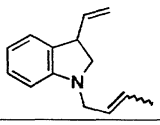
(1) Tributylmanganese magnesium bromide, *n*-$Bu_3MnMgBr$, was equally as effective as *n*-Bu_3MnLi.

(2) The corresponding bromo compound such as 2-bromophenyl prenyl ether afforded phenyl prenyl ether (30%), 3-isopropenyl-2,3-benzofuran (**2a**, 10%) along with the starting material (52%) upon treatment with tributylmanganate(II).[10]

(3) The addition of a THF solution of *n*-Bu_2Mn to 2-lithiophenyl prenyl ether, generated from **1a** and *n*-BuLi in THF gave a complex mixture that did not contain the cyclized product **2a**.

(4) The reaction of 2-iodophenyl homoallyl ether **1e** with

Table 1. Tributylmanganate-Induced Cyclization of Allyl 2-Iodophenyl Ethers and *N,N*-Diallyl-2-iodoaniline[a)]

Entry	Substrate		Product		Yield (%)
1		**1b**		**2b**	40
2		**1c**		**2c**	63
3		**1d**		**2d**	70[b)]
4		**1e**		**2e**	30
5		**3a**		**4a**	92 (90)[c)]
6		**3b**		**4b**	72 (72)[c)]
7		**3c**		**4c**	74

a) *n*-Bu_3MnLi (1.5 mmol) and substrate (1.0 mmol) were employed. b) *cis*/*trans*=15/85. c) *n*-$Bu_3MnMgBr$ was used instead of *n*-Bu_3MnLi.

tributylmanganate(II) provided chroman derivative **2e** in only 30% yield.

(5) The relative stereochemistry between the substituents attached to C(2) and C(3) of compound **2d** was *trans*/*cis*=85/15. This isomeric ratio was the same as that of the radical cyclization product, 3-ethyl-2-methyl-2,3-dihydrobenzofuran (*trans*/*cis*=87/13), which was generated by the reaction of **1d** with *n*-Bu_3SnH.

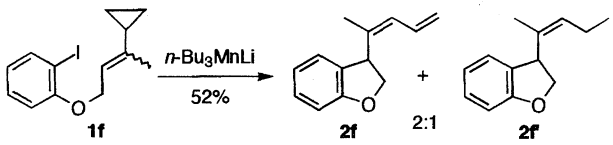
(6) Whereas products (**2b**, **2e**, and **4b**) having methyl group were obtained in the case of the substrates which have terminal olefinic group, alkenes (**2a**, **2c**, **2d**, **4a**, and **4c**) were produced from the iodophenyl ethers and iodoanilines having internal olefinic moiety.

Based on these facts, we are tempted to assume the following reaction mechanism (Scheme 2). Single electron transfer from tributylmanganate(II) to 2-iodophenol derivative **1a** would give an anion radical **5** which generates phenyl radical **6** under departure of the iodide anion. *Exo* mode radical cyclization should afford tertiary carbon radical **7** which recombines with *n*-BuMn[11] to give dialkylmanganese(II) compound **8**. Dehydromanganation would provide the final product **2a**.[12,13]

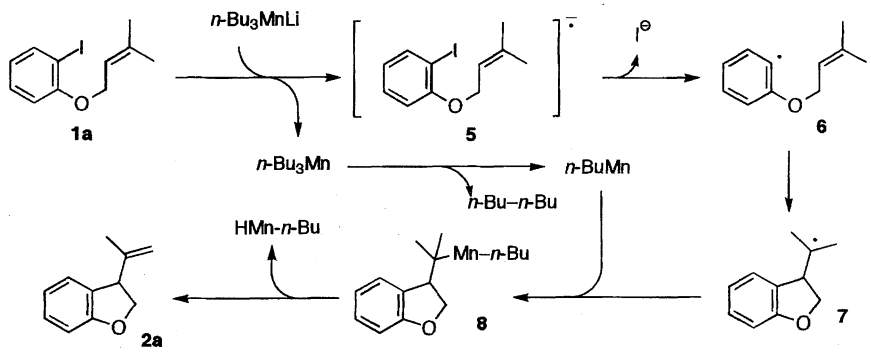
The intermediacy of the radical species was confirmed by the following experiment. Treatment of allylic ether **1f** having a cyclopropane ring on the alkenyl carbon with tributylmanganate(II) provided a mixture of dienyl-substituted dihydrobenzofuran derivative **2f** and alkenyl-substituted compound **2f'** (**2f**:**2f'**=2:1) in 52% combined yield (Scheme 3). No trace of the product having the cyclopropane ring could be observed in the reaction mixture.[14]

The intermediary manganese species could be trapped by various electrophiles.[15] An addition of tributylmanganate(II) to *N,N*-diallylaniline derivative **3b**, followed by treatment with allyl bromide, provided the corresponding allylated product **10a** (E=$CH_2CH{=}CH_2$) in 70% yield. Trapping the reaction by acid chlorides such as acetyl chloride and benzoyl chloride afforded methyl ketone and phenyl ketone, respectively (Scheme 4).

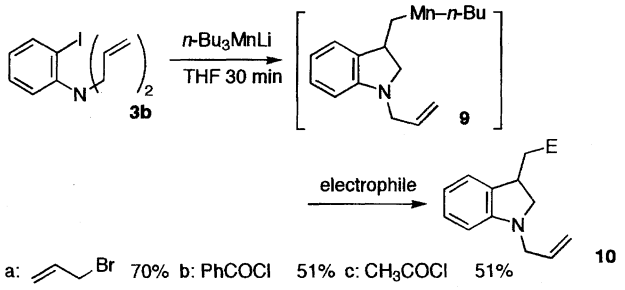
Unexpectedly, the reaction proved to proceed in the presence of a catalytic amount of manganese(II) chloride.[16] For instance, treatment of **1a** (1.0 mmol) or **3a** (1.0 mmol) with excess *n*-BuMgBr (4.0 mmol) in the presence of a catalytic amount of $MnCl_2$ (0.2 mmol) in THF at 25 °C for 12 h provided **2a** or **4a** in 70 or 81% yield, respectively. The reactions



Scheme 3.



Scheme 2.



Scheme 4.

were performed in a flask equipped with a balloon filled with argon. Atmospheric oxygen could diffuse into the balloon to equilibrate the partial pressures, and the concentration of oxygen reached 10% (volume%) after 12 h.[17] The presence of oxygen was essential for the catalytic reaction.[3e] Without oxygen, the cyclization reaction did not complete under $MnCl_2$ catalysis.

(2) Trialkylmanganate(II)-Induced Cyclization of 2-Iodoethanal Acetal. Carbon–carbon bond formation via radical reaction is one of the most important synthetic steps in the construction of organic molecules.[18] In Section 1, we have shown that intramolecular radical cyclization of aryl iodide having alkenyl group has been carried out by using tributylmanganate(II). Further exploitation of this method and development of an intramolecular radical reaction of alkyl iodide carrying alkene moiety in the molecule will be discussed here.

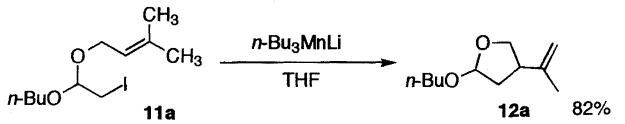
The radical cyclization reaction of unsaturated 2-iodoethanal acetals **11a** was examined. A suspension of manganese(II) chloride in THF was sonicated for 20 min under argon atmosphere. The mixture was cooled to 0 °C and 3 molar amounts of butyllithium was added. After this was stirred for 20 min, a solution of 2-iodoethanal acetal **11a** in THF was added. The resulting mixture was stirred for 1 h at 0 °C and poured into water. Extraction with hexane followed by silica-gel column chromatography afforded tetrahydrofuran derivative **12a** in 82% yield (Scheme 5).

The representative results are summarized in Table 2. These 2-iodoethanal acetals **11** were prepared by the reactions of allylic or 2-propynylic alcohols with butyl vinyl ether or silyl enol ether in the presence of *N*-iodosuccinimide in dichloromethane.[19] Several comments are worth noting.

(1) The use of the iodide derivative was essential to obtain the cyclization product in high yield. Whereas 2-iodoethanal mixed acetal **11a** provided **12a** in 82% yield, the corresponding 2-bromoethanal acetal **11e** gave **12a** in only 41% yield.

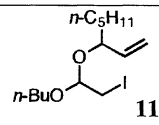
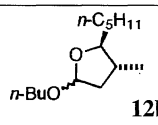
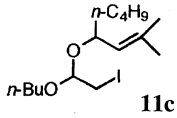
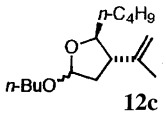
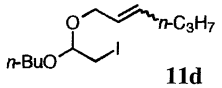
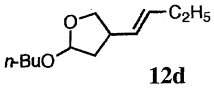
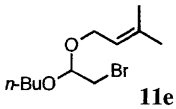
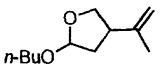
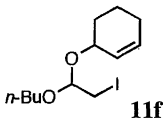
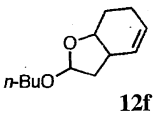
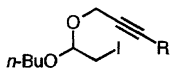
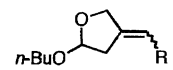
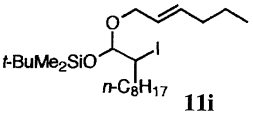
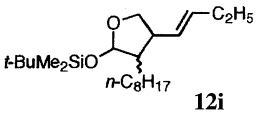
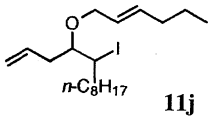
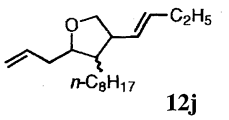
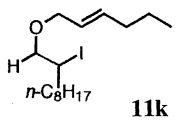
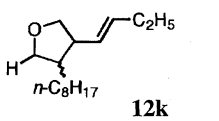
(2) The carbon–carbon triple bonds were as effective as olefinic linkage to trap an radical intramolecularly (Entry 6).[20]

(3) The use of tributylmanganate(II) (*n*-$Bu_3MnMgBr$), derived from $MnCl_2$ and 3 molar amounts of butylmagnesium bromide, instead of *n*-Bu_3MnLi gave **11a** in 42% yield.



Scheme 5.

Table 2. Radical Cyclization of Iodo Acetals by Means of Tributylmanganate (*n*-Bu_3MnLi)

Entry	Substrate	Product (%)	
1	 **11b**	 **12b**	68
2	 **11c**	 **12c**	70
3	 **11d**	 **12d**	73
4	 **11e**	 **12e = 12a**	41
5	 **11f**	 **12f**	48
6	 **11g** R=$SiMe_3$ **11h** R=Ph	 **12g** **12h**	83 65
7	 **11i**	 **12i**	79
8	 **11j**	 **12j**	77
9	 **11k**	 **12k**	35

(4) 2-Iodoethanal silyl acetal **11i** derived from silyl enol ether also provided the corresponding 2-siloxytetrahydrofuran **12i** in good yield.

(5) Whereas the relative stereochemistry of the anomeric carbon is not controlled, a high diastereocontrol is observed between C(4) and C(5) giving the *trans*-product in over 98% stereoselectivity.[21] Thus, treatment of **11b** or **11c** with *n*-

Bu_3MnLi gave **12b** or **12c** as a mixture of two stereoisomers which could be converted into single isomeric *trans*-lactone **18b** or **18c** by oxidation (vide infra). The reaction of **11f** with *n*-Bu_3MnLi gave the cyclized product **12f** as a stereoisomeric mixture which was contaminated by the corresponding saturated compound. However, a single stereoisomer was obtained concerning to the ring-junction. The *cis*-stereochemistry of the ring-junction of **12f** was confirmed by hydrogenation (H_2, PtO_2) and oxidation (Jones oxidation) to the known lactone. In contrast, the lactone **18i**, derived from **12i**, consisted of two stereoisomers (*cis*/*trans* = 1/1) and therefore the relative stereochemistry between C(3) and C(4) of **12i** was *cis*/*trans* = 1/1.

(6) (*E*)-Alkenes were produced selectively (*E*/*Z* => 95/5) in the cyclization of 2-alkenyl ethers (**11d**, **11i**, **11j**, and **11k**) irrespective of the geometry of the starting olefins.

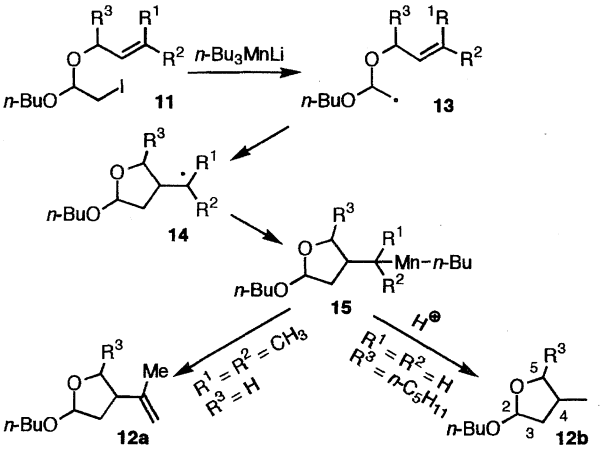
(7) 2-Alkenyl 2-iodoalkyl ethers (**11j** and **11k**) as well as 2-iodoalkanal acetals afforded tetrahydrofuran derivatives in good yields upon treatment with *n*-Bu_3MnLi.

(8) Not only primary alkyl iodides but also secondary iodides (**11i**, **11j**, and **11k**) proved to cyclize effectively to give the desired products.

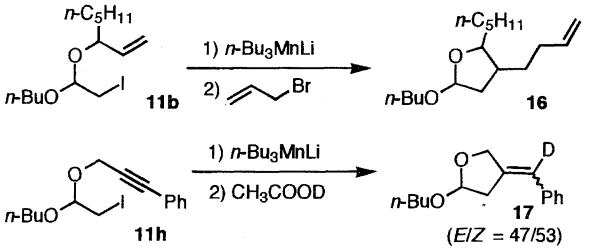
We are tempted to assume the following reaction mechanism.[22] Single electron transfer from tributylmanganate(II) to the 2-iodoethanal acetal **11** would give a 2,2-dialkoxyethyl radical **13** under departure of iodide anion. 5-*Exo* mode cyclization could afford a carbon radical **14** which recombines with *n*-BuMn to give alkylmanganese compound **15**. Protonation or dehydromanganation of **15** would provide the final product **12a** or **12b** (Scheme 6).

The intermediary manganese species could be trapped by various electrophiles. For instance, the addition of tributylmanganate(II) to **11b** followed by treatment with allyl bromide gave an allylated product **16** in 38% yield. Quenching the reaction mixture, derived from **11h** and *n*-Bu_3MnLi, with CH_3COOD provided a deuterated product **17** (**12h**-*d* 85%D) (Scheme 7).

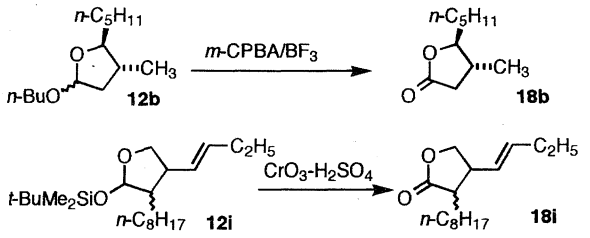
The cyclized products were easily transformed into γ-butyrolactones. For instance, treatment of **12b** or **12i** with *m*CPBA/BF_3·Et_2O[23] or CrO_3·H_2SO_4[24] provided lactone



Scheme 6.



Scheme 7.



Scheme 8.

18b or **18i** (*cis*/*trans* = 1/1) in 70 or 99% yield, respectively (Scheme 8).

The catalytic reaction (0.1 molar amount of $MnCl_2$) using *n*-BuMgBr could also be applied to iodo acetal **11** to give **12**, in case of which the presence of oxygen was not neccesary.[25] For instance, treatment of **11a** or **11d** (1.0 mmol) with *n*-BuMgBr (2.0 mmol) in the presence of $MnCl_2$ (0.1 mmol) afforded **12a** or **12d** in 80 or 78% yield, respectively.

In conclusion:

(1) Treatment of allyl 2-iodophenyl ether or *N*,*N*-diallyl-2-iodoaniline with tributylmanganate(II) provided the corresponding dihydrobenzofuran or indoline derivative in good yield.

(2) The reaction of 2-iodoethanal acetals with tributylmanganate(II) proceeded effectively to give tetrahydrofuran derivatives.

(3) Whereas the latter reaction took place in the presence of a catalytic amount of $MnCl_2$ without oxygen, the former reaction required the coexistence of oxygen under catalytic process.

(4) The radical cyclization mechanism was postulated for these reaction.

Experimental

Distillation of the products was performed using Kugelrohr (Büchi); the boiling points are indicated by the air-bath temperature values without any correction. The NMR spectra (^1H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. The IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Starting Materials. The following starting materials, 2-iodophenyl prenyl (3-methyl-2-butenyl) ether (**1a**), 2-iodophenyl allyl ether (**1b**), and 2-iodophenyl crotyl ether (**1c**), were prepared according to literature procedure.[7] The ether **1d** and **1e** was prepared in similar fashion.

2-Iodophenyl 1-Methyl-2-butenyl Ether (1d): Bp 135 °C (0.5 Torr, 1 Torr = 133.322 Pa); IR (neat) 2976, 1581, 1469, 1439,

1373, 1242, 1144, 1120, 1042, 1017, 963, 926, 745, 648 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.47 (d, J = 6.3 Hz, 3H), 1.69 (d, J = 6.3 Hz, 3H), 4.76 (dq, J = 6.3, 6.3 Hz, 1H), 5.56 (dd, J = 6.3, 15.3 Hz, 1H), 5.71 (dq, J = 15.3, 6.3 Hz, 1H), 6.68 (dd, J = 7.8, 7.8 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 7.8, 7.8 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 17.57, 21.56, 76.40, 88.32, 115.02, 122.55, 127.67, 129.13, 131.84, 139.46, 156.97. HRMS Found: *m/z* 288.0004. Calcd for $C_{11}H_{13}OI$: M, 288.0012.

2-Iodophenyl 3-Butenyl Ether (1e): Bp 120 °C (0.5 Torr); IR (neat) 2926, 1518, 1570, 1478, 1464, 1439, 1289, 1277, 1248, 1121, 1050, 1018, 988, 918, 746, 647 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.60 (dt, J = 6.8, 6.6 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 5.13 (d, J = 10.0 Hz, 1H), 5.21 (d, J = 17.1 Hz, 1H), 5.98 (ddt, J = 10.0, 17.1, 6.8 Hz, 1H), 6.70 (dd, J = 7.7, 7.8 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 7.28 (ddd, J = 1.5, 8.1, 7.8 Hz, 1H), 7.76 (dd, J = 1.5, 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 33.50, 68.52, 86.71, 112.19, 117.35, 122.55, 129.47, 134.41, 139.54, 157.53. Found: C, 43.80; H, 4.05%. Calcd for $C_{10}H_{11}OI$: C, 43.82; H, 4.04%.

Preparation of *N,N*-Diallylic 2-Iodoaniline 3. The title compounds, **3a**, **3b**, and **3c** were prepared by diallylation of a 2-iodoaniline (allylic bromide/Na_2CO_3 in DMF) according to the reported procedure.[4)]

2-Iodo-*N,N*-diprenylaniline (3a): Bp 175 °C (0.5 Torr); IR (neat) 2964, 2912, 2850, 1578, 1467, 1444, 1434, 1376, 1223, 1132, 1089, 1013, 919, 754, 720, 643 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.59 (s, 6H), 1.68 (s, 6H), 3.56 (d, J = 6.6 Hz, 4H), 5.21 (t, J = 6.6 Hz, 2H), 6.76 (ddd, J = 1.5, 7.5, 8.0 Hz, 1H), 6.98 (dd, J = 1.7, 8.0 Hz, 1H), 7.26 (ddd, J = 1.7, 7.5, 7.8 Hz, 1H), 7.84 (dd, J = 1.5, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 17.87, 25.67, 50.98, 100.38, 121.45, 123.84, 125.15, 128.37, 134.82, 139.89, 152.61. Found: C, 54.35; H, 6.36%. Calcd for $C_{16}H_{22}NI$: C, 54.09; H, 6.24%.

2-Iodo-*N,N*-diallylaniline (3b): Bp 145 °C (0.5 Torr); IR (neat) 3070, 1643, 1578, 1468, 1435, 1417, 1214, 1013, 992, 920, 758, 722, 642 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.63 (dt, J = 6.1, 1.4 Hz, 4H), 5.12 (ddd, J = 1.4, 1.4, 10.3 Hz, 2H), 5.17 (ddd, J = 1.4, 1.4, 17.0 Hz, 2H), 5.83 (ddt, J = 10.3, 17.0, 6.1 Hz, 2H), 6.79 (ddd, J = 1.5, 7.8, 7.8 Hz, 1H), 7.03 (dd, J = 1.5, 7.8 Hz, 1H), 7.27 (ddd, J = 1.5, 7.8, 7.8 Hz, 1H), 7.86 (dd, J = 1.5, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 56.06, 100.38, 117.79, 124.24, 125.66, 128.52, 134.91, 140.03, 151.90. Found: C, 48.25; H, 4.73%. Calcd for $C_{12}H_{14}NI$: C, 48.18; H, 4.72%.

2-Iodo-*N,N*-dicrotylaniline (3c, 38 : 62 Strereoisomeric Mixture): Bp 155 °C (0.5 Torr); IR (neat) 3012, 2960, 2912, 1579, 1468, 1435, 1205, 1105, 1013, 966, 939, 752, 720, 642 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.59 (d, J = 6.6 Hz, 1.14H), 1.65 (dd, J = 1.1, 5.9 Hz, 3.72H), 1.67, (d, J = 6.6 Hz, 1.14), 3.53 (d, J = 6.0 Hz, 2.48H), 3.53 (d, J = 6.3 Hz, 0.76H), 3.65 (d, J = 6.3 Hz, 0.76H), 5.36—5.67 (m, 4H), 6.77 (ddd, J = 1.5, 7.8, 7.8 Hz, 1H), 6.98 (dd, J = 1.5, 7.8 Hz, 1H), 7.26 (ddd, J = 1.5, 7.8, 7.8 Hz, 1H), 7.85 (dd, J = 1.5, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.12, 17.77, 49.10, 55.15, 55.95, 77.21, 100.38, 124.01, 124.19, 125.23, 125.31, 126.73, 126.98, 127.60, 127.78, 128.32, 128.61, 128.74, 139.81, 139.85, 152.23. Found: C, 51.18; H, 5.60%. Calcd for $C_{14}H_{18}NI$: C, 51.39; H, 5.54%.

Preparation of Cyclization Precursors of 11. Preparation of 2-iodoethanal butyl prenyl acetal (**11a**) is representative. The preparation of the iodide **11a** was carried out according to the literature procedure[26)] with butyl vinyl ether (2.0 g, 20 mmol), 3-methyl-2-buten-1-ol (1.72 g, 20 mmol), and NIS (4.5 g, 20 mmol). Silica-gel column purification (hexane/ethyl acetate=20/1) of crude product afforded the title compound **11a** (4.8 g) in 80% yield as a colorless liquid: Bp 140 °C (0.5 Torr); IR (neat) 2954, 2930, 2868, 1460, 1450, 1415, 1378, 1175, 1107, 1033 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.93 (t, J = 7.2 Hz, 3H), 1.41 (tq, J = 6.9, 7.2 Hz, 2H), 1.59 (tt, J = 6.9, 6.6 Hz, 2H), 1.70 (s, 3H), 1.76 (s, 3H), 3.24 (d, J = 5.6 Hz, 2H), 3.49 (dt, J = 9.3, 6.6 Hz, 1H), 3.60 (dt, J = 9.3, 6.6 Hz, 1H), 4.05 (dd, J = 7.8, 11.4 Hz, 1H), 4.18 (dd, J = 7.2, 11.4 Hz, 1H), 4.65 (t, J = 5.6 Hz, 1H), 5.31—5.40 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 5.32, 13.73, 17.92, 19.21, 25.69, 31.64, 62.85, 65.97, 101.09, 120.32, 137.84. Found: C, 42.24; H, 7.07%. Calcd for $C_{11}H_{21}O_2I$: C, 42.32; H, 6.78%.

2-Iodoethanal Butyl 1-Vinylhexyl Acetal (11b, 1 : 1 Diastereomixture): Bp 165 °C (0.5 Torr); IR (neat) 2954, 2928, 2866, 1466, 1415, 1379, 1343, 1322, 1177, 1106, 1023, 926 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, J = 6.6 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H), 1.20—1.72 (m, 12H), 3.14—3.25 (m, 2H), 3.40 (dt, J = 9.3, 6.6 Hz, 0.5H), 3.49 (dt, J = 9.2, 6.5 Hz, 0.5H), 3.54 (dt, J = 9.2, 6.5 Hz, 0.5H), 3.62 (dt, J = 9.3, 6.5 Hz, 0.5H), 3.87 (dt, J = 7.5, 6.6 Hz, 0.5H), 3.99 (dt, J = 8.0, 6.8 Hz, 0.5H), 4.59 (t, J = 5.2 Hz, 0.5H), 4.62 (t, J = 5.4 Hz, 0.5H), 5.12—5.19 (m, 1H), 5.19—5.26 (m, 1H), 5.68 (ddd, J = 8.0, 10.5, 16.8 Hz, 0.5H), 5.78 (ddd, J = 7.5, 10.4, 17.7 Hz, 0.5H); ^{13}C NMR ($CDCl_3$) δ = 6.01, 6.26, 13.75, 13.91, 19.13, 19.24, 22.46, 24.72, 24.82, 31.46, 31.60, 31.63, 31.74, 35.17, 35.33, 65.07, 66.63, 78.62, 79.29, 99.14, 100.87, 116.50, 117.79, 138.67, 139.42. Found: C, 47.31; H, 7.62%. Calcd for $C_{14}H_{27}O_2I$: C, 47.46; H, 7.68%.

2-Iodoethanal Butyl 1-Butyl-3-methyl-2-butenyl Acetal (11c, 1 : 1Diastereomixture): Bp 165 °C (0.5 Torr); IR (neat) 2954, 2926, 2866, 1674, 1458, 1414, 1377, 1342, 1245, 1225, 1177, 1104, 1031, 982, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.89 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 1.5H), 0.94 (t, J = 7.2 Hz, 1.5H), 1.17—1.66 (m, 10H), 1.67 (s, 3H), 1.74 (s, 1.5H), 1.76 (s, 1.5H), 3.17 (d, J = 5.4 Hz, 1H), 3.19 (d, J = 5.4 Hz, 1H), 3.38 (dt, J = 9.5, 6.8 Hz, 0.5H), 3.48 (t, J = 6.5 Hz, 1H), 3.60 (dt, J = 9.5, 6.5 Hz, 0.5H), 4.17 (dt, J = 9.4, 6.5 Hz, 0.5H), 4.32 (dt, J = 9.4, 6.6 Hz, 0.5H), 4.56 (t, J = 5.4 Hz, 0.5H), 4.57 (t, J = 5.4 Hz, 0.5H), 5.02 (d, J = 9.4 Hz, 0.5H), 5.14 (d, J = 9.4 Hz, 0.5H); ^{13}C NMR ($CDCl_3$) δ = 6.34, 6.56, 13.78, 13.94, 18.21, 19.16, 19.29, 22.59, 25.71, 25.76, 27.36, 27.44, 31.46, 31.80, 35.34, 35.49, 64.46, 66.52, 73.22, 74.07, 98.66, 100.50, 125.79, 126.65, 134.69, 136.19. Found: C, 49.15; H, 7.92%. Calcd for $C_{15}H_{29}O_2I$: C, 48.92; H, 7.94%.

2-Iodoethanal Butyl 2-Hexenyl Acetal (11d): Bp 140 °C (0.5 Torr); IR (neat) 2954, 2926, 2868, 1460, 1431, 1416, 1379, 1344, 1177, 1111, 1039, 969 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.91 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 1.41 (tq, J = 7.3, 7.2 Hz, 2H), 1.41 (tq, J = 7.5, 7.4 Hz, 2H), 1.59 (tt, J = 6.6, 7.5 Hz, 2H), 2.04 (dt, J = 7.0, 7.3 Hz, 2H), 3.23 (d, J = 5.4 Hz, 2H), 3.48 (dt, J = 9.3, 6.6 Hz, 1H), 3.60 (dt, J = 9.3, 6.6 Hz, 1H), 4.00 (dd, J = 6.2, 11.6 Hz, 1H), 4.10 (dd, J = 6.2, 11.6 Hz, 1H), 4.65 (t, J = 5.4 Hz, 1H), 5.56 (dt, J = 15.3, 6.2 Hz, 1H), 5.73 (dt, J = 15.3, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 5.35, 13.57, 13.72, 19.20, 22.05, 31.62, 34.25, 66.16, 67.33, 101.02, 125.73, 135.30. Found: C, 44.16; H, 7.04%. Calcd for $C_{12}H_{23}O_2I$: C, 44.18; H, 7.11%.

2-Bromoethanal Butyl Prenyl Acetal (11e): Bp 110 °C (0.5 Torr): IR (neat) 2866, 1460, 1450, 1424, 1379, 1354, 1185, 1109, 1003, 686 cm^{-1}; ^1H NMR ($CDCL_3$) δ = 0.93 (t, J = 7.2 Hz, 3H), 1.41 (tq, J = 7.5, 7.2 Hz, 2H), 1.60 (tt, J = 6.3, 7.5 Hz, 2H), 1.70 (s, 3H), 1.76 (s, 3H), 3.39 (d, J = 5.5 Hz, 2H), 3.52 (dt, J = 9.6, 6.3 Hz, 1H), 3.63 (dt, J = 9.6, 6.3 Hz, 1H), 4.07 (dd, J = 7.5, 11.4 Hz, 1H), 4.15 (dd, J = 6.9, 11.4 Hz, 1H), 4.70 (t, J = 5.5 Hz, 1H), 5.31—5.40 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.71, 17.89, 19.16, 25.68, 31.66, 63.11, 66.25, 100.79, 120.28, 137.93. Found: C, 49.68; H, 7.99%. Calcd for $C_{11}H_{21}O_2Br$: C, 49.82; H, 7.98%.

2- Iodoethanal Butyl 2- Cyclohexenyl Acetal (11f, 1 : 1

Diastereomixture): Bp 140 °C (0.5 Torr); IR (neat) 2930, 2866, 1459, 1414, 1341, 1317, 1175, 1107, 1035, 950, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.4 Hz, 3H), 1.40 (tq, J = 7.4, 7.4 Hz, 2H), 1.48—1.65 (m, 3H), 1.67—1.86 (m, 3H), 1.86—2.15 (m, 2H), 3.16—3.28 (m, 2H), 3.48 (dt, J = 9.0, 6.6 Hz, 0.5H), 3.53 (dt, J = 10.5, 6.5 Hz, 0.5H), 3.57 (dt, J = 10.5, 6.5 Hz, 0.5H), 3.60 (dt, J = 9.0, 6.6 Hz, 0.5H), 4.08—4.18 (m, 1H), 4.74 (t, J = 5.7 Hz, 0.5H), 4.76 (t, J = 5.7 Hz, 0.5H), 5.69—5.79 (m, 1H), 5.84—5.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 6.00, 6.19, 13.75, 18.67, 19.03, 19.21, 24.91, 28.37, 29.63, 31.62, 31.69, 64.84, 65.54, 70.26, 70.63, 100.61, 101.15, 127.19.127.63, 131.51, 131.61. Found: C, 44.30; H, 6.67%. Calcd for $C_{12}H_{21}O_2I$: C, 44.46; H, 6.53%.

2-Iodoethanal Butyl 3-Trimethylsilyl-2-propynyl Acetal (11g): Bp 135 °C (0.5 Torr); IR (neat) 2954, 2930, 2868, 2174, 1415, 1344, 1251, 1177, 1112, 1045, 993, 844, 759, 699, 639 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.19 (s, 9H), 0.94 (t, J = 7.3 Hz, 3H), 1.41 (tq, J = 8.1, 7.3 Hz, 2H), 1.59 (tt, J = 6.6, 8.1 Hz, 2H), 3.26 (d, J = 5.4 Hz, 2H), 3.52 (dt, J = 9.3, 6.6 Hz, 1H), 3.66 (dt, J = 9.3, 6.6 Hz, 1H), 4.23 (s, 2H), 4.78 (t, J = 5.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −0.40, 4.90, 13.71, 19.15, 31.54, 54.47, 66.87, 91.90, 100.74, 100.96. Found: C, 40.40; H, 6.52%. Calcd for $C_{12}H_{23}O_2ISi$: C, 40.68; H, 6.54%.

2-Iodoethanal Butyl 3-Phenyl-2-propynyl Acetal (11h): Bp 170 °C (0.5 Torr); IR (neat) 2956, 2928, 2866, 1490, 1459, 1443, 1415, 1375, 1342, 1176, 1110, 1040, 999, 754, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.4 Hz, 3H), 1.42 (tq, J = 7.5, 7.4 Hz, 2H), 1.62 (tt, J = 6.7, 7.5 Hz, 2H), 3.31 (d, J = 5.3 Hz, 2H), 3.57 (dt, J = 9.3, 6.7 Hz, 1H), 3.70 (dt, J = 9.3, 6.7 Hz, 1H), 4.50 (s, 2H), 4.86 (t, J = 5.3 Hz, 1H), 7.28—7.38 (m, 3H), 7.41—7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 4.98, 13.72, 19.19, 31.59, 54.48, 66.86, 84.53, 86.53, 100.74, 122.47, 128.40, 128.68, 131.83. Found: C, 50.24; H, 5.33%. Calcd for $C_{15}H_{19}O_2I$: C, 50.29; H, 5.35%.

2-Iododecanal *t*-Butyldimethylsilyl 2-Hexenyl Acetal (11i, 1 : 1 Diastereomixture): Bp 180 °C (0.5 Torr); IR (neat) 2952, 2924, 2854, 1464, 1253, 1135, 1108, 1036, 1003, 968, 836, 816, 777 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.84 (s, 1.5H), 0.10 (s, 1.5H), 0.11 (s, 1.5H), 0.12 (s, 1.5H), 0.86 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H), 0.90 (s, 4.5H), 0.91 (s, 4.5H), 1.16—1.36 (m, 12H), 1.39 (tq, J = 6.9, 6.9 Hz, 2H), 1.68—1.85 (m, 2H), 2.00 (dt, J = 7.7, 6.9 Hz, 2H), 3.87—4.00 (m, 2H), 4.03—4.14 (m, 1H), 4.50 (d, J = 3.9 Hz, 0.5H), 4.78 (d, J = 3.3 Hz, 0.5H), 5.44—5.60 (m, 1H), 5.61—5.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = −4.73, −4.65, −4.34, −4.14, 13.57, 13.98, 18.00, 22.11, 22.54, 25.63, 25.69, 28.71, 28.78, 29.14, 29.29, 29.38, 29.50, 31.49, 31.76, 32.28, 34.23, 34.29, 40.68, 41.15, 67.50, 67.86, 97.77, 98.32, 125.91, 126.06, 134.66, 134.81. Found: C, 53.27; H, 9.43%. Calcd for $C_{22}H_{45}O_2ISi$: C, 53.21; H, 9.13%.

1-Allyl-2-iododecyl 2-Hexenyl Ether (11j): Bp 180 °C (0.5 Torr); IR (neat) 2954, 2922, 2852, 1641, 1460, 1438, 1377, 1341, 1100, 1061, 997, 969, 914 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, J = 6.9 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H), 1.17—1.41 (m, 13H), 1.52—1.90 (m, 3H), 2.03 (dt, J = 6.9, 6.9 Hz, 2H), 2.34—2.53 (m, 2H), 3.18 (ddd, J = 4.9, 4.9, 6.9 Hz, 1H), 3.99 (dd, J = 6.0, 11.3 Hz, 1H), 4.05 (dd, J = 6.0, 11.3 Hz, 1H), 4.20 (ddd, J = 3.9, 4.9, 9.6 Hz, 1H), 5.09 (dd, J = 1.8, 10.2 Hz, 1H), 5.14 (dd, J = 1.8, 17.1 Hz, 1H), 5.56 (dt, J = 15.5, 6.0 Hz, 1H), 5.70 (dt, J = 15.5, 6.9 Hz, 1H), 5.85 (ddt, J = 10.2, 17.1, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.58, 13.97, 22.06, 22.53, 28.72, 29.13, 29.30, 29.70, 31.74, 34.23, 35.27, 37.72, 41.53, 71.04, 81.20, 117.48, 126.41, 134.36, 134.91. Found: C, 55.87; H, 8.57%. Calcd for $C_{19}H_{35}OI$: C, 56.16; H, 8.68%.

2-Iododecyl 2-Hexenyl Ether (11k): Bp 150 °C (0.5 Torr); IR (neat) 2952, 2920, 2852, 1464, 1378, 1362, 1300, 1247, 1105, 1063, 1005, 970, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H), 1.16—1.47 (m, 11H), 1.41 (tq, J = 7.2, 7.3 Hz, 2H), 1.47—1.62 (m, 1H), 1.68—1.90 (m, 2H), 2.04 (dt, J = 6.8, 7.2 Hz, 2H), 3.60 (dd, J = 7.5, 10.6 Hz, 1H), 3.71 (dd, J = 5.9, 10.6 Hz, 1H), 3.98 (d, J = 6.2 Hz, 2H), 4.11—4.22 (m, 1H), 5.55 (dt, J = 15.5, 6.2 Hz, 1H), 5.71 (dt, J = 15.5, 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.57, 13.98, 22.08, 22.54, 28.74, 29.13, 29.22, 29.30, 31.74, 34.25, 34.62, 36.40, 71.67, 75.44, 126.10, 135.20. Found: C, 52.75; H, 8.67%. Calcd for $C_{16}H_{31}OI$: C, 52.46; H, 8.53%.

General Procedure for the Manganate-Promoted Cyclization of 2-Iodophenyl Allylic Ether. Formation of 3-isopropenyl-2,3-dihydrobenzofuran (**2a**) is representative. A suspension of manganese(II) chloride (0.19 g, 1.5 mmol) in tetrahydrofuran (THF, 5 mL) was sonicated for 20 min. Butyllithium (1.5 M hexane solution, 3.0 mL, 4.5 mmol) was added to $MnCl_2$ at 0 °C. The mixture immediately turned brown. After the solution was stirred for 15 min at 0 °C, 2-iodophenyl prenyl (3-methyl-2-butenyl) ether **1a** (0.29 g, 1.0 mmol) in THF (2 mL) was added over 1—2 min. The resulting mixture was stirred at 0°C for 2 h. The reaction was quenched with 1.0 M HCl and extracted with ethyl acetate (20 mL×3). The organic extracts were combined and washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude products were purified by silica gel column chromatography (hexane : ethyl acetate = 40 : 1) to give dihydrobenzofuran derivative **2a** (0.14 g) in 88% yield: Bp 100 °C (10 Torr); IR (neat) 2970, 2890, 1597, 1482, 1460, 1228, 1015, 965, 897, 826, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.64—1.65 (m, 3H), 4.17 (dd, J = 6.8, 9.8 Hz, 1H), 4.35 (dd, J = 6.8, 9.0 Hz, 1H), 4.65 (dd, J = 9.0, 9.8 Hz, 1H), 4.84—4.87 (m, 1H), 4.89—4.90 (m, 1H), 6.79—6.89 (m, 2H), 7.09—7.17 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 18.68, 50.18, 75.26, 109.55, 112.85, 120.53, 125.06, 128.52, 128.80, 144.76, 160.37. Found: C, 82.20; H, 7.53%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

Physical data for **2b** were identical with those reported in the literature.[7)]

3-Ethenyl-2,3-dihydrobenzofuran (2c): IR (neat) 3076, 2960, 2926, 2880, 1641, 1610, 1598, 1481, 1459, 1226, 1165, 1097, 1015, 979, 921, 838, 748, 725, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 4.10—4.25 (m, 1H), 4.23 (dd, J = 8.0, 8.0 Hz, 1H), 4.71 (dd, J = 9.0, 8.0 Hz, 1H), 5.16 (dd, J = 10.0, 1.5 Hz, 1H), 5.22 (dd, J = 17.0, 1.5 Hz, 1H), 5.88 (ddd, J = 17.0, 10.8, 8.0 Hz, 1H), 6.80—7.00 (m, 2H), 7.14—7.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 46.91, 76.18, 109.67, 116.69, 120.66, 124.96, 128.57, 129.31, 137.94, 159.98. No analytically pure sample could be obtained because of small impurities which could not be separated. Thus, the sample **2c** was converted into 3-ethyl-2,3-dihydrobenzofuran which was identical with the authentic sample.[7)]

3-Ethenyl-2-methyl-2,3-dihydrobenzofuran (2d, 85 : 15 Stereoisomeric Mixture): Bp 80 °C (10 Torr); IR (neat) 2972, 1598, 1460, 1384, 1280, 1231, 1175, 1106, 1056, 911,874, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.51 (d, J = 6.0 Hz, 3H), 3.64 (dd, J = 8.7, 8.7 Hz, 0.85H), 3.97 (dd, J = 8.7, 8.7 Hz, 0.15H), 4.52 (dq, J = 8.7, 6.0 Hz, 0.85H), 4.94 (dq, J = 8.7, 6.0 Hz, 0.15H), 5.15—5.30 (m, 2H), 5.84 (ddd, J = 17.1, 10.2, 8.7 Hz, 1H), 6.74—6.91 (m, 2H), 7.03—7.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 19.551, 21.675, 50.50, 54.90, 84.84, 85.13, 109.44, 109.52, 117.51, 120.10, 120.53, 124.52, 124.84, 128.14, 128.59, 129.92, 137.36, 159.42. Found: C, 82.16; H, 7.76%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

Triethylborane-Induced Radical Cyclization of 1d. A hexane solution of Et_3B (1.0 M, 0.07 mL, 0.07 mmol) was added to a solution of **1d** (199 mg, 0.7 mmol), *n*-Bu_3SnH (0.20 mL, 0.76

mmol) in toluene (14 mL). After being stirred for 12 h at 25 °C, the resulting mixture was concentrated in vacuo. The residual oil was dissolved in ethyl acetate (20 mL) and KF (2 g) and saturated aqueous KF solution (4 mL) was added. The mixture was stirred at 25 °C for another 12 h. Workup followed by silica gel column chromatography (hexane : ethyl acetate = 40 : 1) afforded 3-ethyl-2-methyl-2,3-dihydrobenzofuran (*trans*/*cis* = 87/13) in 65% yield.

4-Methylchroman (2e): Bp 98 °C (10 Torr); IR (neat) 2956, 2870, 1581, 1489, 1448, 1309, 1270, 1253, 1226, 1121, 1059, 1050, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.33 (d, J = 7.2 Hz, 3H), 1.72 (dddd, J = 3.6, 6.6, 6.6, 13.7 Hz, 1H), 2.03—2.13 (m, 1H), 2.95 (tq, J = 6.6, 6.6 Hz, 1H), 4.12—4.25 (m, 2H), 6.76—6.90 (m, 2H), 7.04—7.17 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 22.07, 28.36, 30.17, 63.79, 116.75, 120.25, 127.26, 127.67, 128.71, 154.43. Found: C, 80.98; H, 8.13%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

General Procedure for the Manganate(II) Promoted Cyclization of *N,N*-Diallylic 2-Iodoaniline. Preparation of 3-isopropenyl-1-prenylindoline (**4a**) is representative. A THF (2 mL) solution of *N,N*-diprenyl-2-iodoaniline **3a** (0.36 g, 1.0 mmol) was added at 0 °C to a solution of *n*-Bu_3MnLi (1.5 mmol), generated from $MnCl_2$ (0.19 g, 1.5 mmol) and *n*-BuLi (1.5 M, 3.0 mL, 4.5 mmol), and the resulting mixture was stirred for 2 h at 0 °C. The reaction was quenched with water and extracted with ethyl acetate (20 mL×3). The organic extracts were combined and washed with brine, then purified as above to give 3-isopropenyl-1-prenylindoline (**4a**, 0.21 g) in 92% yield: Bp 85 °C (0.5 Torr); IR (neat) 3068, 2966, 2914, 2854, 1646, 1605, 1488, 1460, 1376, 1318, 1235, 1195, 1156, 1022, 893, 744 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.67—1.80 (m, 9H), 3.14 (dd, J = 9.0, 9.0 Hz, 1H), 3.49 (dd, J = 9.0, 9.0 Hz, 1H), 3.64 (dd, J = 14.7, 6.9 Hz, 1H), 3.75 (dd, J = 14.7, 6.9 Hz, 1H), 3.90 (dd, J = 9.0, 9.0 Hz, 1H), 4.82—4.92 (m, 2H), 5.22—5.34 (m, 1H), 6.53 (d, J = 7.8 Hz, 1H), 6.66 (dd, J = 7.2, 7.2 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 7.09 (dd, J = 7.8, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 152.53, 145.52, 135.53, 131.85, 127.79, 124.53, 120.06, 117.60, 112.40, 107.50, 57.62, 48.83, 46.39, 25.67, 19.37, 17.90. Found: C, 84.46; H, 9.60%. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31%.

1-Allyl-3-methylindoline (4b): Bp 65 °C (0.5 Torr); IR (neat) 3044, 2956, 2808, 1608, 1487, 1460, 1243, 1159, 990, 920, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.31 (d, J = 6.9 Hz, 3H), 2.85 (dd, J = 8.4, 8.4 Hz, 1H), 3.28 (q, J = 7.8 Hz, 1H), 3.55 (dd, J = 8.4, 8.4 Hz, 1H), 3.61 (ddt, J = 15.3, 6.0, 1.2 Hz, 1H), 3.78 (ddt, J = 15.3, 6.0, 1.2 Hz, 1H), 5.16—5.31 (m, 2H), 5.91 (ddt, J = 17.1, 9.9, 6.0 Hz, 1H), 6.51 (d, J = 7.5 Hz, 1H), 6.69 (dd, J = 7.2, 7.2 Hz, 1H), 7.01—7.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 18.41, 35.05, 51.92, 61.19, 107.38, 117.29, 117.77, 123.17, 127.42, 134.31, 135.31, 151.89. Found: C, 83.14; H, 8.79%. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73%.

1-Butyl-3-ethylindoline (4c′): 1-(2-Butenyl)-3-ethenylindoline (**4c**) contained *cis* and *trans*-butenyl groups. These compounds were hydrogenated (H_2, PtO_2) and purified by silica gel column chromatography to give 1-butyl-3-ethylindoline (**4c′**) in 89% from **4c**. Bp 75 °C (0.5 Torr); IR (neat) 3044, 2954, 1607, 1489, 1459, 1378, 1273, 1239, 1179, 1127, 1026, 916, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.96 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H), 1.28—1.63 (m, 5H), 1.77—1.90 (m, 1H), 2.92—3.12 (m, 4H), 3.52 (t, J = 8.4 Hz, 1H), 6.47 (d, J = 7.8 Hz, 1H), 6.63 (dd, J = 7.5, 7.5 Hz, 1H), 7.00—7.10 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 11.70, 13.86, 20.29, 26.88, 29.34, 42.10, 48.64, 58.77, 106.73, 117.02, 123.60, 127.51, 133.78, 152.70. Found: C, 82.91; H, 10.69%. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41%.

General Procedure for Electrophilic Trapping of Manganese Reagents. Preparation of 1-allyl-3-(3-butenyl)indoline (**10a**) is representative. A THF solution of **3b** (0.30 g, 1.0 mmol) was added to a solution of *n*-Bu_3MnLi (1.5 mmol) at 0 °C. After 2 h, allyl bromide (0.39 mL, 4.5 mmol) was added and the resulting mixture was stirred at 0 °C for another 30 min. The reaction was quenched with water and extracted with ethyl acetate (20 mL×3). Purification by silica gel column chromatography afforded allylated product **10a** (0.15 g) in 70% yield: Bp 80 °C (0.5 Torr); IR (neat) 3070, 2920, 2850, 1642, 1607, 1488, 1332, 1245, 1158, 992, 914, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.63 (m, 1H), 1.93 (m, 1H), 2.16 (m, 2H), 2.97 (dd, J = 8.4, 8.4 Hz, 1H), 3.21 (m, 1H), 3.51 (dd, J = 8.4, 8.4 Hz, 1H), 3.65 (dd, J = 15.3, 6.0 Hz, 1H), 3.75 (dd, J = 15.3, 6.0 Hz, 1H), 4.97—5.31 (m, 4H), 5.79—5.97 (m, 2H), 6.50 (d, J = 8.1 Hz, 1H), 6.675 (dd, J = 7.5, 7.5 Hz, 1H), 7.07 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 31.53, 33.23, 39.93, 51.85, 59.20, 107.36, 114.88, 117.32, 117.63, 123.67, 127.59, 133.91, 134.24, 138.49, 152.02. Found: C, 84.21; H, 8.94%. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98%.

1-Allyl-3-phenacylindoline (10b): Bp 120 °C (0.5 Torr); IR (neat) 2920, 1687, 1606, 1489, 1246, 992, 923, 748, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.05 (dd, J = 9.0, 3.0 Hz, 1H), 3.27 (dd, J = 17.7, 9.0 Hz, 1H), 3.45 (dd, J = 17.7, 4.5 Hz, 1H), 3.66—3.74 (m, 3H), 3.80—3.92 (m, 1H), 5.14—5.32 (m, 2H), 5.89 (ddt, J = 17.1, 10.2, 6.0 Hz, 1H), 6.53 (d, J = 9.0 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 7.05—7.15 (m, 2H), 7.42—7.50 (m, 2H), 7.52—7.62 (m, 1H), 7.94—8.02 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 35.97, 43.67, 51.60, 59.36, 107.47, 117.53, 117.73, 123.86, 128.01, 128.12, 128.71, 132.84, 133.29, 133.94, 136.95, 151.93, 199.16. Found: C, 82.06; H, 6.96%. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.86%.

1-Allyl-3-acetonylindoline (10c): Bp 95 °C (0.5 Torr); IR (neat) 2918, 2810, 1716, 1606, 1489, 1460, 1418, 1364, 1247, 1159, 992, 923, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.17 (s, 3H), 2.71 (dd, J = 8.4, 8.4 Hz, 1H), 2.89—2.96 (m, 2H), 3.58—3.71 (m, 4H), 5.16—5.30 (m, 2H), 5.88 (ddt, J = 16.2, 9.9, 5.7 Hz, 1H), 6.50 (d, J = 7.8 Hz, 1H), 6.66 (dd, J = 7.5, 7.5 Hz, 1H), 7.00—7.16 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 30.25, 35.65, 48.44, 51.60, 59.20, 107.46, 117.51, 117.75, 123.68, 127.96, 132.62, 133.93, 151.82, 207.86. Found: C, 77.85; H, 8.08%. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96%.

The Reaction of 2-Iodophenyl 3-Cyclopropyl-2-butenyl Ether (1f) with *n*-Bu_3MnLi. A THF solution of **1f** (0.17 g, 0.56 mmol) was added to *n*-Bu_3MnLi (0.89 mmol) at 0 °C under argon atmosphere. After 1 h, the reaction was quenched with water. Extractive workup followed by silica gel column chromatography gave a mixture which contains the diene product **2f** plus the monoolefin **2f′** in a ratio of 2 : 1 in 52% combined yield. These two compounds were inseparable on analytical TLC. The mixture was hydrogenated (H_2, PtO_2) to give 3-(1-methylbutyl)-2,3-dihydrobenzofuran (6 : 4 diastereomeric mixture) in 80% yield: Bp 110 °C (10 Torr); IR (near) 2956, 2922, 2870, 1596, 1484, 1460, 1228, 1016, 958, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.79 (d, J = 6.9 Hz, 1.2H), 0.87 (d, J = 6.6 Hz, 1.8H), 0.88 (t, J = 6.9 Hz, 1.8H), 0.92 (t, J = 6.9 Hz, 1.2H), 1.05—1.50 (m, 4H), 1.70—1.82 (m, 0.6H), 1.82—1.94 (m, 0.4H), 3.41 (dt, J = 9.3, 4.5 Hz, 0.6H), 3.48 (dt, J = 9.0, 5.4 Hz, 0.4H), 4.32—4.40 (m, 1H), 4.49 (dd, J = 9.3, 9.3 Hz, 0.6H), 4.55 (dd, J = 9.3, 9.3 Hz, 0.4H), 6.77 (d, J = 8.1 Hz, 1H), 6.80—6.90 (m, 1H), 7.10—7.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.08, 14.12, 14.66, 16.25, 20.32, 20.40, 35.14, 35.96, 36.49, 36.66, 46.57, 47.07, 72.87, 74.67, 109.30, 109.34, 120.06, 120.20, 124.69, 125.31, 128.09, 128.17, 129.00, 129.86, 160.51, 160.76. Found: C, 81.78; H, 9.54%. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53%.

General Procedure for the Reaction of 2-Iodophenol and 2-

Iodoaniline Derivative with Butylmagnesium Bromide in the Presence of Catalytic Amount of $MnCl_2$. Manganese(II) chloride (24 mg, 0.2 mmol) was placed in a flask equipped with a balloon filled with argon. THF (5 mL) was added and a suspension was sonicated for 15 min. Butylmagnesium bromide (1.1 M, ether solution, 3.7 mL, 4.1 mmol) was added at 0 °C and the resulting brown solution was stirred for 10 min. A solution of **1a** (0.29 g, 1.0 mmol) in THF (2 ml) was added and the whole was stirred for 12 h. Extractive workup followed by silica gel column purification provided 3-isopropenyl-2,3-dihydrobenzofuran **2a** (0.11 g) in 70% yield.

General Procedure for the Manganate Promoted Cyclization of 2-Iodoethanal Acetal. The reaction of **11a** with *n*-Bu_3MnLi is representative. A suspension of manganese(II) chloride (0.15 g, 1.2 mmol) in THF (10 mL) was sonicated for 20 min under argon atmosphere. The mixture was cooled to 0 °C and butyllithium (1.5 M hexane solution, 2.2 mL, 3.3 mmol) was added. After the mixture was stirred for 20 min, a solution of **11a** (0.31 g, 1.0 mmol) in THF (3 mL) was added. The resulting mixture was stirred for 1 h at 0 °C and then poured into water (20 mL). Extraction with hexane (20 mL×3) followed by silica-gel column chromatography afforded tetrahydrofuran derivative **12a** (0.15 g) in 82% yield. (7 : 3 diastereomeric mixture): Bp 110 °C (10 Torr); IR (neat) 2956, 2868, 1648, 1458, 1378, 1345, 1189, 1103, 1036, 1009, 929, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.4 Hz, 3H), 1.37 (tq, J = 7.4, 7.4 Hz, 2H), 1.56 (m, 2H), 1.72 (s, 0.9H), 1.75 (s, 2.1H), 1.77 (m, 0.7H), 1.88 (ddd, J = 5.6, 9.5, 13.0 Hz, 0.3H), 2.03 (dd, J = 7.7, 13.0 Hz, 0.3H), 2.29 (ddd, J = 5.6, 9.5, 13.0 Hz, 0.7H), 2.84 (ddt, J = 8.0, 8.0, 8.0 Hz, 0.7H), 3.11 (ddt, J = 8.1, 8.1, 8.1 Hz, 0.3H), 3.37 (dt, J = 6.6, 9.6 Hz, 0.3H), 3.40 (dt, J = 6.6, 9.6 Hz, 0.7H), 3.61—3.74 (m, 2H), 3.92 (t, J = 8.0 Hz, 0.7H), 4.06 (t, J = 8.1 Hz, 0.3H), 4.73—4.80 (m, 2H), 5.12—5.18 (m, 1H); ^{13}C NMR ($CDCl_3$) major product δ = 13.72, 19.25, 20.50, 31.75, 37.38, 45.71, 67.51, 69.53, 104.64, 111.15, 143.87, minor product δ = 13.72, 19.25, 20.26, 31.71, 37.59, 43.89, 66.99, 70.71, 104.20, 110.47, 144.83. Found: C, 71.62; H, 11.06%. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%.

2-Butoxy-4-methyl-5-pentyltetrahydrofuran (12b, 74 : 26 Mixture of Stereoisomers): Bp 110 °C (1 Torr); IR (neat) 2954, 2928, 2868, 1460, 1379, 1344, 1098, 994, 921, 901 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, 0.78H), 1.04 (d, J = 6.6 Hz, 2.22H), 1.22—1.62 (m, 13H), 1.74 (dtq, J = 6.6, 8.1, 9.2 Hz, 0.74H), 2.05 (dd, J = 6.6, 11.7 Hz, 0.26H), 2.00—2.18 (m, 0.26H), 2.32 (ddd, J = 5.7, 9.2 13.2 Hz, 0.74H), 3.33 (dt, J = 6.5, 9.3 Hz, 0.26H), 3.38 (dt, J = 6.6, 9.6 Hz, 0.74H), 3.46—3.56 (m, 1H), 3.68 (dt, J = 6.9, 9.3 Hz, 0.26H), 3.69 (dt, J = 6.8, 9.6 Hz, 0.74H), 5.00 (d, J = 5.1 Hz, 0.26H), 5.07 (dd, J = 3.0, 5.7 Hz, 0.74H); ^{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%.

2-Butoxy-5-butyl-4-isopropenyltetrahydrofuran (12c, 1 : 1 Mixture of Stereoisomers): Bp 100 °C (0.5 Torr); IR (neat) 2954, 2928, 2868, 1095, 1051, 999, 976, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.87 (t, J = 6.6 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H), 1.22—1.61 (m, 10H), 1.69 (s, 1.5H), 1.71 (s, 1.5H), 1.72—1.82 (m, 0.5H), 1.85—2.06 (m, 1H), 2.22—2.41 (m, 1H), 2.74 (ddd, J = 11.4, 7.8, 7.8 Hz, 0.5H), 3.32 (dt, J = 9.6, 6.6 Hz, 0.5H), 3.37 (dt, J = 9.6, 6.6 Hz, 0.5H), 3.66 (dt, J = 9.6, 6.9 Hz, 1H), 3.75—3.87 (m, 1H), 4.72—4.80 (m, 2H), 5.02 (d, J = 4.8 Hz, 0.5H), 5.07 (dd, J = 5.4, 3.3 Hz, 0.5H); ^{13}C NMR ($CDCl_3$) δ = 13.73, 13.78, 13.91, 19.28, 19.31, 19.75, 22.64, 22.72, 28.46, 28.52, 31.76, 31.80, 33.33, 36.20, 38.54, 38.85, 50.12, 52.00, 66.65, 67.14, 79.44, 82.79, 103.11, 103.32, 112.01, 112.43, 144.25, 144.31. Found: C, 74.72; H, 11.72%. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%.

2-Butoxy-4-(1-butenyl)tetrahydrofuran (12d, 4 : 1 Diastereomeric Mixture): Bp 125 °C (10 Torr); IR (neat) 2956, 2930, 2870, 1460, 1343, 1099, 1070, 1029, 1004, 968, 929 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H), 1.30—1.44 (m, 2H), 1.51—1.61 (m, 2H), 1.62 (ddd, J = 3.5, 8.1, 13.6 Hz, 0.8H), 1.71 (ddd, J = 5.3, 9.3, 12.8 Hz, 0.2H), 2.00 (dq, J = 7.5, 6.3 Hz, 2H), 2.28 (ddd, J = 5.5, 9.3, 13.2 Hz, 1H), 2.68—2.84 (m, 0.8H), 2.98—3.15 (m, 0.2H), 3.38 (dt, J = 6.6, 9.6 Hz, 1H), 3.51 (dd, J = 8.7, 8.7 Hz, 1H), 3.68 (dt, J = 6.6, 9.6 Hz, 1H), 3.90 (dd, J = 8.7, 8.7 Hz, 0.8H), 4.04 (dd, J = 8.7, 8.7 Hz, 0.2H), 5.08—5.16 (m, 1H), 5.38 (ddt, J = 8.4, 15.3, 1.5 Hz, 1H), 5.52 (dt, J = 15.3, 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) major product δ = 13.54, 13.72, 19.25, 25.33, 31.75, 39.59, 42.05, 67.42, 71.24, 104.64, 129.15, 133.43. Found: C, 72.88; H, 11.34%. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%.

8-Butoxy-7-oxabicyclo[4.3.0]nonane (12f′). Treatment of **11f** with tributylmanganate(II) according to the general procedure provided 8-butoxy-7-oxabicyclo[4.3.0]non-2-ene (**12f**) which was contaminated by a saturated compound: 8-butoxy-7-oxabicyclo-[4.3.0]nonane (**12f′**) (< 10%). Thus, the product was converted into **12f′** by hydrogenation (H_2/PtO_2). Two stereoisomers were separated by silica-gel column chromatography. Faster moving band, R_f = 0.50 (hexane/ethyl acetate = 20/1): Bp 85 °C (0.5 Torr); IR (neat) 2928, 2862, 1449, 1348, 1335, 1179, 1101, 1068, 1044, 998 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.91 (t, J = 7.4 Hz, 3H), 1.16—1.25 (m, 2H), 1.35 (tt, J = 7.4, 7.4 Hz, 2H), 1.29—1.48 (m, 2H), 1.48—1.62 (m, 5H), 1.89 (dd, J = 4.8, 4.8 Hz, 2H), 1.94 (ddt, J = 3.9, 3.9, 14.4 Hz, 1H), 2.06 (dt, J = 4.8, 14.4 Hz, 1H), 3.39 (dt, J = 9.6, 6.8 Hz, 1H), 3.73 (dt, J = 9.6, 6.8 Hz, 1H), 4.08 (dd, J = 3.9, 7.7 Hz, 1H), 5.17 (dd, J = 4.8, 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.73, 19.21, 20.29, 24.07, 27.68, 28.41, 31.77, 36.91, 40.21, 67.77, 75.31, 103.63. Found: C, 72.65; H, 11.46%. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%. Slower moving band, R_f = 0.42 (hexane/ethyl acetate = 20/1): Bp 85 °C (0.5 Torr); IR (neat) 2928, 2860, 1449, 1353, 1172, 1122, 1090, 1071, 1042, 1019, 993 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.3 Hz, 3H), 1.18—1.34 (m, 2H), 1.40 (tt, J = 7.3, 7.3 Hz, 2H), 1.50—1.69 (m, 6H), 1.72—1.79 (m, 2H), 1.80—1.92 (m, 1H), 2.09 (ddt, J = 7.7, 7.7, 10.7 Hz, 1H), 2.13 (dt, J = 6.1, 7.7 Hz, 1H), 3.38 (dt, J = 9.5, 6.5 Hz, 1H), 3.73 (dt, J = 9.5, 6.8 Hz, 1H), 3.94 (dd, J = 5.1, 10.7 Hz, 1H), 5.10 (dd, J = 3.1, 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.69, 19.27, 21.52, 22.74, 26.66, 29.04, 31.86, 36.33, 38.02, 67.80, 78.06, 104.58. Found: C, 72.41; H, 11.03%. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%.

2-Butoxy-4-trimethylsilylmethylenetetrahydrofuran (12g, 56 : 44 Stereoisomeric Mixture): Bp 120 °C (10 Torr); IR (neat) 2954, 2864, 1638, 1348, 1248, 1182, 1097, 1068, 1039, 1004, 926, 872, 838, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.05 (s, 3.96H), 0.07 (s, 5.04H), 0.88 (t, J = 7.2 Hz, 3H), 1.33 (dt, J = 7.2, 7.2 Hz, 2H), 1.52 (tt, J = 7.2, 7.2 Hz, 2H), 2.49 (d, J = 16.5 Hz, 1H), 2.56—2.70 (m, 0.56H), 2.70—2.80 (m, 0.44H), 3.38 (dt, J = 9.6, 7.2 Hz, 1H), 3.66 (dt, J = 9.6, 7.2 Hz, 1H), 4.22—4.42 (m, 2H), 5.12 (d, J = 5.1 Hz, 0.44H), 5.22 (d, J = 5.1 Hz, 0.56H), 5.36—5.42 (m, 0.56H), 5.46—5.52 8m, 0.44H); ^{13}C NMR ($CDCl_3$) δ = −0.77, −0.73, 13.74, 19.22, 31.59, 38.58, 42.70, 66.89, 67.00, 68.25, 71.50, 102.79, 104.42, 117.82, 119.26, 154.32, 154.37. Found: C, 62.80; H, 10.59%. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59%.

2-Butoxy-4-phenyl[^2H]methylenetetrahydrofuran (17, *E*/*Z*=47/53 Stereoisomeric Mixture): Bp 140 °C (0.5 Torr);

IR (neat) 2954, 2926, 2864, 1180, 1098, 1068, 1037, 1014, 971, 926, 766, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.91 (t, J = 7.5 Hz, 3H), 1.35 (tq, J = 7.5, 8.4 Hz, 2H), 1.55 (tt, J = 6.6, 8.4 Hz, 2H), 2.71 (d, J = 16.7 Hz, 0.53H), 2.83 (dd, J = 1.5, 16.7 Hz, 0.53H), 2.90 (d, J = 5.1 Hz, 0.47H), 2.93 (dd, J = 5.1, 16.7 Hz, 0.47H), 3.43 (dt, J = 6.6, 9.6 Hz, 1H), 3.72 (dt, J = 6.6, 9.6 Hz, 1H), 4.52 (d, J = 12.9 Hz, 0.53H), 4.62 (d, J = 12.9 Hz, 0.53H), 4.69 (s, 0.94H), 5.21 (d, J = 5.1 Hz, 0.47H), 5.33 (dd, J = 1.5, 5.1 Hz, 0.53H), 7.11—7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 13.71, 19.22, 31.60, 37.78, 40.96, 66.99, 67.07, 67.83, 70.76, 102.18, 104.34, 120.15, 121.57, 126.49, 126.58, 127.87, 128.02, 128.40, 128.51, 137.46, 138.67, 139.11. Elemental analysis was performed for 2-butoxy-4-phenylmethylenetetrahydrofuran (**12h**). Found: C, 77.40; H, 8.96%. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

4-(1-Butenyl)-2-*t*-butyldimethylsiloxy-3-octyltetrahydrofuran (12i): Bp 150 °C (1 Torr); IR (neat) 2952, 2922, 2852, 1464, 1252, 1137, 1109, 1020, 998, 974, 938, 837, 777 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.07 (s, 3H), 0.09 (s, 3H), 0.85 (t, J = 7.3 Hz, 3H), 0.88 (s, 9H), 0.94 (t, J = 7.4 Hz, 3H), 1.17—1.36 (m, 14H), 1.97 (ddq, J = 1.4, 6.1, 7.3 Hz, 2H), 1.90—2.04 (m, 1H), 2.70 (dddd, J = 3.3, 8.3, 10.4, 10.7 Hz, 1H), 3.69 (dd, J = 3.3, 8.2 Hz, 1H), 4.02 (dd, J = 8.2, 8.3 Hz, 1H), 5.26 (d, J = 4.2 Hz, 1H), 5.34 (dt, J = 15.3, 6.1 Hz, 1H), 5.57 (dd, J = 10.4, 15.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −5.79, −4.27, 13.68, 14.00, 17.74, 22.58, 25.27, 25.57, 25.73, 28.00, 29.21, 29.51, 29.91, 31.77, 43.70, 48.51, 73.17, 99.44, 130.37, 132.84. Found: C, 71.90; H, 12.30%. Calcd for $C_{22}H_{44}O_2Si$: C, 71.67; H, 12.03%.

2-Allyl-4-(1-butenyl)-3-octyltetrahydrofuran (12j): Bp 125 °C (1 Torr); IR (neat) 3072, 2956, 2922, 2852, 1642, 1462, 1378, 1123, 1069, 1051, 999, 970, 910, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, J = 6.6 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H), 1.10—1.35 (m, 14H), 1.70—2.50 (m, 5.37H), 2.75—2.83 (m, 0.63H), 3.39—3.70 (m, 2H), 3.84—4.10 (m, 1H), 5.03—5.15 (m, 2H), 5.19—5.42 (m, 1H), 5.45—5.56 (m, 1H), 5.88 (ddt, J = 17.1, 9.9, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.78, 13.97, 22.55, 25.57, 27.66, 27.75, 29.18, 29.38, 29.71, 31.77, 39.27, 45.50, 47.48, 72.72, 82.50, 116.69, 126.93, 134.08, 135.51. Found: C, 82.44; H, 12.22%. Calcd for $C_{19}H_{34}O$: C, 82.25; H, 11.99%.

3-(1-Butenyl)-4-octyltetrahydrofuran (12k). Faster moving band, R_f = 0.50 hexane/ethyl acetate = 20/1): ^1H NMR ($CDCl_3$) δ = 0.88 (t, J = 6.8 Hz, 3H), 0.98 (dt, J = 1.8, 7.5 Hz, 3H), 1.10—1.40 (m, 14H), 1.80—1.94 (m, 1H), 2.02 (ddq, J = 1.5, 7.5, 7.5 Hz, 2H), 2.34 (dddd, J = 8.4, 8.4, 8.4, 8.4 Hz, 1H), 3.39 (dd, J = 8.4, 8.4 Hz, 1H), 3.45 (dd, J = 8.4, 8.4 Hz, 1H), 3.94 (dd, J = 8.1, 4.5 Hz, 1H), 4.01 (dd, J = 8.1, 8.1 Hz, 1H), 5.24 (ddt, J = 15.3, 8.4, 1.8 Hz, 1H), 5.53 (dt, J = 15.3, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.70, 13.98, 22.55, 25.50, 28.38, 29.17, 29.41, 29.44, 29.76, 31.77, 45.87, 49.80, 73.41, 74.08, 128.76, 134.15. Slower moving band, R_f = 0.40 (hexane/ethyl acetate = 20/1): ^1H NMR ($CDCl_3$) δ = 0.88 (t, J = 6.8 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H), 1.10—1.40 (m, 14H), 2.04 (dq, J = 7.5, 7.5 Hz, 2H), 2.12—2.24 (m, 1H), 2.71—2.81 (m, 1H), 3.44 (dd, J = 8.3, 8.3 Hz, 1H), 3.61 (dd, J = 8.3, 4.5 Hz, 1H), 3.90 (dd, J = 8.1, 6.6 Hz, 1H), 3.92 (dd, J = 8.1, 8.1 Hz, 1H), 5.36 (dd, J = 15.3, 9.0 Hz, 1H), 5.52 (dt, J = 15.3, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.81, 13.99, 22.56, 25.58, 27.98, 28.31, 29.19, 29.46, 29.75, 31.78, 43.28, 45.49, 72.56, 73.41, 126.79, 134.04. HRMS Found: m/z 238.2305. Calcd for $C_{16}H_{30}O$: M, 288.2298.

Conversion of 12 into Lactone 18. Oxidation of **12b** was performed according to the literature.[23] A drop of $BF_3 \cdot Et_2O$ was added to a solution of **12b** (0.14 g, 0.6 mmol) in CH_2Cl_2 (3 mL) under argon atmosphere. Then *m*CPBA (0.66 mmol) was added and the whole was stirred at 25 °C for 3 h. Ether (15 mL) was added and the mixture was poured into saturated sodium hydrogencarbonate. Extraction with ethyl acetate followed by silica gel column purification gave lactone **18b** (85 mg, 85% yield) whose spectral data ware identical with those reported in the literature.[27]

***trans*-5-Butyl-4-isopropenyltetrahydro-2-furanone (18c):** Bp 120 °C (1 Torr); IR (neat) 2954, 2932, 2862, 1784, 1649, 1456, 1422, 1382, 1199, 1171, 1097, 978, 924, 899 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.91 (t, J = 7.2 Hz, 3H), 1.25—1.73 (m, 6H), 1.76 (s, 3H), 2.51 (dd, J = 9.3, 17.5 Hz, 1H), 2.67 (dd, J = 8.6, 17.5 Hz, 1H), 2.81 (ddd, J = 8.0, 8.6, 9.3 Hz, 1H), 4.31 (dt, J = 4.2, 8.2 Hz, 1H), 4.86 (s, 1H), 4.88—4.92 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.71, 19.47, 22.27, 27.59, 34.01, 48.50, 83.62, 113.58, 141.99, 176.21. Found: C, 72.33; H, 10.07%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

***cis*-7-Oxabicyclo[4.3.0]nonan-8-one (18f′):** Bp 120 °C (0.5 Torr); IR (neat) 2934, 2856, 1769, 1449, 1424, 1348, 1335, 1226, 1176, 1143, 1097, 1021, 1003, 988, 942, 877, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.19—1.35 (m, 2H), 1.40—1.55 (m, 2H), 1.57—1.82 (m, 3H), 2.08 (dddd, J = 4.5, 4.5, 4.5, 14.7 Hz, 1H), 2.25 (dd, J = 2.4, 16.8 Hz, 1H), 2.32—2.45 (m, 1H), 2.62 (dd, J = 7.0, 16.8 Hz, 1H), 4.52 (ddd, J = 4.5, 4.5, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 19.69, 22.62, 26.96, 27.61, 34.71, 37.34, 79.10, 177.75. Found: C, 68.35; H, 8.70%. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63%.

4-(1-Butenyl)-3-octyltetrahydro-2-furanone (18i, 1 : 1 Stereoisomeric Mixture). Faster moving band R_f = 0.62 (hexane/ethyl acetate = 5/1): IR (neat) 2954, 2922, 2852, 1782, 1464, 1379, 1353, 1160, 1097, 1067, 1024, 969 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.84 (t, J = 6.8 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H), 1.16—1.31 (m, 10H), 1.32—1.46 (m, 2H), 1.46—1.59 (m, 1H), 1.64—1.78 (m, 1H), 2.01 (ddq, J = 1.5, 6.6, 7.1 Hz, 2H), 2.24 (dt, J = 10.7, 6.1 Hz, 1H), 2.80 (dddd, J = 8.2, 8.3, 9.9, 10.7 Hz, 1H), 3.78 (dd, J = 9.3, 9.9 Hz, 1H), 4.26 (dd, J = 8.2, 9.3 Hz, 1H), 5.49 (ddt, J = 8.3, 15.3, 1.5 Hz, 1H), 5.63 (dt, J = 15.3, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.30, 13.93, 22.49, 25.35, 26.39, 28.53, 29.07, 29.19, 29.38, 31.71, 44.93, 45.57, 70.37, 126.32, 136.48, 178.98. Slower moving band, R_f = 0.58 (hexane/ethyl acetate = 5/1): IR (neat) 2918, 2852, 1769, 1463, 1369, 1180, 1151, 1112, 1032, 985, 968 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85 (t, J = 6.8 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 1.13—1.30 (m, 10H), 1.30—1.46 (m, 3H), 1.61—1.75 (m, 1H), 2.02 (ddq, J = 1.5, 6.9, 7.5 Hz, 2H), 2.50 (ddd, J = 7.7, 4.8, 9.0 Hz, 1H), 3.07 (dddd, J = 2.9, 5.9, 7.7, 9.8 Hz, 1H), 4.06 (dd, J = 2.9, 9.1 Hz, 1H), 4.26 (dd, J = 5.9, 9.1 Hz, 1H), 5.30 (ddt, J = 9.8, 15.3, 1.5 Hz, 1H), 5.61 (dt, J = 15.3, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.43, 13.97, 22.53, 25.40, 25.46, 27.00, 29.10, 29.20, 29.30, 31.72, 42.46, 43.51, 71.73, 124.15, 136.34, 178.99.

4-(3-Butenyl)-5-pentyltetrahydro-2-furanone (16′). Allyl bromide (3.0 mmol) was added to a reaction mixture of **11b** (1.0 mmol) and tributylmanganate(II) (1.2 mmol) at 0 °C. Extractive workup followed by silica gel column purification provided 4-(3-butenyl)-2-butoxy-5-pentyltetrahydrofuran (**16**) as a mixture of two diastereomers in 38% combined yield. Faster moving band (R_f = 0.60, hexane/ethyl acetate = 20/1): IR (neat) 2954, 2926, 2858, 1643, 1457, 1380, 1345, 1098, 1073, 1030, 984, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.84—0.95 (m, 6H), 1.20—1.75 (m, 16H), 1.92—2.20 (m, 2H), 2.29 (ddd, J = 16.2, 12.4, 8.6 Hz, 1H), 3.37 (dt, J = 9.6, 6.6 Hz, 1H), 3.62 (dt, J = 3.3, 7.4 Hz, 1H), 3.67 (dt, J = 9.6, 6.6 Hz, 1H), 4.95 (ddt, J = 10.3, 1.9, 1.1 Hz, 1H), 5.02 (ddt, J = 17.1, 1.9, 1.7 Hz, 1H), 5.08 (dd, J = 3.3, 2.4 Hz, 1H), 5.80 (ddt, J = 17.6, 10.3, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.74, 13.97, 19.28, 22.52, 25.95, 31.81, 31.92, 32.23, 32.50, 34.18, 39.10, 43.03, 67.10, 82.66, 103.42, 114.65, 138.64. Slower moving band (R_f = 0.52, hexane/ethyl acetate = 20/1): ^1H NMR ($CDCl_3$)

δ = 0.84—0.96 (m, 6H), 1.20—1.65 (m, 17H), 1.95—2.16 (m, 4H), 3.33 (dt, J = 9.3, 6.6 Hz, 1H), 3.60 (dt, J = 4.8, 6.9 Hz, 1H), 3.67 (dt, J = 9.3, 6.6 Hz, 1H), 4.93—5.07 (m, 2H), 5.02 (d, J = 4.8 Hz, 1H), 5.82 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.78, 13.93, 19.33, 22.52, 26.09, 31.75, 31.84, 32.50, 32.80, 36.68, 39.86, 42.08, 66.63, 85.65, 103.46, 114.67, 138.57. Because of the contamination by 2-butoxy-4-methyl-5-pentyltetrahydrofuran, **16** was converted into the title lactone **16′** to obtain an analytically pure sample: Bp 142 °C (1 Torr); IR (neat) 2926, 2856, 1779, 1643, 1456, 1422, 1203, 1172, 996, 944, 912 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.90 (t, J = 6.6 Hz, 3H), 1.23—1.37 (m, 4H), 1.37—1.57 (m, 3H), 1.58—1.74 (m, 3H), 1.99—2.20 (m, 3H), 2.21 (dd, J = 7.7, 16.5 Hz, 1H), 2.69 (dd, J = 7.5, 16.5 Hz, 1H), 4.11 (dt, J = 4.8, 7.4 Hz, 1H), 5.02 (ddt, J = 10.2, 1.4, 1.4 Hz, 1H), 5.05 (ddt, J = 17.1, 1.4, 1.4 Hz, 1H), 5.78 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H); ^{13}C NMR δ = 13.84, 22.35, 25.24, 31.43, 31.58, 32.09, 34.45, 35.06, 40.48, 85.95, 115.67, 137.30, 176.71. Found: C, 74.31; H, 10.59%. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54%.

The Reaction of 2-Iodoethanal Acetal 11a with *n*-BuMgBr in the Presence of Catalytic Amount of $MnCl_2$. Butylmagnesium bromide (1.1 M, ether solution, 1.8 mL, 2.0 mmol) was added to a suspension of $MnCl_2$ (12 mg, 0.1 mmol) in THF (5 mL) at 0 °C under argon atmosphere. After being stirred for 20 min at 0 °C, a solution of **11a** (0.31 g, 1.0 mmol) in THF (2 mL) was added and the whole was stirred for 3 h at 0 °C under a sealed system. Usual workup and purification by silica gel column chromatography of the residual oil afforded 2-butoxy-4-isopropenyltetrahydrofuran **12a** (0.15 g) in 80% yield.

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References

1) a) R. J. K. Taylor, "Organocopper Reagents A Practical Approach," Oxford University Press, Oxford (1994); b) B. H. Lipshutz and S. Sengupta, *Org. React.*, **41**, 135 (1992); c) B. H. Lipshutz, in "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, New York (1991), Vol. 1, Chap. 1.4, p. 107; d) B. H. Lipshutz, in "Encyclopedia of Inorganic Chemistry," ed by R. B. King, Wiley, New York (1994); e) Y. Ymamoto, *Angew. Chem., Int. Ed. Engl.*, **25**, 947 (1986); f) E. Nakamura, *Synlett*, **1991**, 539; g) P. Knochel and R. D. Singer, *Chem. Rev.*, **93**, 2117 (1993).

2) a) M. Isobe, S. Kondo, N. Nagasawa, and T. Goto, *Chem. Lett.*, **1977**, 679; b) D. Seebach and W. Langer, *Helv. Chim. Acta*, **62**, 1701 and 1710 (1979); c) T. Harada, T. Katsuhira, K. Hattori, and A. Oku, *J. Org. Chem.*, **58**, 2958 (1993); d) T. Harada, H. Wada, and A. Oku, *J. Org. Chem.*, **60**, 5370 (1995).

3) a) G. Cahiez, "*n*-Butylmanganese Chloride and Related Reagents in Encyclopedia of Reagents for Organic Synthesis," ed by L. Paquette, Wiley, Chichester (1995), p. 925; b) G. Cahiez, "Manganese(II) Chloride in Encyclopedia of Reagents for Organic Synthesis," ed by L. Paquette, Wiley, Chichester (1995), p. 3227; c) G. Cahiez, *An. Quim.*, **91**, 561 (1995); d) E. J. Corey and G. H. Posner, *Tetrahedron Lett.*, **1970**, 315; e) K. Okada, K. Oshima, and K. Utimoto, *J. Am. Chem. Soc.*, **118**, 6076 (1996); f) R. Inoue, H. Shinokubo, and K. Oshima, *Tetrahedron Lett.*, **37**, 5377 (1996).

4) a) D. Zhang and L. S. Liebeskind, *J. Org. Chem.*, **61**, 2594 (1996); b) W. F. Bailey and X.-L. Jiang, *J. Org. Chem.*, **61**, 2596 (1996); c) M. Uchiyama, M. Koike, M. Kameda, Y. Kondo, and T. Sakamoto, *J. Am. Chem. Soc.*, **118**, 8733 (1996).

5) a) C. P. Sloan, J. C. Cuevas, C. Quesnelle, and V. Snieckus, *Tetrahedron Lett.*, **29**, 4685 (1988); b) S. Wolff and H. M. R. Hoffmann, *Synthesis*, **1988**, 760; c) D. L. Boger and M. S. S. Palanki, *J. Am. Chem. Soc.*, **114**, 9318 (1992); d) A. V. R. Rao, M. K. Gurjar, D. S. Bose, and R. R. Devi, *J. Org. Chem.*, **56**, 1320 (1991); e) D. L. Boger, W. Yun, and B. R. Teegarden, *J. Org. Chem.*, **57**, 2873 (1992); f) D. L. J. Clive, N. Etkin, T. Joseph, and J. W. Lown, *J. Org. Chem.*, **58**, 2442 (1993); g) G. Boisvert and R. Giasson, *Tetrahedron Lett.*, **33**, 6587 (1992); h) R. Rai and D. B. Collum, *Tetrahedron Lett.*, **35**, 6221 (1994); i) T. Itoh, H. Ohara, and S. Emoto, *Tetrahedron Lett.*, **36**, 3531 (1995).

6) J. Iqbal, B. Bhatia, and N. K. Nayyar, *Chem. Rev.*, **94**, 519 (1994); Palladium-catalyzed cyclization: R. C. Larock and D. E. Stinn, *Tetrahedron Lett.*, **29**, 4687 (1988); R. C. Larock and S. Babu, *Tetrahedron Lett.*, **28**, 5291 (1987); R. C. Larock and D. E. Stinn, *Tetrahedron Lett.*, **30**, 2767 (1989); L. S. Hegedus, *Angew. Chem., Int. Ed. Engl.*, **27**, 1113 (1988); T. Sakamoto, Y. Kondo, and H. Yamanaka, *Heterocycles*, **27**, 2225 (1988); Nickel: M. Mori, S. Kudo, and Y. Ban, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 771; S. Olivero, J. C. Clinet, and E. Dunach, *Tetrahedron Lett.*, **36**, 4429 (1995); Cobalt: G. Pattenden, *Chem. Soc. Rev.*, **17**, 361 (1988); Zn–Mn: E. Riguet, I. Klement, C. K. Reddy, G. Cahiez, and P. Knochel, *Tetrahedron Lett.*, **37**, 5865 (1996); Zn–Ni: A. Vaupel and P. Knochel, *J. Org. Chem.*, **61**, 5743 (1996).

7) D. P. Curran and M. J. Totleben, *J. Am. Chem. Soc.*, **114**, 6050 (1992).

8) A part of this paper was published in a communication. J. Nakao, R. Inoue, H. Shinokubo, and K. Oshima, *J. Org. Chem.*, **62**, 1910 (1997).

9) Treatment of **1a** with Me_3MnLi followed by an addition of D_2O provided 2-deuteriophenyl prenyl ether in 93% yield (>98%*d*).

10) In the case of the reaction of 2-bromophenyl prenyl ether with *n*-Bu_3MnLi, formation of anionic species might compete with formation of a radical which is generated by single electron transfer form manganate(II) to halo ether.

11) Dodecane was obtained in 20% yield in addition to **2a** in the reaction of **1a** with (*n*-Hex)$_3$MnLi.

12) Decomposition of the dialkylmanganese species has been reported. M. Tamura and J. Kochi, *J. Organomet. Chem.*, **29**, 111 (1971).

13) An alternative mechanism, an iodine-manganese exchange followed by anionic carbomanganation giving **8**, could not be negated. A more detailed study is obviously necessary to conclude the mechanism.

14) J. Fossey, D. Lefort, and J. Sorba, in "Free Radicals in Organic Chemistry," John Wiley & Sons, Chichester (1995), p. 159.

15) Examples of sequences: (1) radical cyclization, (2) reduction to an organometallic, and (3) electrophilic trapping: a) W. A. Nugent and T. V. RajanBabu, *J. Am. Chem. Soc.*, **110**, 8561 (1988); b) K. Takai, K. Nitta, O. Fujimura, and K. Utimoto, *J. Org. Chem.*, **54**, 4732 (1989); c) See Ref. 7.

16) Anionic cyclization of **3** with *t*-BuLi has been reported.[4] However, an addition of a Grignard reagent (*n*-BuMgBr) to **1a** or **3a** in the absence of $MnCl_2$ afforded only the reduced product, phenyl prenyl ether, or *N*,*N*-diprenylaniline in 20 or 30% yield along with the recovered starting materials.

17) The catalytic reaction also proceeded in the atmosphere. Stirring a mixture of **3a** (1.0 mmol), *n*-BuMgBr (4.0 mmol), and

$MnCl_2$ (0.1 mmol) or $MnCl_2$ (0.3 mmol) in the atmosphere afforded **4a** in 60 or 80% yield, respectively, along with the recovered starting material **3a** in 30 or 14% yield. The reaction in a flask under argon balloon gave a better yield of **3a** than the reaction in the atmosphere. Thus, slow injection of oxygen might be essential for the catalytic reaction. The role of oxygen is not clear at this stage. However, we are tempted to assume following explanation. Zero-valent manganese could not react with iodoaniline, thus, Mn(0) must be reoxidized to Mn(II) species ($MnCl_2$ or MnI_2) by oxygen to complete a catalytic cycle.

18) a) B. Giese, "Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds," ed by J. E. Baldwin, Pergamon Press, Oxford (1986); b) B. Giese, *Angew. Chem., Int. Ed. Engl.*, **28**, 969 (1989); c) D. P. Curran, W. Shen, J. Zhang, and T. A. Heffner, *J. Am. Chem. Soc.*, **112**, 6738 (1990); d) N. A. Porter, D. M. Scott, I. J. Rosenstein, B. Giese, A. Veit, and H. G. Zeitz, *J. Am. Chem. Soc.*, **113**, 1791 (1991).

19) G. Stork, P. M. Sher, and H.-L. Chen, *J. Am. Chem. Soc.*, **108**, 6384 (1986).

20) Treatment of **11g** with tributylstannane in the presence of Et_3B afforded **12g** in 99% yield ($E/Z=44/56$) (Chart 1).

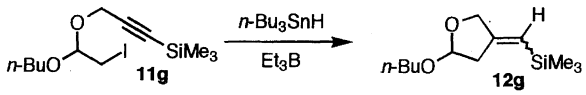

Chart 1.

21) A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, **41**, 3925 (1985).

22) Recently nickel or cobalt-catalyzed radical cyclization reaction has been reported. A. Vaupel and P. Knochel, *Tetrahedron Lett.*, **35**, 8349 (1994); T. Bamhaoud and J. Prandi, *J. Chem. Soc., Chem. Commun.*, **1996**, 1229.

23) P. A. Grieco, T. Oguri, and Y. Yokoyama, *Tetrahedron Lett.*, **1978**, 419.

24) T. Morikawa, T. Nishiwaki, Y. Iitake, and Y. Kobayashi, *Tetrahedron Lett.*, **28**, 671 (1987).

25) In contrast to the catalytic reaction of **1a**, in which the presence of oxygen was essential, the catalytic reaction of **11** was complete in 3 h at 0 °C under argon atmosphere in a sealed system. Thus, single electron transfer from zero-valent manganese to 2-iodoethanal acetal would provide alkyl radical and manganese(I) species as shown below (Chart 2).

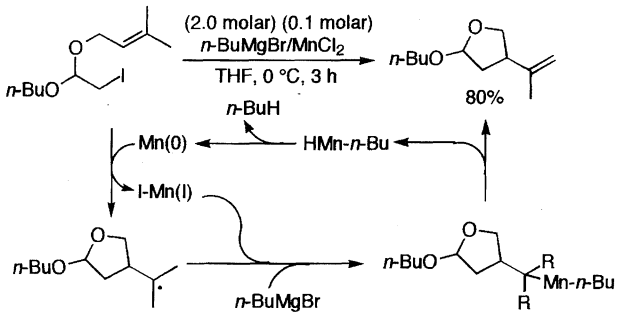

Chart 2.

26) D. S. Middelton and N. S. Simpkins, *Synth. Commun.*, **19**, 21 (1987).

27) K. Briner and A. Vasella, *Helv. Chim. Acta*, **72**, 1371 (1989).