Hydroindation of allenes and its application to radical cyclization†

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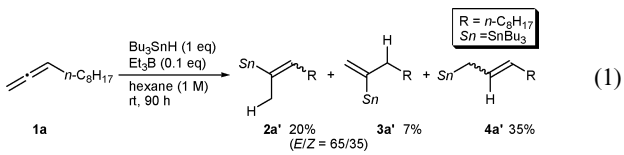
Received 26th February 2008, Accepted 11th March 2008
First published as an Advance Article on the web 9th April 2008
DOI: 10.1039/b803314e

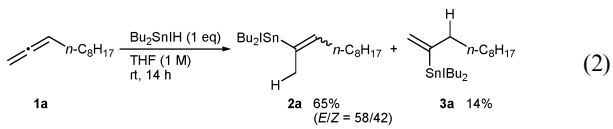
Hydroindation of allenes and radical cyclization of 1,2,7-trienes (allenenes) were accomplished by $HInCl_2$ with high regioselectivity to afford a variety of cyclic compounds. The resulting vinylic indiums could be used for successive coupling reactions in a one-pot procedure. The use of $HInCl_2$ generated slowly *in situ* is extremely effective for the radical cyclization.

Introduction

Radical carbon–carbon bond-forming reactions have been widely used in synthetic chemistry.[1] In particular, tandem reactions, including cyclization, have been widely studied, in which organic halides and/or unsaturated bonds such as dienes, enynes and diynes are generally used as starting substrates, while allene functionalities have rarely been used for cyclization.[2,3] In most of the reported cyclizations, tri-*n*-butyltin hydride (Bu_3SnH) has been exclusively used as a conventional radical agent.[4] However, reaction of allenes with Bu_3SnH gives organotin compounds as a mixture of isomers (eqn (1)). Recently we reported the central-carbon selective stannation of allenes using dibutyliodotin hydride (Bu_2SnIH) and the successive one-pot coupling with an aromatic iodide (eqn (2)–(4)).[5] The characteristic feature of the Bu_2SnIH promoted reaction is the stereoselectivity of hydrostannation which was well controlled by the substituents of the allenes, and unsymmetrically tri- and tetrasubstituted alkenes **5b** and **5c** were obtained stereoselectively in a one-pot procedure (eqn (3) and (4)).



(1)



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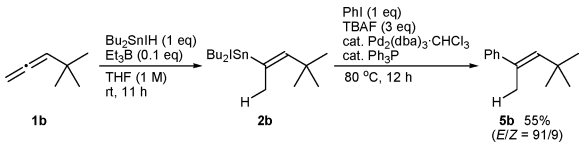
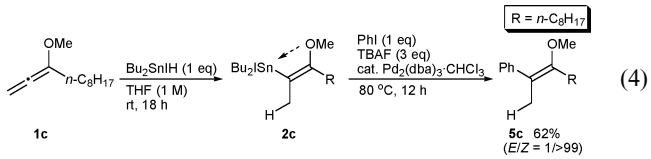


(3)



(4)

On the other hand, we have recently developed dichloroindium hydride ($HInCl_2$) as an alternative radical reagent that is more environmentally benign than Bu_3SnH. In addition, $HInCl_2$ can provide several types of radical reactions that cannot be attained using Bu_3SnH.[6] In this paper, we report the first hydroindation of allenes and radical cyclization of 1,2,7-trienes (allenenes). $HInCl_2$ presents similar regioselectivity to Bu_2SnIH and is more effective than Bu_2SnIH in the radical cyclization to give cyclized products. The resulting vinylindium product can also be used for further coupling reactions in a one-pot procedure.

Results and discussion

Initially, we examined the hydroindation of various allenes by $HInCl_2$ generated *in situ*, as shown in Table 1. The reactivity of $HInCl_2$ was found to be strongly dependent upon the hydride source in transmetallation with $InCl_3$. Among the metal hydrides examined, Et_3SiH was found to be the most effective hydride source, furnishing a mixture of 2-undecene (**6a**) (65%) and 1-undecene (**7a**) (20%) in the reaction of *n*-octylallene (**1a**) (entries 1–4). The hydroindation proceeded in a radical manner as demonstrated by complete suppression by a radical inhibitor (entry 5). The ratio of **6** : **7** depended on the substituents of allene **1**, and a bulky tertiary alkyl group afforded internal alkene **6d** with good regioselectivity (entry 6). Interestingly, the oxygen-substituted substrate **1e** afforded only the *E*-isomer of **6e** by coordination of oxygen to indium (entry 7). The reaction of disubstituted allenes **1f** and **1g** also gave alkenes **6f** and **6g** in moderate yields (entries 8 and 9). To confirm the regioselectivity of hydroindation, the resulting reaction mixture in entry 3 was treated with iodine, furnishing two types of vinyl iodides, **2a**″ and **3a**″, in which iodine was attached to the central carbon (Scheme 1). This result indicates that the indation took place selectively at the central carbon of the allene moiety.

Although central-carbon selective metallation could be achieved, the successive hydrogenation was not regioselective and produced a mixture of two types of vinylindiums. If the reaction took place *via* allyl radical species, this drawback could be overcome by the application to cyclization, which could cause

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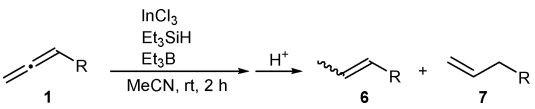
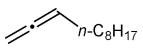
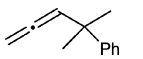
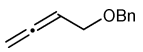
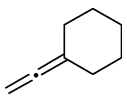
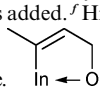
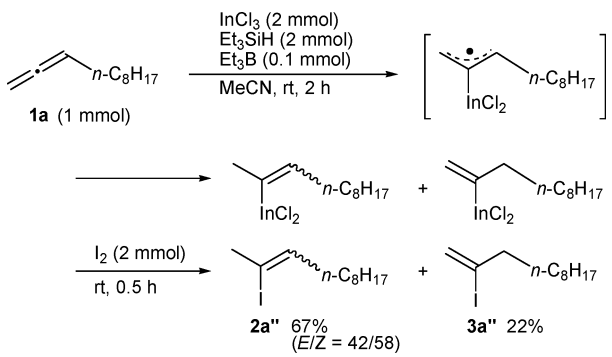
† Electronic supplementary information (ESI) available: Experimental procedures and characterizations. See DOI: 10.1039/b803314e

Table 1 Hydroindation of allenes[a]



Entry	Allene **1**		Yield (%) **6** (*E* : *Z*)	**7**
1[b]		**1a**	**6a** 40	**7a** 6
2[c]		**1a**	**6a** 4	**7a** 2
3		**1a**	**6a** 65 (57 : 43)	**7a** 20
4[d]		**1a**	**6a** 30 (70 : 30)	**7a** 8
5[e]		**1a**	**6a** 3	**7a** 0
6		**1d**	**6d** 71 (60 : 40)	**7d** 5
7		**1e**	**6e** 79 (>99 : 1)[f]	**7e** 10
8		**1f**	**6f** 32	**7f** 10
9		**1g**	**6g** 57[g]	

[a] $InCl_3$–Et_3SiH–MeCN system was used to generate $HInCl_2$. Reagents: allene **1** (1 mmol), $InCl_3$ (2 mmol), Et_3SiH (2 mmol), Et_3B (0.1 mmol), MeCN (2 mL). [b] $InCl_3$–Bu_3SnH–THF system was used to generate $HInCl_2$. [c] $InCl_3$–$NaBH_4$–MeCN system at −30 °C was used to generate $HInCl_2$. [d] $InCl_2OMe$–$PhSiH_3$–THF system was used to generate $HInCl_2$. [e] Galvinoxyl (0.1 mmol) was added. [f] High stereoselectivity should depend on the chelation shown here.  [g] Cyclononene was obtained.

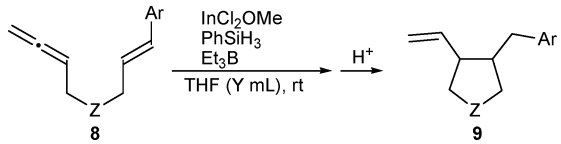


Scheme 1 Regioselective indation of the central carbon of the allene.

the regioselective intramolecular addition of the intermediate allyl radicals to alkenes.

As expected, when 1,2,7-triene (allenene) **8a** was treated with the $InCl_3$–Et_3SiH system, the desired cyclic product **9a** was obtained in 60% yield under the conditions noted in Table 2 (entry 1). This result indicates that the regioselective reaction with the allyl radical was caused by cyclization. When an $InCl_2OMe$–hydrosilane system was used, cyclic product **9a** was also obtained in 81% yield (entry 2). When allenene **8b** was treated with the

Table 2 Radical cyclization of allenenes using $HInCl_2$[a]



Entry	Allenene **8**	Ar	Z	Y	*t*/h	Yield (%) (dr)[c]
1[b]	**8a**	Ph	$C(COOEt)_2$	30	20	**9a** 60 (56 : 44)
2	**8a**	Ph	$C(COOEt)_2$	10	20	**9a** 81 (56 : 44)
3[b]	**8b**	Ph	O	2	2	Complicated
4[b]	**8b**	Ph	O	10	2	Complicated
5	**8b**	Ph	O	10	20	**9b** >99 (87 : 13)
6	**8b**	Ph	O	2	2	**9b** 32 (89 : 11)
7	**8b**	Ph	O	2	20	**9b** 47 (87 : 13)
8	**8c**	*p*-ClC_6H_4	O	10	20	**9c** >99 (83 : 17)
9	**8d**	*p*-$MeOC_6H_4$	O	10	20	**9d** 62 (87 : 13)
10	**8e**	1-naphthyl	O	10	20	**9e** >99 (85 : 15)

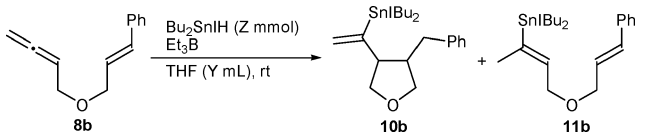
[a] Reagents: allenene **8** (1 mmol), $InCl_2OMe$ (2 mmol), $PhSiH_3$ (2.4 mmol), Et_3B (0.1 mmol). [b] Indium hydride was generated by the $InCl_3$ (2 mmol), Et_3SiH (2 mmol), MeCN (30 mL) system instead of $InCl_2OMe$–$PhSiH_3$–THF respectively. [c] Stereochemistry is given in the ESI.

$InCl_3$–Et_3SiH system, only a complicated mixture was obtained, regardless of the amount of solvent, perhaps due to its strong Lewis acidity (entries 3 and 4).[6e,7] In contrast, when an $InCl_2OMe$–hydrosilane system was used, cyclic product **9b** was obtained quantitatively (entry 5). Stereoselectivity was found to improve up to 87 : 13 in comparison with **8a**. We have already shown that this $InCl_2OMe$–hydrosilane system has an advantage under neutral and mild conditions, where in contrast to the $InCl_3$–Et_3SiH system, a strong Lewis acid such as silyl chloride was not formed during the formation of $HInCl_2$.[6d,e] In the reaction of **8a**, cyclopentane derivative **9a** was obtained by both systems, where the choice of method for generating $HInCl_2$ did not matter because allenene **8a** did not have an ether moiety, which might have been decomposed by acidic conditions (entries 1 and 2). In the $InCl_2OMe$–hydrosilane system, the diluted conditions and long reaction period were essential because the conditions noted in entries 6 and 7 gave only 32% and 47% yields respectively. Allenenes **8c** and **8d** functionalized by substituents such as Cl and OMe also gave cyclic products, **9c** and **9d**, in moderate to excellent yields (entries 8 and 9). Naphthalene derivative **8e** gave the corresponding product **9e** in a quantitative yield (entry 10).

When Bu_2SnIH, which has regioselectivity similar to $HInCl_2$,[5a] was applied to the reaction of **8b**, non-cyclized vinyltin **11b** was obtained in 28% yield with cyclized product **10b** in 43% yield (Table 3, entry 1). As anticipated, more concentrated conditions gave a reduced amount of the cyclic product **10b** (entries 2 and 3).

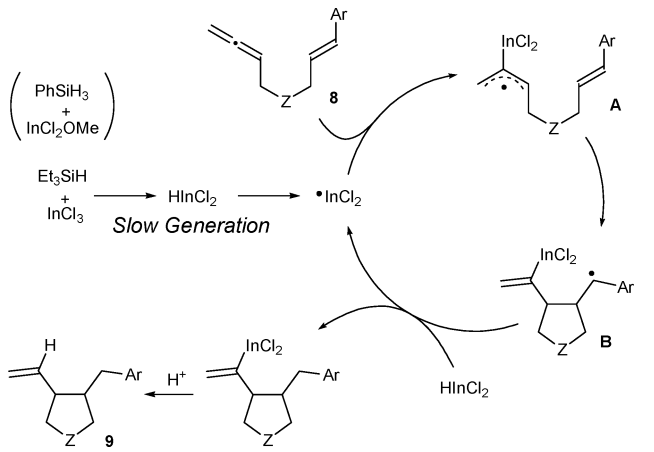
A plausible cyclization mechanism for $HInCl_2$-promoted cyclization using allenene **8** is illustrated in Scheme 2. The $HInCl_2$ formed *in situ* affords an indium radical (•$InCl_2$). The resulting indium radical adds to the central carbon of the allene moiety to give stable allylic radical **A**, which reacts with the remaining internal alkene moiety to give cyclized radical **B**. Probably due to the higher hydrogen donating ability of Bu_2SnIH than $HInCl_2$, hydrogenation of intermediate **A** occurred in the Bu_2SnIH-promoted reaction. Thus $HInCl_2$, which is generated slowly by the

Table 3 Radical cyclization of allenene **8b** using Bu_2SnIH[a]



Entry	Y	Z	*t*/h	Yield (%) 10b	11b
1	10 mL	1 mmol	20	43	28
2	10 mL	2 mmol	20	26	42
3	2 mL	2 mmol	68	10	68

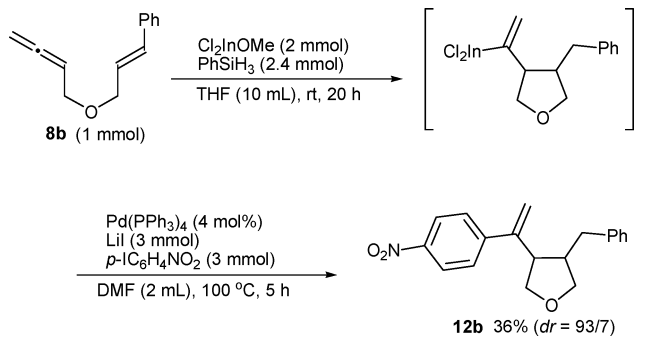
[a] Reagents: allenene **8b** (1 mmol), Et_3B (0.1 mmol).



Scheme 2 A plausible mechanism for cyclization.

transmetallation, is more effective for this cyclization step than Bu_2SnIH. After cyclization, radical **B** is hydrogenated by $HInCl_2$ followed by protonation to give cyclic product **9**.

Finally, we tried a one-pot coupling of the generated cyclized vinylindium species.[8] After cyclization, instead of the above-mentioned protonolysis of the resulting product, Pd-catalyzed coupling with *p*-nitrophenyl iodide was performed under heating (Scheme 3). As a result, the desired product **12b** was obtained in a moderate yield (36%). Although a more appropriate coupling procedure should be developed, this result presents a direct route to *gem*-disubstituted alkenes *via* hydroindation, cyclization and coupling reactions. The yield of the desired coupling product **12b** was not very high at this stage, because of steric hindrance in the



Scheme 3 Successive coupling reaction of vinylindium.

vinylic indium species. However, this result proved the utility of the bulky group substituted-vinylindium for the coupling reaction at the internal carbon.

Conclusions

In summary, the usefulness of hydroindation of allenes was indicated. As an application of hydroindation, the first radical cyclization of 1,2,7-trienes (allenenes) was accomplished. In the radical cyclization, $HInCl_2$ is superior to Bu_2SnIH. The nature of $HInCl_2$ slowly generated *in situ* is extremely effective for the radical cyclization to give a vinylindium which could be used for a coupling reaction.

Experimental

General

IR spectra were recorded as thin films on a Horiba FT-720 spectrometer. All ^1H and ^{13}C NMR spectra were recorded with a JEOL JMTC-400/54/SS (400 and 100 MHz, respectively) in deuterochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane as an internal standard. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed using MERCK Silica gel 60. Purification of products by a recycle GPC system was performed by JAPAN ANALYTICAL INDUSTRY CO., LTD. LC-908. Yields were determined by ^1H NMR analysis using an internal standard. Stereochemistry of products was determined from the NOE-difference spectrum or coupling constant in the ^1H NMR spectrum.

Typical procedure for radical cyclization of allenene 8b using Bu_2SnIH (Table 3)

A 30 mL round bottom flask was dried by flame under reduced pressure. After the flask was filled with nitrogen, THF (10 mL) was added. Bu_2SnH_2 (0.234 g, 1.0 mmol) and Bu_2SnI_2 (0.486 g, 1.0 mmol) were added successively to generate Bu_2SnIH (2.0 mmol) by the redistribution reaction. To the mixture was added allenene **8b** (0.186 g, 1.0 mmol) and the resulting mixture was stirred at rt for 20 h. To the resulting solution was added $CHCl_3$ (5 mL) to completely decompose the remaining tin hydride and the volatiles were removed under reduced pressure. Products were determined from ^1H NMR spectroscopy. Purification was performed by recycle GPC eluting with $CHCl_3$. Products **10b** and **11b** were not isolated as pure compunds. The identifiable signals in the crude mixture are given here. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.65 (d, J = 15.7 Hz, 1H, **11b**), 6.28–6.16 (m, 2H, **11b**), 5.81 (s, 1H, **10b**), 5.56 (s, 1H, **10b**).

Typical procedure for hydroindation of allenes using $HInCl_2$ ($InCl_3$–Et_3SiH system, Table 1)

A 10 mL round bottom flask charged with $InCl_3$ (0.442 g, 2 mmol) was heated at 110 °C *in vacuo* for 1 h. After the flask was filled with nitrogen, MeCN (2 mL) and Et_3SiH (0.233 g, 2.0 mmol) were added and the mixture was stirred at rt for 5 min. Then the allene (1.0 mmol) and Et_3B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively. The resulting mixture was stirred at rt for 2 h. After 1M HCl aq was added, the reaction

mixture was extracted with ether (10 mL × 3). The combined organic layer was dried over $MgSO_4$ and concentrated. The product was determined from ^{1}H NMR spectroscopy. Purification was performed by silica gel column chromatography eluting with hexane. Further purification was performed by distillation under reduced pressure.

((*E*)-1,1-Dimethyl-but-2-enyl)benzene, 6d-*E*. IR (neat) 1597 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (d, J = 8.0 Hz, 2H), 7.29 (dd, J = 8.0 and 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 5.64 (dq, J = 15.5 and 1.4 Hz, 1H), 5.45 (dq, J = 15.5 and 6.3 Hz, 1H), 1.71 (dd, J = 6.3 and 1.4 Hz, 3H), 1.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.40, 141.08, 127.97, 126.11, 125.57, 120.95, 40.27, 28.86, 18.03; MS (EI, 70 eV) m/z 160 (M^+, 39), 145 ($M^+ - CH_3$, 100), 117 (22); HRMS calcd for $C_{12}H_{16}$: 160.1252, found: m/z 160.1257 (EI, (M^+), +0.5 mmu).

((*Z*)-1,1-Dimethyl-but-2-enyl)benzene, 6d-*Z*. IR (neat) 1601 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, J = 8.0 Hz, 2H), 7.28 (dd, J = 8.0 and 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 5.69 (dq, J = 11.4 and 1.7 Hz, 1H), 5.41 (dq, J = 11.4 and 7.2 Hz, 1H), 1.43 (s, 6H), 1.20 (dd, J = 7.2 and 1.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.42, 140.56, 127.99, 126.11, 125.26, 124.77, 39.92, 31.12, 14.19; MS (EI, 70 eV) m/z 160 (M^+, 36), 145 ($M^+ - CH_3$, 100), 117 (23); HRMS calcd for $C_{12}H_{16}$: 160.1252, found: m/z 160.1250 (EI, (M^+), −0.2 mmu).

Typical procedure for radical cyclization of allenenes 8 using $HInCl_2$ ($InCl_2OMe$–$PhSiH_3$ system, Table 2)

A 30 mL round bottom flask charged with $InCl_3$ (0.442 g, 2.0 mmol) and NaOMe (0.108 g, 2.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After the flask was filled with nitrogen, THF (10 mL) was added to dissolve the $InCl_3$. The resulting mixture was stirred at rt for 0.5 h. Then $PhSiH_3$ (0.260 g, 2.4 mmol), allenene **8** (1.0 mmol) and Et_3B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively, and the resulting solution was stirred at rt for 20 h. After 1M HCl aq was added, the reaction mixture was extracted with ether (10 mL × 3). The combined organic layer was dried over $MgSO_4$ and concentrated. The cyclized product was determined from ^{1}H NMR spectroscopy. Purification was performed by silica gel column chromatography eluting with hexane. Further purification was performed by distillation under reduced pressure.

Diethyl 3-benzyl-4-vinylcyclopentane-1,1-dicarboxylate, 9a. 81%; (**major**) IR (neat) 1732 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30–7.14 (m, 5H), 5.69 (ddd, J = 17.1, 10.2 and 8.2 Hz, 1H), 5.09 (dd, J = 17.1 and 1.9 Hz, 1H), 5.05 (dd, J = 10.2 and 1.9 Hz, 1H), 4.22–4.09 (m, 4H), 2.92 (dd, J = 13.5 and 3.6 Hz, 1H), 2.50 (dd, J = 13.5 and 7.5 Hz, 1H), 2.36–2.21 (m, 3H), 2.05 (dd, J = 13.5 and 10.9 Hz, 1H), 2.00–1.87 (m, 2H), 1.23 (t, J = 7.0 Hz, 3H), 1.19 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.63, 172.47, 140.74, 139.96, 128.81, 128.24, 125.83, 115.83, 61.41, 61.36, 58.21, 50.04, 46.71, 40.30, 39.56, 39.17, 14.00, 13.96; MS (EI, 70 eV) m/z 330 (M^+, 28), 256 (52), 239 (36), 211 (26), 183 (33), 182 (20), 173 (36), 165 (63), 143 (79), 91 (CH_2Ph, 100); HRMS calcd for $C_{20}H_{26}O_4$: 330.1831, found: m/z 330.1813 (EI, (M^+), −1.8 mmu); (**minor**) This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC are given here. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.85 (ddd, J = 17.1, 10.3 and 8.5 Hz, 1H), 5.08 (dd, J = 10.3 and 1.9 Hz, 1H), 5.04 (dd, J = 17.1 and 1.9 Hz, 1H), 2.51 (dd, J = 14.0 and 7.2 Hz, 1H), 2.08 (dd, J = 13.8 and 8.2 Hz, 1H), 1.24 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.77, 172.69, 141.16, 138.10, 128.87, 128.22, 125.75, 115.84, 61.45, 61.42, 58.75, 46.57, 44.81, 38.80, 38.24, 36.30, 14.02, 13.97; MS (EI, 70 eV) m/z 330 (M^+, 22), 256 (59), 239 (49), 229 (24), 184 (23), 183 (37), 182 (30), 173 (46), 165 (65), 143 (56), 91 (CH_2Ph, 100); HRMS calcd for $C_{20}H_{26}O_4$: 330.1831, found: m/z 330.1820 (EI, (M^+), −1.1 mmu).

3-Benzyl-4-vinyltetrahydrofuran, 9b. >99%; (**major**, **9b-*trans***) the stereochemistry of the products was determined from NOE observations. See ESI†. IR (neat) 1639 (C=C) cm^{-1}, 1053 (C–O–C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (dd, J = 7.5 and 7.4 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.5, 2H), 5.69 (ddd, J = 17.1 and 10.1 and 8.5 Hz, 1H), 5.08 (dd, J = 17.1 and 1.7 Hz, 1H), 5.05 (dd, J = 10.1 and 1.7 Hz, 1H), 4.03 (dd, J = 8.2 and 8.2 Hz, 1H), 3.88 (dd, J = 8.5 and 7.5 Hz, 1H), 3.54 (dd, J = 8.2 and 8.7 Hz, 1H), 3.53 (dd, J = 8.5 and 7.9 Hz, 1H), 2.91 (dd, J = 13.8 and 4.8 Hz, 1H), 2.58–2.48 (m, 2H), 2.31–2.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.28, 137.85, 128.62, 128.38, 126.09, 116.46, 73.35, 72.85, 50.32, 47.24, 37.75; MS (EI, 70 eV) m/z 188 (M^+, 1), 157 (27), 129 (30), 104 (32), 92 (51), 91 ($PhCH_2$, 100); HRMS calcd for $C_{13}H_{16}O$: 188.1201, found: m/z 188.1210 (EI, (M^+), +0.9 mmu); anal. calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57, found: C, 82.92; H, 8.31%; (**minor**, **9b-*cis***) This compound was a minor product and was not isolated as a pure compound. The identifiable signals in the crude mixture after GPC are given here. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.89 (ddd, J = 17.1, 10.3 and 9.4 Hz, 1H), 3.96 (dd, J = 8.5 and 6.5 Hz, 1H), 3.81 (dd, J = 8.6 and 7.2 Hz, 1H), 3.74 (dd, J = 8.5 and 4.8 Hz, 1H), 2.78 (dd, J = 13.5 and 5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.78, 136.13, 128.75, 128.49, 125.97, 116.88, 72.67, 71.93, 46.74, 44.82, 34.25; MS (EI, 70 eV) m/z 188 (M^+, 2), 157 (27), 105 (25), 104 (29), 92 (47), 91 (CH_2Ph, 100); HRMS calcd for $C_{13}H_{16}O$: 188.1201, found: m/z 188.1198 (EI, (M^+), −0.3 mmu).

3-(4-Chlorophenylmethyl)-4-vinyltetrahydrofuran, 9c. >99%; the stereochemistry of the products was determined from comparison of ^{1}H NMR spectrum with **9b**. These compounds were not isolated as pure compounds and were obtained as a mixture of diastereomers (**9c-*trans*** : **9c-*cis*** = 83 : 17). The observed data are given here. IR (neat) 1639 (C=C) cm^{-1}, 1095 (C–O–C) cm^{-1}, 1053 (C–O–C) cm^{-1}; anal. calcd for $C_{13}H_{15}ClO$: C, 70.11; H, 6.79; Cl, 15.92, found: C, 69.84; H, 6.58; Cl, 16.20%; (**major**, **9c-*trans***) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 5.67 (ddd, J = 17.0, 10.1 and 8.5 Hz, 1H), 5.07 (dd, J = 17.0 and 1.7 Hz, 1H), 5.05 (dd, J = 10.1 and 1.7 Hz, 1H), 4.02 (dd, J = 8.5 and 8.2 Hz, 1H), 3.86 (dd, J = 8.5 and 7.5 Hz, 1H), 3.54 (dd, J = 8.5 and 8.5 Hz, 1H), 3.49 (dd, J = 8.5 and 8.2 Hz, 1H), 2.87 (dd, J = 13.8 and 5.1 Hz, 1H), 2.56–2.46 (m, 2H), 2.28–2.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.69, 137.69, 131.87, 129.95, 128.50, 116.60, 73.17, 72.85, 50.26, 47.13, 37.13; MS (EI, 70 eV) m/z 222 (M^+, 9), 138 (27), 125 ($CH_2C_6H_4Cl$, 100), 91 (22); HRMS calcd for $C_{13}H_{15}ClO$: 222.0811, found: m/z 222.0808 (EI, (M^+), −0.3 mmu); (**minor**, **9c-*cis***) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.86 (ddd, J = 17.0, 10.1 and 9.2 Hz, 1H), 5.16 (dd, J = 10.1 and 1.7 Hz, 1H), 5.10 (dd, J = 17.0 and 1.7 Hz, 1H), 3.96 (dd,

J = 8.5 and 6.5 Hz, 1H), 3.80 (dd, J = 8.5 and 7.0 Hz, 1H), 3.74 (dd, J = 8.5 and 4.8 Hz, 1H), 2.74 (dd, J = 13.5 and 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.20, 135.94, 131.75, 117.10, 72.69, 71.81, 46.66, 44.71, 33.62; MS (EI, 70 eV) m/z 222 (M^+, 3), 167 (32), 139 (30), 138 (29), 127 (36), 125 ($CH_2C_6H_4Cl$, 100), 91 (20); HRMS calcd for $C_{13}H_{15}ClO$: 222.0811, found: m/z 222.0818 (EI, (M^+), + 0.7 mmu).

3-(4-Methoxyphenylmethyl)-4-vinyltetrahydrofuran, 9d. 62%; the stereochemistry of the products was determined by comparison of the ^{1}H NMR spectrum with **9b**; (**major**, **9d-*trans***) IR (neat) 1639 (C=C) cm^{-1}, 1250 (C–O–C) cm^{-1}, 1111 (C–O–C) cm^{-1}, 1038 (C–O–C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 5.69 (ddd, J = 17.0, 10.1 and 8.5 Hz, 1H), 5.08 (dd, J = 17.0 and 1.4 Hz, 1H), 5.05 (dd, J = 10.1 and 1.4 Hz, 1H), 4.02 (dd, J = 8.5 and 8.2 Hz, 1H), 3.87 (dd, J = 8.5 and 7.5 Hz, 1H), 3.79 (s, 3H), 3.54 (dd, J = 8.5 and 8.5 Hz, 1H), 3.51 (dd, J = 8.5 and 8.2 Hz, 1H), 2.85 (dd, J = 13.8 and 4.8 Hz, 1H), 2.56–2.43 (m, 2H), 2.28–2.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.89, 137.92, 132.32, 129.53, 116.39, 113.73, 73.34, 72.85, 55.19, 50.21, 47.43, 36.80; MS (EI, 70 eV) m/z 218 (M^+, 16), 121 ($CH_2C_6H_4OMe$, 100); HRMS calcd for $C_{14}H_{18}O_2$: 218.1307, found: m/z 218.1313 (EI, (M^+), +0.6 mmu); (**minor**, **9d-*cis***) this compound was a minor product and was not isolated as a pure compound. The identifiable signals in the crude mixture after GPC are given here. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.88 (ddd, J = 16.9, 10.4 and 9.2 Hz, 1H), 5.15 (dd, J = 10.4 and 1.9 Hz, 1H), 5.11 (dd, J = 16.9 and 1.9 Hz, 1H), 3.96 (dd, J = 8.5 and 6.8 Hz, 1H), 2.72 (dd, J = 13.5 and 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.20, 132.80, 129.52, 116.81, 72.70, 71.98, 46.73, 45.04, 33.32; MS (EI, 70 eV) m/z 218 (M^+, 14), 163 (22), 148 (24), 121 ($CH_2C_6H_4OMe$, 100); HRMS calcd for $C_{14}H_{18}O_2$: 218.1307, found: m/z 218.1309 (EI, (M^+), +0.2 mmu).

3-(Naphthalen-1-ylmethyl)-4-vinyltetrahydrofuran, 9e. >99%; the stereochemistry of the products was determined from comparison of the ^{1}H NMR spectrum with **9b**; (**major**, **9e-*trans***) IR (neat) 1639 (C=C) cm^{-1}, 1065 (C–O–C) cm^{-1}, 1041 (C–O–C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.53–7.45 (m, 2H), 7.37 (dd, J = 8.2 and 7.0 Hz, 1H), 7.27 (d, J = 7.0 Hz, 1H), 5.73 (ddd, J = 17.0, 10.0 and 8.5 Hz, 1H), 5.14 (dd, J = 17.0 and 1.7 Hz, 1H), 5.10 (dd, J = 10.1 and 1.7 Hz, 1H), 4.07 (dd, J = 8.5 and 8.0 Hz, 1H), 3.80 (dd, J = 8.5 and 7.5 Hz, 1H), 3.60 (dd, J = 8.5 and 8.2 Hz, 1H), 3.54 (dd, J = 8.5 and 8.5 Hz, 1H), 3.45 (dd, J = 14.0 and 4.6 Hz, 1H), 2.85 (dd, J = 14.0 and 9.9 Hz, 1H), 2.65 (dddd, J = 8.5, 8.5, 8.2 and 8.0 Hz, 1H), 2.50–2.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.80, 136.43, 133.84, 131.67, 128.80, 127.02, 126.21, 125.87, 125.52, 125.39, 123.48, 116.72, 73.58, 72.90, 50.85, 46.20, 34.98; MS (EI, 70 eV) m/z 238 (M^+, 32), 142 (100), 141 (CH_2Np, 96); HRMS calcd for $C_{17}H_{18}O$: 238.1358, found: m/z 238.1362 (EI, (M^+), +0.4 mmu); (**minor**, **9e-*cis***) This compound was a minor product and was not isolated as a pure compound. The identifiable signals in the crude mixture after GPC are given here. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.03 (ddd, J = 16.9, 10.1 and 9.2 Hz, 1H), 3.99 (dd, J = 8.5 and 7.0 Hz, 1H), 3.31 (dd, J = 13.8 and 4.3 Hz, 1H), 3.05–2.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.78, 136.12, 133.90, 131.74, 128.84, 126.92, 126.42, 123.55, 117.26, 72.46, 72.06, 47.08, 43.83, 31.22; MS (EI, 70 eV) m/z 238 (M^+, 35), 155 (28), 142 (88), 141 (CH_2Np, 100), 115 (25); HRMS calcd for $C_{17}H_{18}O$: 238.1358, found: m/z 238.1371 (EI, (M^+), +1.3 mmu).

Typical procedure for radical cyclization of allenene 8b and successive coupling ($InCl_2OMe$–$PhSiH_3$ system, Scheme 3)

A 30 mL round bottom flask charged with $InCl_3$ (0.442 g, 2.0 mmol) and NaOMe (0.108 g, 2.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After the flask was filled with nitrogen, THF (10 mL) was added to dissolve the $InCl_3$. The resulting mixture was stirred at rt for 0.5 h. Then $PhSiH_3$ (0.260 g, 2.4 mmol), allenene **8b** (1.0 mmol) and Et_3B (0.1 mL, 1 M solution in hexane, 0.1 mmol) were added successively, and the resulting solution was stirred at rt for 20 h. After DMF (2 mL) was added, the THF was removed under reduced pressure. Then $IC_6H_4NO_2$-*p* (0.204 g, 1.0 mmol), $Pd(Ph_3P)_4$ (0.046 g, 4 mol%) and LiI (3.0 mmol) were added and the mixture was stirred at 100 °C for 5 h. After the reaction, the resulting solution was filtrated through celite. After concentration of the filtrate, the yield of product **12b** was determined from the ^{1}H NMR spectrum (36% yield). Further purification was performed by silica gel column chromatography eluting with hexane–AcOEt = 9 : 1.

3-Benzyl-4-(1-(4-nitrophenyl)vinyl)tetrahydrofuran, 12b. 36%; (**major**) IR (neat) 1597 (C=C) cm^{-1}, 1516 (NO_2) cm^{-1}, 1346 (NO_2) cm^{-1}, 1111 (C–O–C) cm^{-1}, 1061 (C–O–C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J = 8.9 Hz, 2H), 7.31–7.19 (m, 5H), 7.10 (d, J = 8.2 Hz, 2H), 5.45 (s, 1H), 5.38 (s, 1H), 4.15 (dd, J = 8.7 and 7.2 Hz, 1H), 4.01 (dd, J = 8.5 and 7.0 Hz, 1H), 3.77 (dd, J = 8.7 and 6.0 Hz, 1H), 3.65 (dd, J = 8.5 and 6.0 Hz, 1H), 3.03 (ddd, J = 7.2, 6.8 and 6.0 Hz, 1H), 2.81 (dd, J = 13.8 and 7.2 Hz, 1H), 2.70 (dd, J = 13.8 and 8.0 Hz, 1H), 2.57–2.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.15, 147.48, 146.88, 139.63, 128.68, 128.47, 127.06, 126.32, 123.48, 115.56, 73.04, 73.00, 48.79, 46.85, 38.96; MS (EI, 70 eV) m/z 309 (M^+, 1), 218 ($M^+ - CH_2Ph$, 33), 130 (35), 92 (45), 91 ($PhCH_2$, 100); HRMS calcd for $C_{19}H_{19}NO_3$: 309.1365, found: m/z 309.1359 (EI, (M^+), −0.6 mmu); (**minor**) this compound was a minor product and was not isolated as a pure compound. The identifiable signals in the crude mixture after silica gel column chromatography are given here. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.61 (s, 1H), 5.28 (s, 1H); MS (EI, 70 eV) m/z 309 (M^+, 5), 278 (36), 177 (24), 160 (20), 146 (22), 133 (26), 132 (21), 131 (23), 130 (78), 129 (22), 128 (24), 117 (100), 115 (37), 105 (92), 92 (21), 91 ($PhCH_2$, 98); HRMS calcd for $C_{19}H_{19}NO_3$: 309.1365, found: m/z 309.1364 (EI, (M^+), −0.1 mmu).

Acknowledgements

This research has been supported by the JSPS Research Fellowships for Young Scientists, and by the Grant-in-Aid for Scientific Research on Priority Areas (459 and 460) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by the JFE 21st Foundation and Nihonshouken Foundation.

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