Allylindation of Cyclopropenes in Organic and Aqueous Media: Switching the Regio- and Stereoselectivity Based on the Chelation with a Hydroxyl Group and the Crystal Structure of the Cyclopropylindium Product

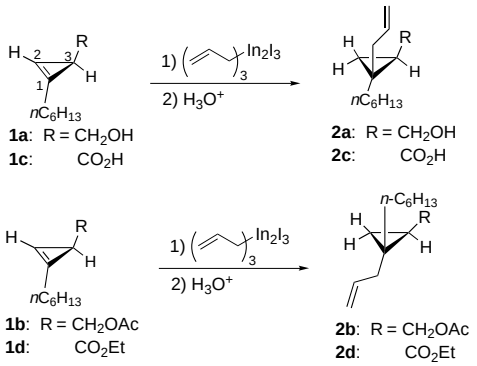
Shuki Araki,* Fumio Shiraki, Takashi Tanaka, Hiroyuki Nakano, Kandasamy Subburaj, Tsunehisa Hirashita, Hatsuo Yamamura, and Masao Kawai[a]

Abstract: Hydroxy-bearing cyclopropenes react with allylindium reagents to undergo clean allylindation both in organic and aqueous media, in which the chelation of the hydroxyl group to indium plays the central role. The regio- and stereoselectivity have been regulated both by the location of the hydroxyl group in the molecules and the reaction solvents. In particular, the allylindation in water shows marked differences from that in organic solvents; the regio- and stereoselectivity have totally been reversed compared with those in organic solvents. Unusually stable cyclopropylindium compounds have been isolated from the reaction of 1-(ω-hydroxyalkyl)-cyclopropenes and the structure has fully been established by X-ray crystallography.

Keywords: C–C coupling · indium · metalation · neighboring-group effects · solvent effects

Introduction

Addition of organometalic compounds to unsaturated molecules (carbometalation) is a fundamental reaction in organic synthesis.[1] Various main group metals and transition metals have hitherto been utilized for carbometalation, of which indium has emerged as a versatile metal only recently. Allylindium reagents have been found to undergo smooth addition reactions to carbon–carbon multiple bonds of alkynes,[2] alkenes,[3] and allenes.[4] In our work on the first allylindation of cyclopropenes,[5, 6] it was shown that the reaction of 1-hexyl-3-hydroxymethylcyclopropene (**1a**) with allylindium sesquiiodide gave the corresponding allylcyclopropane **2a** *cis*-selectively[7] (Scheme 1). The allyl group was introduced exclusively to the substituted C^1 carbon and the indium atom to the less-hindered C^2 carbon, minimizing the steric repulsion between the bulky indium and the hexyl group. The observed high *cis* selectivity can be explained in terms of the chelation of the hydroxyl group to the indium atom of the allylindium reagent. This chelation-controlled *cis* preference was reversed by the protection of the hydroxyl group, that is, allylindation of the acetate **1b** proceeded with the complete *trans* selectivity to give **2b**.



Scheme 1. Allylindation of cyclopropenes **1a–d**.

Similarly, the *cis* preference of the carboxylic acid **1c** was reversed in the ethyl ester **1d**. Thus, the hydroxymethyl and carboxy groups at the C^3 carbon of the cyclopropenes have been found to excert an important effect in attaining the *cis* selectivity. A similar chelation effect can, in principle, be expected also for a hydroxyl group in an appropriate position of cyclopropene substrates. We now demonstrate that this is the case; both the regio- and stereoselectivity can be regulated by changing the relative position of the hydroxyl group. Furthermore, we disclose that allylindation of hydroxy-bearing cyclopropenes in water shows marked differences from that in organic solvents; the regio- and stereoselectivity have totally been reversed compared with those in organic solvents.[8]

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Results and Discussion

The hydroxy-bearing cyclopropenes used in this work were readily prepared by the rhodium-catalyzed carbene addition to ω-acetoxy-1-alkynes. Selective hydrolysis of the acetoxy group of the resulting 2-(ω-acetoxyalkyl)cyclopropene-1-carboxylates furnished the hydroxy esters **1e**–**g**. The reduction of **1e**–**g** with Dibal-H gave dihydroxycyclopropenes **1h**–**j**. Allylindation of these cyclopropenes was conducted with preformed allylindium reagents (Grignard-type reaction) or, more conveniently, by mixing allyl halides, indium, and the cyclopropenes all together (Barbier-type reaction). Both the methods gave almost coincident results. First, cyclopropene **1e** with a 2-hydroxyethyl group at the C^1 carbon was treated with allylindium sesquiiodide in THF. The reaction mixture was quenched with 1M hydrochloric acid. Cyclopropylindium **3** (36% yield) was isolated as colorless crystals after column chromatographic purification, together with a small amount (13%) of the minor product **4** (Scheme 2).

The structure of **3** was unambiguously determined by X-ray analysis. Compound **3** crystallizes in the triclinic ($P\bar{1}$) space group from chloroform. It is important to note that the iodine atoms in the allylindium reagent have been replaced by chlorine atoms during the acidic workup with hydrochloric acid. As shown in Figure 1, both the hydroxyl and carbonyl groups are coordinated to the indium atom, thus revealing that **3** is the C^2-allylated *cis*-adduct. One of the chlorine atoms is coordinated to the neighboring indium atom, which results in the chlorine-bridged dimeric structure. The bridging In–Cl bond lengths are 2.543(3) and 2.626(3) Å, which are longer than the non-bridged Cl–In bond length (2.356(3) Å); accordingly, the geometry at the indium atom is distorted octahedral with a coordination number of six at the indium atom. Surprisingly, cyclopropylindium **3** is unusually stable to hydrolysis; it is stable towards 1M hydrochloric acid for a short time, but the protolysis occurred readily with 10M hydrochloric acid giving the protonated cyclopropane **5** (Scheme 3).

For the corresponding cyclopropylindium precursor of the *trans* adduct **4**, on the other hand, such stabilization through

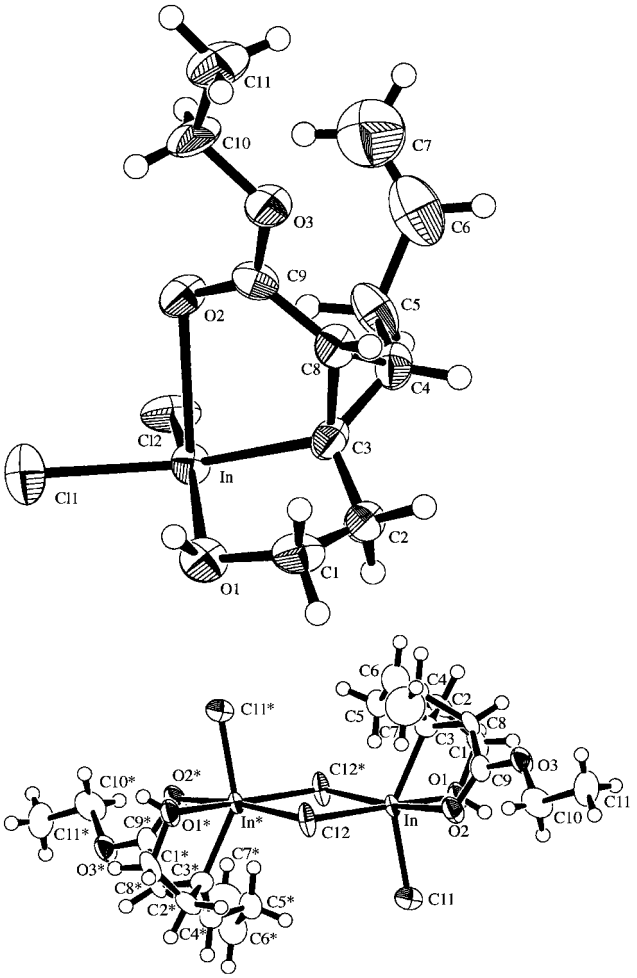
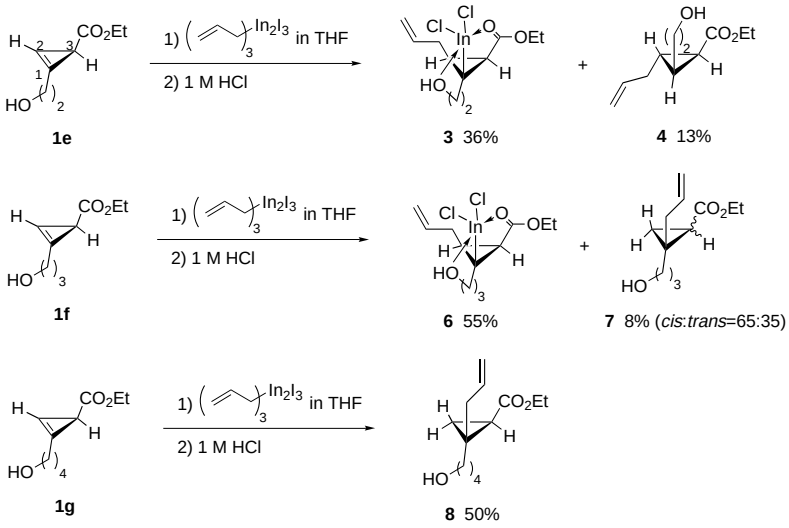
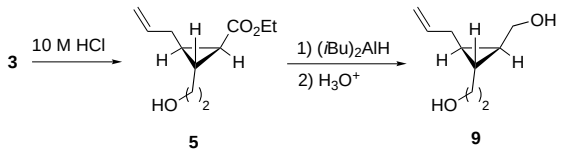


Figure 1. Molecular structure of **3** with crystallographic numbering scheme. Selected bond lengths [Å] and angles [°]: In–Cl1 2.356(3), In–Cl2 2.543(3), In–Cl2* 2.626(3), In–O1 2.521(8), In–O2 2.532(7), In–C3 2.15(1); Cl1-In-Cl2 4.2(1), Cl1-In-Cl2* 100.4(1), Cl1-In-O1 84.0(2), Cl1-In-O2 87.6(2), Cl1-In-C3 147.2(3), Cl2-In-Cl2* 82.81(9), Cl2-In-O1 163.4(2), Cl2-In-O2 92.0(2), Cl2-In-C3 114.4(3), Cl2*-In-O1 81.3(2), Cl2*-In-O2 170.8(2), Cl2*-In-C3 98.8(3), O1-In-O2 104.3(2), O1-In-C3 72.9(4), O2-In-C3 76.3(3), In-Cl2-In* 97.19(9).

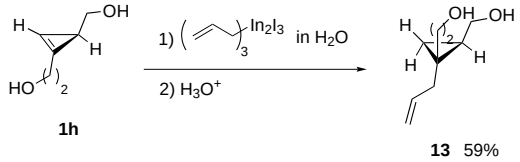


Scheme 2. Allylindation of 1-(ω-hydroxyalkyl)cyclopropenes **1e**–**g**.

the double chelation of the hydroxyl and carbonyl groups can not be expected; hence the protolysis occurred readily even with 1M HCl. Similarly, the 3-hydroxypropyl analogue **1f** gave the corresponding cyclopropylindium **6** in 55% yield. The minor product **7** (8%) of this reaction is not the stereoisomer but the C^1-allylated regioisomer. Interestingly, the allylation of (4-hydroxybutyl)cyclopropene **1g**, which bears a longer side chain, proceeded with complete regio- (C^1 allylation) and stereoselectivity (*cis* addition) to give the



Scheme 3. The protolysis and the subsequent reduction of cyclopropylindium **3**.

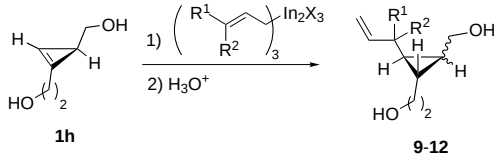


Scheme 4. Allylindation of **1h** in water.

adduct **8** as the sole product. These results on the series of 1-(ω-hydroxyalkyl)cyclopropenes **1e–g** clearly demonstrate that the allylindation is controlled by the chelation of the hydroxyl group in the side chain; when the side chain is short ($n=2$ and 3), indium atom trends to attack the C^1 carbon, whereas the 4-hydroxybutyl group ($n=4$) is long enough to direct the indium to the C^2 carbon; consequently, the allyl group is introduced to the C^1 carbon. In these cyclopropenes, the ester group at the C^3 carbon assists the *cis*-allylation in cooperation with the chelation of the hydroxyl group. Cyclopropenes **1e–g** were unsusceptible to allylindation in aqueous media.

Next, we undertook the second series of cyclopropenes **1h–j** which possess two hydroxyl groups in the C^1- and C^3-substituents. As shown in Table 1, **1h** readily reacted with various allylic indium reagents at the γ carbon. As is expected from the reaction of **1e**, the allylindation of **1h** proceeded regioselectively (C^1 indation and C^2 allylation) and stereoselectively (*cis*-preference) to give **9–12**. The *cis* selectivity is generally very high (>90%), except for the cinnamylindium case (entry 4). The product *cis*-**9** was identical to the compound obtained by the Dibal-H reduction of **5** (Scheme 3). Strikingly, when this allylindation was conducted in water, both the regio- and stereoselectivity were totally reversed and **13** was formed exclusively (Scheme 4). This is because the solvent water coordinates to the allylindium reagent breaking the chelation of the hydroxyl groups; accordingly, the solvated reagent attacks from the less-hindered *trans* face with preference of C^2 indation to avoid the steric crowding of the hydroxyethyl group at the C^1 carbon. In the allylindation of the analogues **1i** and **1j** with a 3-hydroxypropyl or 4-hydroxybutyl group, respectively, the longer side chains facilitate the C^2 indation even in organic solvents giving C^1-allylation products **14** and **15**, regioselectively (Table 2). Again, the *cis*/*trans* ratio largely depends on the solvents; the more polar solvent was used, the larger *trans* selectivity was obtained. Eventually, the highest *trans* selectivity (94%) was attained in water. The conversion of the hydroxyl groups to sodium alkoxides increased the *cis* selectivity in THF owing to the enhanced chelation. The diol obtained by the Dibal-H reduction of **8** was identical to the major stereoisomer *cis*-**15** from the reaction of **1j** in THF. For the reactions of diacetate **1k–m**, such chelation effect is not expected and, indeed, these cyclopropenes gave, regardless of the length of the side chain, *trans*-adducts **16–18**, exclusively (Table 3). Compound **16** was identical to the acetylation product of diol **13**. Table 4 summarizes the results of the allylindation of **1i** with different allylindium reagents, and demonstrates that the stereoselectivity can also be changed, to

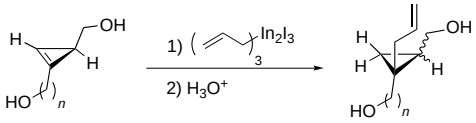
Table 1. Allylindation of **1h**.



	R^1	R^2	X	Solvent	Conditions	Product	Yield [%]	*cis*:*trans*
1	H	H	I	THF	RT, 2 h	**9**	72	95:5
2	H	H	I	DMF	RT, 2 h	**9**	92	90:10
3	Me	H	Br	THF	RT, 2 h	**10**[a]	43	100:0
4	Ph	H	Br	DMF	RT, 4 h	**11**[b]	45	65:35
5	Me	Me	Br	DMF	RT, 5 h	**12**	40	100:0

[a] Diastereomeric ratio 58:42. [b] Diastereomeric ratios 71:29 (*cis* isomers) and 58:42 (*trans* isomers).

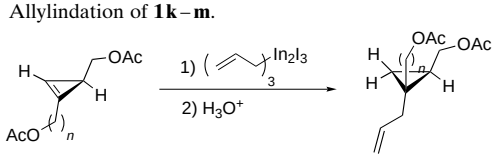
Table 2. Allylindation of **1i** and **1j** in various solvents.



	1	Solvent	Conditions	Product	Yield [%]	*cis*:*trans*
1	**1i**	THF	RT, 2 h	**14**	72	72:28
2[a]	**1i**	THF	RT, 2 h	**14**	65	80:20
3	**1i**	NMP	RT, 4 h	**14**	69	58:42
4	**1i**	DMF	RT, 4 h	**14**	56	26:74
5	**1i**	THF/H_2O[b]	RT, 9 h	**14**	45	12:88
6	**1i**	H_2O	RT, 6 h	**14**	75	6:94
7	**1j**	THF	RT, 2 h	**15**	75	89:11
8	**1j**	DMF	RT, 2 h	**15**	68	48:52
9	**1j**	H_2O	RT, 4 h	**15**	77	7:93

[a] The reaction was carried out with NaH (2 equiv). [b] Ratio 1:1.

Table 3. Allylindation of **1k–m**.



Entry	1	*n*	Conditions	Products	Yield [%]
1	**1k**	2	THF, RT, 21 h	**16**	73
2	**1l**	3	DMF, RT, 8 h	**17**	74
3	**1m**	4	THF, RT, 5 h	**18**	71

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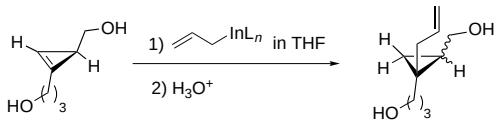
Table 4. Allylindation of **1i** with various allylindium reagents.



1i **14**

	Allylindium	Conditions	Yield [%]	*cis*:*trans*
1	(allyl)$_3$In$_2$I$_3$	RT, 2 h	72	72:28
2	(allyl)$_3$In$_2$Br$_3$	RT, 2 h	58	56:44
3	(allyl)$_3$In	RT, 3 h	36	53:47
4	(allyl)InBr$_2$	RT, 12 h	48	31:69
5	(allyl)InI$_2$	RT, 12 h	54	23:77

some extent, by selecting the indium reagents; allylindium sesquihalides[9] tends to give higher *cis* selectivity than allylindium dihalides.

Conclusion

In summary, it has been shown that the allylindation of hydroxy-bearing cyclopropenes proceeds both in organic and aqueous media, where the chelation of the hydroxyl group to the allylindium reagent plays the central role. It is recognized that such chelation effects are important also for other indium-mediated reactions such as carbonyl allylation reactions.[10] This work demonstrates that the regio- and stereoselectivity can be switched by changing the location of or by protection of the hydroxyl group. Furthermore, depending on the reaction solvents the selectivities are reversed sharply owing to the solvation to the allylindium reagent which competes with the chelation of the hydroxyl group. In particular, water has been found to show distinct features from those in organic solvents, thus providing a good example of intriguing possibilities of organic synthesis in water. The methodologies demonstrated here allow an easy access to regio- and stereodivergent syntheses of substituted cyclopropanes.[11] The cyclopropylindium intermediates **3** and **6** are useful not only for mechanistic investigations, but also as synthetic intermediates with defined stereochemistry. Further synthetic utilization of these cyclopropylindium compounds is now under investigation.

Experimental Section

General methods: All reactions were carried out under a positive pressure of argon. Indium powder (99.99%) was purchased from Aldrich Chemical Co. and used as received. Ethyl diazoacetate was prepared from glycine ethyl ester.[12] 4-Acetoxy-1-butyne, 5-acetoxy-1-pentyne, and 6-acetoxy-1-heptyne were prepared by the acetylation of the corresponding commercial alcohols. Infrared spectra were recorded on a JASCO IRA-102 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz). All NMR data were obtained using tetramethylsilane as an internal standard; *J* values are given in Hz. Elemental analyses were performed at Nagoya Institute of Technology or Elemental Analysis Centre of Kyoto University.

Synthesis of cyclopropenes: Ethyl 2-(ω-acetoxyalkyl)-2-cyclopropene-1-carboxylates were synthesized by the rhodium-catalyzed reaction of appropriate alkynes with ethyl diazoacetate, according to the method in literature.[13, 14] Selective hydrolysis[15] of the acetoxy group gave ethyl 2-(ω-hydroxyalkyl)-2-cyclopropene-1-carboxylates (**1e–g**). The following synthesis of **1e** represents the procedures.

Ethyl 2-(2-acetoxyethyl)-2-cyclopropene-1-carboxylate: A solution of ethyl diazoacetate (4.6 g, 40 mmol) in dichloromethane was added at a rate of two drops per min to a solution of 4-acetoxy-1-butyne (2.5 g, 22 mmol) and $Rh_2(OAc)_4$ (30 mg, 0.066 mmol) in dichloromethane (10 mL). After the addition was complete, the solvent was removed and the residue was chromatographed on silica gel (EtOAc/hexane 1:6) to give the cyclopropene (2.8 g, 66%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.50$ (d, $J = 1.5$ Hz, 1H), 4.33–4.07 (m, 4H), 2.85 (t, $J = 6.5$ Hz, 2H), 2.18 (d, $J = 1.5$ Hz, 1H), 2.05 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H); IR (neat): $\tilde{\nu}_{max} = 3150$, 3000, 1738, 1444, 1370, 1340, 1242, 1190, 1044, 736 cm^{-1}. The following cyclopropenes were prepared in a similar manner.

Ethyl 2-(3-acetoxypropyl)-2-cyclopropene-1-carboxylate: 64% yield; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.41$ (d, $J = 1.5$ Hz, 1H), 4.16–4.08 (m, 4H), 2.60 (t, $J = 7.2$ Hz, 2H), 2.16 (d, $J = 1.5$ Hz, 1H), 2.05 (s, 3H), 1.94 (quint, $J = 7.2$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 3H); IR (neat): $\tilde{\nu}_{max} = 3150$, 2990, 1740, 1442, 1368, 1340, 1244, 1186, 1040, 736 cm^{-1}.

Ethyl 2-(4-acetoxybutyl)-2-cyclopropene-1-carboxylate: 64% yield; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.38$ (dd, $J = 1.5$, 1.3 Hz, 1H), 4.25–4.05 (m, 4H), 2.54 (dt, $J = 6.3$, 1.3 Hz, 2H), 2.14 (d, $J = 1.5$ Hz, 1H), 2.05 (s, 3H), 1.73–1.67 (m, 4H), 1.26 (t, $J = 7.1$ Hz, 3H); IR (neat): $\tilde{\nu}_{max} = 2965$, 1726, 1446, 1368, 1338, 1242, 1182, 1038 cm^{-1}.

Ethyl 2-(2-hydroxyethyl)-2-cyclopropene-1-carboxylate (1e): Anhydrous K_2CO_3 (4.1 g, 30 mmol) was added in small portions to a solution of ethyl 2-(2-acetoxyethyl)-2-cyclopropene-1-carboxylate (5.3 g, 27 mmol) in ethanol (15 mL) at 0 °C, and the mixture was stirred for 70 h at room temperature. Ethanol was evaporated and water was added to the residue. The product was extracted with diethyl ether. The extracts were washed with brine and dried. The solvent was evaporated and the residue was chromatographed on silica gel (EtOAc/hexane 1:2) to give **1e**[16] (2.2 g, 52%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.54$ (d, $J = 1.4$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 3.84–3.75 (m, 2H), 3.15 (t, $J = 6.9$ Hz, 1H), 2.97 (dq, $J =$ 13.7, 6.9 Hz, 1H), 2.60 (ddt, $J = 15.1$, 4.5, 1.4 Hz, 1H), 2.21 (d, $J = 1.4$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H); IR (neat): $\tilde{\nu}_{max} = 3450$, 3150, 3000, 1800, 1700, 1370, 1340, 1260, 1196, 1098, 1048, 962, 924, 852, 798, 728 cm^{-1}; elemental analysis calcd (%) for $C_8H_{12}O_3$: C 61.62, H 7.74; found: C 61.73, H 7.97. Compounds **1f** and **1g** were prepared similarly.

Ethyl 2-(3-hydroxypropyl)-2-cyclopropene-1-carboxylate (1f): 80% yield; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 6.38 (d, $J = 1.5$ Hz, 1H), 4.14 (q, $J =$ 7.2 Hz, 2H), 3.73 (t, $J = 6.7$ Hz, 2H), 2.63 (t, $J = 6.7$ Hz, 2H), 2.16 (d, $J =$ 1.5 Hz, 1H), 1.88 (brs, 1H), 1.87 (quint, $J = 6.7$ Hz, 2H), 1.26 (t, $J = 7.2$ Hz, 3H); IR (neat): $\tilde{\nu}_{max} = 3450$, 3150, 2950, 1800, 1716, 1440, 1366, 1338, 1252, 1184, 1030, 960, 918, 802, 726 cm^{-1}; elemental analysis calcd (%) for $C_9H_{14}O_3$: C 63.51, H 8.29; found: C 63.38, H 8.57.

Ethyl 2-(4-hydroxybutyl)-2-cyclopropene-1-carboxylate (1g): 58% yield; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.36$ (dd, $J = 1.5$, 1.3 Hz, 1H), 4.14 (q, $J =$ 7.1 Hz, 2H), 3.67 (t, $J = 5.9$ Hz, 2H), 2.56 (dt, $J = 6.9$, 1.3 Hz, 2H), 2.14 (d, $J = 1.5$ Hz, 1H), 1.73–1.63 (m, 4H), 1.57 (s, 1H), 1.26 (t, $J = 7.1$ Hz, 3H); IR (neat): $\tilde{\nu}_{max} = 3435$, 2950, 1800, 1708, 1448, 1372, 1340, 1258, 1186, 1036, 964 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{16}O_3$: C 65.19, H 8.75; found: C 64.87, H 8.93.

Dihydroxycyclopropenes (**1h–j**) were prepared by the diisobutylaluminum hydride (Dibal-H) reduction of the corresponding carboxylates **1e–g**. The following preparation of **1h** is representative.

1-(2-Hydroxyethyl)-3-(hydroxymethyl)cyclopropene (1h): A solution of Dibal-H (0.95 M in hexane, 13 mL, 12 mmol) was added to a solution of **1e** (0.62 g, 4.0 mmol) in dichloromethane (9 mL) at −78 °C, and the mixture was stirred at that temperature for 16 h. Methanol (10 mL) was added at −78 °C and the mixture was warmed to room temperature. After being filtered, the filtrate was evaporated and the residue was chromatographed on silica gel (EtOAc) to give **1h** (0.33 g, 72%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.70$ (s, 1H), 4.00–3.75 (m, 3H), 3.65 (brs, 1H), 3.30 (dd, $J =$ 10.7, 5.5 Hz, 1H), 2.90 (ddd, $J = 16.1$, 7.3, 3.9 Hz, 1H), 2.67 (dddd $J = 16.1$, 6.3, 4.2, 1.9 Hz, 1H), 2.37 (brs, 1H), 1.75 (ddd, $J = 5.5$, 2.8, 1.5 Hz, 1H); IR (neat): $\tilde{\nu}_{max} = 3340$, 2940, 2330, 1770, 1420, 1150, 1050, 1010, 970 cm^{-1}.

In a similar manner, **1i** and **1j** were synthesized. Owing to the hygroscopic nature of diols **1h–j**, the elemental analyses did not give satisfactory

results. Hence, the elemental analyses were carried out on the corresponding diacetates **1k–m**.

1-(3-Hydroxypropyl)-3-(hydroxymethyl)cyclopropene (1i): 57% yield; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.65$ (s, 1H), 3.73 (dt, $J = 10.4$, 6.3 Hz, 1H), 3.72 (dt, $J = 10.4$, 6.3 Hz, 1H), 3.63 (dd, $J = 10.7$, 3.6 Hz, 1H), 3.45 (dd, $J = 10.7$, 4.7 Hz, 1H), 2.63 (dt, $J = 7.0$, 1.1 Hz, 1H), 2.18 (br s, 2H), 1.86 (quint, $J = 6.6$ Hz, 2H), 1.72 (ddd, $J = 4.7$, 3.6, 1.4 Hz, 1H); IR (neat): $\tilde{\nu}_{max} =$ 3340, 2930, 2870, 1426, 1374, 1240, 1044, 1020 cm^{-1}.

1-(4-Hydroxybutyl)-3-(hydroxymethyl)cyclopropene (1j): 51% yield; ^{1}H NMR (200 MHz,$CDCl_3$): $\delta = 6.65$ (s, 1H), 3.68 (t, $J = 6.0$ Hz, 1H), 3.61–3.47 (m, 2H), 2.55 (t, $J = 6.5$ Hz, 2H), 1.73–1.63 (m, 5H), 1.52 (br s, 2H); IR (neat): $\tilde{\nu}_{max} = 3335$, 2940, 2875, 1424, 1056, 1018 cm^{-1}.

3-(Acetoxymethyl)-1-(2-acetoxyethyl)cyclopropene (1k): Acetic anhydride (15 mL) was added to a cooled solution of **1h** (0.23 g, 2.0 mmol) in pyridine (10 mL), and the mixture was stirred overnight. Water (20 mL) was added and the product was extracted with diethyl ether. The extracts were washed successively with 1M hydrochloric acid, saturated aqueous $NaHCO_3$ and brine. The solvent was removed to give **1k** (88 mg, 22%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.73$ (s, 1H), 4.28 (t, $J = 6.8$ Hz, 2H), 4.01 (dd, $J = 11.0$, 5.1 Hz, 1H), 3.88 (dd, $J = 11.0$, 5.1 Hz, 1H), 2.83 (t, $J = 6.8$ Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.73 (dt, $J = 5.1$, 1.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 171.0$, 170.7, 121.2, 103.9, 71.4, 61.6, 25.7, 20.9, 20.7, 16.5; IR (neat): $\tilde{\nu}_{max} = 2950$, 1736, 1426, 1384, 1364, 1228, 1024, 966 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{14}O_4$: C 60.59, H 7.12; found: C 60.34, H 7.16.

Compounds **1l** and **1m** were prepared in a similar manner.

3-(Acetoxymethyl)-1-(3-acetoxypropyl)cyclopropene (1l): 57% yield; ^{1}H NMR (200 MHz, $CDCl_3$):$\delta = 6.64$ (d, $J = 1.4$ Hz, 1H), 4.12 (t, $J =$ 6.5 Hz, 2H), 3.99 (dd, $J = 11.1$, 5.2 Hz, 1H), 3.90 (dd, $J = 11.1$, 5.2 Hz, 1H), 2.57 (dt, $J = 7.2$, 1.2 Hz, 2H), 2.06 (s, 6H), 1.92 (quint, $J = 6.9$ Hz, 2H), 1.71 (dt, $J = 5.2$, 1.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.7$, 170.6, 123.4, 102.1, 71.3, 63.2, 25.8, 22.2, 20.6, 20.4, 16.5; IR (neat): $\tilde{\nu}_{max} = 2970$, 2930, 1738, 1434, 1368, 1234, 1026 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{16}O_4$: C 62.25, H 7.60; found: C 62.31, H 7.75.

3-(Acetoxymethyl)-1-(4-acetoxybutyl)cyclopropene (1m): 69% yield; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.62$ (s, 1H), 4.08 (t, $J = 6.3$ Hz, 2H), 3.95 (dd, $J = 11.4$, 5.4 Hz, 1H), 3.94 (dd, $J = 11.4$, 5.4 Hz, 1H), 2.52 (t, $J =$ 6.2, Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.74–1.63 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 171.0$ ($\times 2$), 124.1, 102.0, 71.8, 63.9, 27.9, 25.4, 23.4, 20.8 ($\times 2$), 16.5; IR (neat): $\tilde{\nu}_{max} = 2955$, 1736, 1432, 1366, 1240, 1034 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{18}O_4$: C 63.70, H 8.02; found: C 63.55, H 8.02.

Allylindation of 1e–f (Scheme 2): The following reaction of **1e** represents the general procedure. A mixture of indium powder (0.23 g, 2.0 mmol) and allyl iodide (0.28 mL, 3.0 mmol) was stirred in THF (1 mL) at room temperature for 1 h. Cyclopropene **1e** (0.16 g, 1.0 mmol) was added and the mixture was stirred at room temperature for 5 h. The reaction was quenched with 1M HCl (6 mL) and the products were extracted with diethyl ether. The extracts were washed with brine and dried. The solvent was evaporated and the residue was chromatographed on silica gel (EtOAc/hexane 1:4) to give **3** (0.14 g, 36%) and **4** (26 mg, 13%).

Cyclopropenes **1f** and **1g** were allylindated similarly.

[(3-Allyl-2-ethoxycarbonyl-1-(2-hydroxyethyl)]cyclopropylindium dichloride (3): m.p. 136–139 °C ($CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.81$ (ddt, $J = 17.2$, 10.4, 6.4 Hz, 1H), 5.12 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.04 (dd, $J =$ 10.4, 1.6 Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 4.15–4.07 (m, 1H), 3.80–3.69 (m, 1H), 3.55 (br s, 1H), 2.38–1.99 (m, 4H), 1.66–1.51 (m, 2H), 1.33 (t, $J =$ 7.2 Hz, 3H); ^{13}C NMR (50 MHz, CD_3CN): $\delta = 181.2$, 136.9, 115.6, 64.1, 61.3, 37.6, 34.3, 34.2, 32.7 (C-In), 27.6, 13.9; IR (neat): $\tilde{\nu}_{max} = 3450$, 2995, 2940, 1642, 1414, 1382, 1352, 1218, 998, 916, 852 cm^{-1}; SIMS: *m*/*z* (%): 349 (20) [*M* – Cl]$^+$, 347 (57) [*M* – Cl]$^+$, 265 (8), 151 (6), 115 (100); elemental analysis calcd (%) for $C_{11}H_{17}Cl_2InO_3$: C 34.50, H 4.47; found: C 34.01, H 4.39.

Ethyl 2-allyl-3-(2-hydroxyethyl)cyclopropane-1-carboxylate (4): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.93–5.73$ (m, 1H), 5.16–4.99 (m, 2H), 4.13 (q, $J =$ 7.1 Hz, 2H), 3.68 (t, $J = 6.2$ Hz, 2H), 2.41–1.98 (m, 2H), 1.97–1.74 (m, 2H), 1.71 (br s, 1H), 1.55 (dd, $J = 8.7$, 5.0 Hz, 1H), 1.49–1.38 (m, 1H), 1.36–1.17 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 172.8, 136.1, 115.6, 62.6, 60.4, 36.5, 29.6, 26.3, 25.4, 24.4, 14.2; IR (neat): $\tilde{\nu}_{max} = 3480$, 3100, 3000, 2950, 1720, 1644, 1446, 1380, 1340, 1300, 1178, 1048, 1000, 918, 860, 736 cm^{-1}.

[(3-Allyl-2-ethoxycarbonyl-1-(3-hydroxypropyl))cyclopropylindium dichloride (6): 55% yield; m.p. 96 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.87$ (ddt, $J = 17.1$, 10.2, 6.6 Hz, 1H), 5.15 (dd, $J = 17.1$, 1.7 Hz, 1H), 5.05 (dd, $J = 10.2$, 1.7 Hz, 1H), 4.30 (m, 2H), 4.24–4.15 (m, 2H), 3.01 (br s, 1H), 2.51–2.12 (m, 3H), 1.90–1.77 (m, 3H), 1.58 (m, 1H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.19–1.08 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 181.2$, 135.8, 116.2, 68.5, 64.2, 39.7 (C-In), 38.6, 35.5, 34.4, 30.2, 28.8, 14.1; IR (KBr): $\tilde{\nu}_{max} = 3370$, 2970, 2940, 2830, 1628, 1410, 1378, 1344, 1286, 1240, 1200, 1096, 1060, 1000, 918, 800 cm^{-1}; MS (EI): *m*/*z* (%): 398 (1) [*M*]$^+$, 396 (1) [*M*]$^+$, 363 (22), 361 (22), 325 (99), 211 (10), 115 (100); elemental analysis calcd (%) for $C_{12}H_{19}Cl_2InO_3$: C 36.30, H 4.82; found: C 35.75, H 4.66.

Ethyl 2-allyl-2-(3-hydroxypropyl)cyclopropane-1-carboxylate (7): 8% yield; *cis*/*trans* ratio 65:35; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.72$ (m, 1H), 5.07 (br d, $J = 10.1$ Hz, 1H), 5.02 (br d, $J = 17.1$ Hz, 1H), 4.13 (q, $J =$ 7.1 Hz, 2H), 3.64 (t, $J = 6.4$ Hz, 2H), 2.42–2.20 (m, 2H), 1.74–1.22 (m, 6H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 4.9$ Hz, 1H), 0.90 (dd, $J = 8.0$, 4.9 Hz, 1H).

Ethyl 2-allyl-2-(4-hydroxybutyl)cyclopropane-1-carboxylate (8): 50% yield; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.71$ (ddt, $J = 17.1$, 10.1, 6.9 Hz, 1H), 5.04 (dd, $J = 10.1$, 1.2 Hz, 1H), 5.02 (dd, $J = 17.1$, 1.2 Hz, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.65 (t, $J = 6.2$ Hz, 2H), 2.35 (dd, $J = 15.0$, 6.9 Hz, 1H), 2.27 (dd, $J = 15.0$, 6.9 Hz, 1H), 1.58 (s, 1H), 1.57–1.42 (m, 6H), 1.30–1.21 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.13 (t, $J = 4.8$ Hz, 1H), 0.88 (dd, $J = 8.0$, 4.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 172.6$, 135.9, 116.2, 62.7, 60.3, 36.7, 33.4, 32.6, 30.1, 25.7, 22.4, 20.2, 14.3; IR (neat): $\tilde{\nu}_{max} = 3430$, 2940, 2875, 1722, 1444, 1404, 1284, 1176, 1100, 1040, 914 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{22}O_3$: C 68.99, H 9.80; found: C 68.70, H 9.61.

Ethyl 3-allyl-2-(2-hydroxyethyl)cyclopropane-1-carboxylate (5): A solution of **3** (37 mg, 0.097 mmol) in acetonitrile (5 mL) was stirred with 10M HCl (1 mL) at room temperature. The product was extracted with diethyl ether. The extracts were washed with brine and dried. The solvent was evaporated to give **5** (16 mg, 83%); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.83$ (ddt, $J = 17.1$, 10.2, 6.5 Hz, 1H), 5.06 (dd, $J = 17.1$, 1.8 Hz, 1H), 4.98 (dd, $J = 10.2$, 1.8 Hz, 1H), 4.12 (q, $J = 7.2$ Hz, 2H), 3.71 (t, $J = 6.2$ Hz, 2H), 2.41–2.18 (m, 2H), 1.72–1.50 (m, 4H), 1.41 (m, 1H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.21 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 172.4$, 137.3, 115.1, 62.3, 60.3, 35.9, 30.8, 27.8, 24.8, 24.2, 14.3; IR (neat): $\tilde{\nu}_{max} = 3430$, 2945, 1720, 1642, 1442, 1380, 1180, 1058, 992, 914, 858 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{18}O_3$: C 66.64, H 9.15; found: C 65.96, H 9.17.

1-Allyl-2-(2-hydroxyethyl)-3-hydroxymethylcyclopropane (*cis*-9): Dibal-H (1.0M in hexane, 0.75 mL, 0.75 mmol) was added at –78 °C to a solution of **5** (50 mg, 0.25 mmol) in dichloromethane (2 mL), and the mixture was stirred at that temperature for 16 h. The reaction was quenched by the addition of ethanol (3 mL) at –78 °C. The resulted solid was filtered and the filtrate was concentrated to give an oil, which was chromatographed on silica gel (EtOAc) to give ***cis*-9** (20 mg, 51%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.93$ (ddt, $J = 17.0$, 10.4, 6.2 Hz, 1H), 5.11 (dd, $J = 17.0$, 1.7 Hz, 1H), 5.02 (dd, $J = 10.4$, 1.7 Hz, 1H), 3.73 (dd, $J = 11.5$, 6.1 Hz, 1H), 3.73 (t, $J = 6.2$ Hz, 2H), 3.56 (dd, $J = 11.5$, 8.0 Hz, 1H), 2.29–2.01 (m, 2H), 1.94 (s, 2H), 1.83–1.68 (m, 1H), 1.45–1.27 (m, 1H), 1.10–0.96 (m, 1H), 0.91–0.78 (m, 1H), 0.56–0.44 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 138.3$, 114.6, 62.6, 62.5, 36.0, 32.5, 25.2, 21.9, 20.9; IR (neat): $\tilde{\nu}_{max} = 3360$, 3090, 3000, 2930, 2850, 2330, 1820, 1640, 1430, 1028, 908, 872, 828 cm^{-1}; MS (CI): *m*/*z* (%): 157 (7) [*M*H]$^+$, 140 (7), 139 (71), 122 (11), 121 (100), 113 (5), 109 (7), 107 (5). This compound was acetylated (Ac_2O in pyridine) and the elemental analysis was performed on the diacetate: elemental analysis calcd (%) for $C_{13}H_{20}O_4$: C 64.98, H 8.39; found: C 64.70, H 8.55.

Allylindation of 1h with allylic indium sesquihalides (Table 1): The following reaction with allylindium sesquiiodide is representative of the general procedure. A mixture of indium powder (0.20 g, 1.7 mmol) and allyl iodide (0.24 mL, 2.6 mmol) was stirred in THF (2 mL) at room temperature for 1 h. Cyclopropene (**1h**) (97 mg, 0.85 mmol) was added and the mixture was stirred at room temperature for 2 h. The reaction was quenched with 1M HCl (6 mL) and the product was extracted with diethyl ether. The extracts were washed with brine and dried. The solvent was evaporated and the residue was chromatographed on silica gel (EtOAc) to give two stereoisomers of *cis*-**9** (90 mg, 68%) and *trans*-**9** (5 mg, 4%). The major isomer was found to be *cis* by comparison with the sample obtained by the

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Dibal-H reduction of **5**. Other reactions were similarly carried out. The results are summarized in Table 1.

1-Allyl-2-(2-hydroxyethyl)-3-hydroxymethylcyclopropane (*trans*-9): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.81$ (ddt, $J = 17.2$, 11.6, 6.2 Hz, 1H), 5.03 (dd, $J = 17.2$, 1.5 Hz, 1H), 4.97 (dd, $J = 11.6$, 1.5 Hz, 1H), 3.99–3.66 (m, 3H), 3.29 (dd, $J = 11.6$, 10.7 Hz, 1H), 3.03 (s, 1H), 2.08–1.39 (m, 4H), 1.26 (s, 1H), 1.06 (m, 1H), 0.61 (m, 1H), 0.40 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 137.5$, 114.5, 62.8, 61.3, 37.1, 30.1, 25.2, 20.9, 20.1.

2-(2-Hydroxyethyl)-3-hydroxymethyl-1-(1-methylallyl)cyclopropane (*cis*-10): Diastereomeric ratio 58:42, ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.99$–5.81 (m, 1H), 5.12–4.93 (m, 2H), 3.79–3.41 (m, 4H), 2.21 (br s, 2H), 1.86–1.62 (m, 2H), 1.48–1.21 (m, 1H), 1.21–1.00 (m, 1H), 1.07/1.15 (2d, $J = 6.0$ Hz, total 3H), 0.71–0.60 (m, 1H), 0.59–0.48 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 144.5$, 143.8, 112.5, 112.3, 63.1, 62.8, 37.6, 36.0, 35.7, 29.6, 29.2, 25.9, 25.5, 20.9, 20.8, 20.3; IR (neat): $\tilde{\nu}_{max} = 3350$, 3100, 2960, 2940, 2870, 2340, 1640, 1444, 1406, 1362, 1020, 904 cm^{-1}; MS (CI): *m*/*z* (%): 171 (2) $[M]^+$, 154 (8), 153 (66), 136 (12), 135 (100), 111 (6), 109 (41), 107 (18). This compound was acetylated (Ac_2O in pyridine) and the elemental analysis was performed on the diacetate: elemental analysis calcd (%) for $C_{14}H_{22}O_4$: C 66.11, H 8.72; found: C 66.05, H 8.97.

2-(2-Hydroxyethyl)-3-hydroxymethyl-1-(1-phenylallyl)cyclopropane (*cis*-11): Diastereomeric ratio 71:29, ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.37$–7.23 (m, 5H), 6.23–6.06 (m, 1H), 5.35–5.02 (m, 2H), 3.81–3.73/3.49–3.41 (m, total 4H), 2.99–2.88 (m, 1H), 1.90–1.65 (br s, 2H), 1.58–1.40 (m, 2H), 1.29–1.19 (m, 1H), 1.17–1.04 (m, 1H), 0.69–0.60 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 143.7$, 141.4, 141.7, 128.5, 127.3, 126.5, 114.4, 113.9, 62.8, 62.5, 49.1, 48.5, 35.7, 35.6, 28.3, 27.9, 26.2, 25.9, 21.5, 20.5; IR (neat): $\tilde{\nu}_{max} = 3350$, 3100, 3070, 3040, 3000, 2940, 2880, 2350, 2250, 1644, 1600, 1580, 1490, 1450, 1430, 1410, 1380, 1300, 1250, 1200, 1100, 1030, 918, 880, 756, 730, 700 cm^{-1}; MS (CI): *m*/*z* (%): 233 (8) $[MH]^+$, 216 (20), 215 (100), 214 (7), 213 (7), 203 (13), 198 (17), 197 (92), 185 (10), 173 (27), 172 (8), 171 (56), 169 (23), 155 (19), 143 (11), 141 (16), 131 (11), 130 (9), 129 (17), 117 (26), 111 (6). This compound was acetylated (Ac_2O in pyridine) and the elemental analysis was performed on the diacetate: elemental analysis calcd (%) for $C_{19}H_{24}O_4$: C 72.12, H 7.65; found: C 71.81, H 7.75.

2-(2-Hydroxyethyl)-3-hydroxymethyl-1-(1-phenylallyl)cyclopropane (*trans*-11): Diastereomeric ratio 58:42; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 7.32–7.19 (m, 5H), 6.18–-5.90 (m, 1H), 5.18–5.02 (m, 2H), 4.02–3.23 (m, 4H), 2.88 (s, 2H), 1.97–1.85 (m, 1H), 1.74–1.50 (m, 2H), 1.12–0.96 (m, 1H), 0.89–0.79 (m, 1H), 0.76–0.66 (m, 1H); IR (neat): $\tilde{\nu}_{max} = 3600$, 3325, 3090, 3075, 3040, 3010, 2940, 2890, 1636, 1600, 1494, 1450, 1068, 1022, 912, 730, 700 cm^{-1}. This compound was acetylated (Ac_2O in pyridine) and the elemental analysis was performed on the diacetate: elemental analysis calcd (%) for $C_{19}H_{24}O_4$: C 72.12, H 7.65; found: C 71.70, H 7.79.

2-(2-Hydroxyethyl)-3-hydroxymethyl-1-(1,1-dimethylallyl)cyclopropane (*cis*-12): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.84$ (dd, $J = 17.5$, 10.6 Hz, 1H), 4.97 (dd, $J = 17.5$, 1.4 Hz, 1H), 4.91 (dd, $J = 10.6$, 1.4 Hz, 1H), 3.85–3.62 (m, 4H), 2.45 (br s, 2H), 1.81 (m, 1H), 1.39–1.21 (m, 1H), 1.11 (s, 3H), 1.05 (s, 3H), 1.00–0.89 (m, 1H), 0.80–0.68 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 147.8$, 110.6, 62.9, 62.3, 36.6, 36.2, 34.8, 28.6, 28.2, 26.8, 17.7; IR (neat): $\tilde{\nu}_{max} = 3350$, 3095, 2970, 1830, 1638, 1462, 1418, 1380, 1360, 1256, 1230, 1184, 1156, 1106, 1012, 910, 878, 840 cm^{-1}; MS (CI): *m*/*z* (%): 185 (2) $[MH]^+$, 168 (11), 167 (82), 155 (2), 149 (100), 137 (6), 124 (8), 123 (74), 121 (15), 111 (22), 107 (16). This compound was acetylated (Ac_2O in pyridine) and the elemental analysis was performed on the diacetate: elemental analysis calcd (%) for $C_{15}H_{24}O_4$: C 67.13, H 9.02; found: C 67.26, H 9.21.

Allylindation of 1h in water (Scheme 4): A mixture of indium powder (0.20 g, 1.8 mmol), allyl iodide (0.24 mL, 2.6 mmol), and **1h** (77 mg, 0.68 mmol) was stirred in water (2 mL) at room temperature for 6 h. The reaction was quenched with 1M HCl (6 mL) and the product was extracted with diethyl ether. The extracts were washed with brine and dried. The solvent was evaporated and the residue was chromatographed on silica gel (EtOAc/hexane 1:2) to give **13** (46 mg, 59%).

1-Allyl-1-(2-hydroxyethyl)-2-hydroxymethylcyclopropane (13): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.81$ (dddd, $J = 17.2$, 10.2, 8.0, 6.2 Hz, 1H), 5.06 (dd, $J = 17.2$, 1.4 Hz, 1H), 5.02 (dd, $J = 10.2$, 1.4 Hz, 1H), 3.99–3.71 (m, 3H), 3.28 (dd, $J = 11.9$, 10.8 Hz, 1H), 2.90 (br s, 2H), 2.52 (dd, $J = 14.7$, 8.0 Hz, 1H), 1.92 (dt, $J = 15.2$, 3.3 Hz, 1H), 1.68 (dd, $J = 14.7$, 6.2 Hz, 1H), 1.57–1.41 (m, 1H), 1.17–1.02 (m, 1H), 0.57 (dd, $J = 8.9$, 4.8 Hz, 1H), 0.05 (t, $J =$ 4.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 136.1$, 116.3, 62.6, 58.9, 41.0, 32.3, 26.1, 20.1, 14.0; IR (neat): $\tilde{\nu}_{max} = 3305$, 3095, 2960, 2340, 1640, 1440, 1260, 1156, 1070, 1040, 1020, 916 cm^{-1}; MS (CI): *m*/*z* (%): 157 (3) $[M]^+$, 140 (5), 139 (63), 122 (11), 121 (100), 109 (7). The acetylation product (Ac_2O in pyridine) of this compound was identical to **16**.

Allylindation of 1i and 1j in various solvents (Table 2): The following reaction of **1i** with allylindium sesquiiodide in water (entry 6) is representative of the general procedure. A mixture of indium powder (0.14 g, 1.3 mmol), allyl iodide (0.17 mL, 1.9 mmol), and **1i** (80 mg, 0.63 mmol) was stirred in water (1 mL) at room temperature for 6 h. The reaction was quenched with 1M HCl (6 mL) and the product was extracted with diethyl ether. The extracts were washed with brine and dried. The solvent was evaporated and the residue was chromatographed on silica gel (EtOAc) to give **14** (80 mg, 75%). The *cis*/*trans* ratio was estimated to be 6:94 by ^{1}H NMR. Other reactions were similarly carried out and the results are listed in the Table 2. Owing to the hygroscopic nature of diol **14** and **15**, the elemental analyses did not give satisfactory results. Hence, **14** and **15** were acetylated (Ac_2O in pyridine) to the diacetates which were confirmed to be identical to **17** and **18**, respectively.

2-Allyl-1-(hydroxymethyl)-2-(3-hydroxypropyl)cyclopropane (*cis*-14): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.89$ (ddt, $J = 17.3$, 10.2, 7.1 Hz, 1H), 5.09 (dd, $J = 10.2$, 1.1 Hz, 1H), 5.05 (dd, $J = 17.3$, 1.1 Hz, 1H), 3.78 (dd, $J =$ 11.6, 6.2 Hz, 1H), 3.65 (t, $J = 6.8$ Hz, 2H), 3.50 (dd, $J = 11.6$, 9.0 Hz, 1H), 2.17 (d, $J = 7.1$ Hz, 2H), 1.82 (br s, 2H), 1.73–1.58 (m, 2H), 1.51–1.34 (m, 2H), 1.11–0.93 (m, 1H), 0.54 (dd, $J = 8.7$, 5.0 Hz, 1H), 0.22 (t, $J = 5.0$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 136.8$, 115.9, 62.8, 62.4, 34.9, 33.7, 29.3, 25.9, 23.4, 16.2.

2-Allyl-1-(hydroxymethyl)-2-(3-hydroxypropyl)cyclopropane (*trans*-14): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.80$ (ddt, $J = 17.1$, 10.1, 7.0 Hz, 1H), 5.06 (dd, $J = 17.1$, 1.2 Hz, 1H), 5.04 (dd, $J = 10.1$, 1.2 Hz, 1H), 3.84–3.47 (m, 4H), 2.02 (m, 2H), 1.90–1.62 (m, 4H), 1.50–1.42 (m, 2H), 1.01 (m, 1H), 0.57 (dd, $J = 8.7$, 4.8 Hz, 1H), 0.14 (t, $J = 4.8$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 136.0$, 116.2, 62.8, 62.1, 41.4, 29.5, 26.4, 25.8, 23.6, 15.6; IR (neat): $\tilde{\nu}_{max} = 3350$, 2940, 2890, 1642, 1440, 1260, 1150, 1060, 1032, 1012, 914 cm^{-1}.

2-Allyl-1-(hydroxymethyl)-2-(4-hydroxybutyl)cyclopropane (*cis*-15): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.89$ (ddt, $J = 17.2$, 10.4, 6.9 Hz, 1H), 5.09 (d, $J = 17.2$ Hz, 1H), 5.07 (d, $J = 10.4$ Hz, 1H), 3.75 (dd, $J = 11.6$, 6.6 Hz, 1H), 3.64 (t, $J = 6.2$ Hz, 2H), 3.53 (dd, $J = 11.6$, 8.7 Hz, 1H), 2.21 (dd, $J = 15.3$, 6.4 Hz, 1H), 2.08 (dd, $J = 15.3$, 7.5 Hz, 1H), 1.63–1.21 (m, 8H), 1.05–0.90 (m, 1H), 0.54 (dd, $J = 8.6$, 4.9 Hz, 1H), 0.20 (t, $J = 4.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 136.9$, 115.8, 63.0, 62.5, 36.9, 35.0, 32.6, 25.9, 23.8, 22.5, 16.3; IR (neat): $\tilde{\nu}_{max} = 3360$, 3090, 2945, 2875, 1640, 1454, 1438, 1416, 1150, 1056, 1036, 912 cm^{-1}.

2-Allyl-1-(hydroxymethyl)-2-(4-hydroxybutyl)cyclopropane (*trans*-15): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.79$ (ddt, $J = 16.9$, 10.3, 7.0 Hz, 1H), 5.05 (dd, $J = 16.9$, 1.1 Hz, 1H), 5.03 (dd, $J = 10.3$, 1.1 Hz, 1H), 3.73 (dd, $J =$ 11.5, 6.6 Hz, 1H), 3.65 (t, $J = 6.1$ Hz, 2H), 3.55 (dd, $J = 11.5$, 8.5 Hz, 1H), 2.02 (m, 2H), 1.72–1.30 (m, 8H), 1.05–0.91 (m, 1H), 0.57 (dd, $J = 8.7$, 4.9 Hz, 1H), 0.16 (t, $J = 4.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 136.1$, 116.1, 62.8, 62.1, 41.4, 32.5, 30.2, 25.4, 24.1, 22.7, 15.9.

Allylindation of 1k-m with allylindium sesquiiodide (Table 3): The following reaction of **1k** (entry 1) is representative of the general procedure. Allyl iodide (0.14 mL, 1.5 mmol) was added to a suspension of indium powder (0.12 g, 1.0 mmol) in THF (2 mL), and the mixture was stirred for 1 h. Cyclopropene **1k** (99 mg, 0.5 mmol) was added to the resulting allylindium reagent, and the mixture was reacted at room temperature for 21 h. The reaction was quenched with 1M HCl (5 mL). The product was extracted with diethyl ether, and the extracts were washed with brine and dried. The solvent was evaporated and the residue was chromatographed on silica gel (EtOAc/hexane 1:2) to give **16** (88 mg, 73%).

2-Acetoxymethyl-1-(2-acetoxyethyl)-1-allylcyclopropane (16): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.76$ (ddt, $J = 17.1$, 10.1, 7.0 Hz, 1H), 5.09 (dd, $J =$ 17.1, 1.3 Hz, 1H), 5.07 (dd, $J = 10.1$, 1.3 Hz, 1H), 4.26 (dd, $J = 11.8$, 6.9 Hz, 1H), 4.17 (t, $J = 7.3$ Hz, 2H), 3.91 (dd, $J = 11.8$, 8.8 Hz, 1H), 2.26–1.87 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 1.67 (m, 2H), 1.07 (m, 1H), 0.66 (dd, $J = 8.6$, 5.1 Hz, 1H), 0.31 (t, $J = 5.1$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 171.1$, 170.9, 135.2, 116.8, 65.0, 62.4, 41.3, 29.4, 21.5, 21.3, 20.9, 16.0; IR (neat): $\tilde{\nu}_{max} = 3075$, 2970, 2925, 1736, 1638, 1436, 1370, 1236, 1034, 968 cm^{-1};

elemental analysis calcd (%) for $C_{13}H_{20}O_4$: C 64.98, H 8.39; found: C 64.52, H 8.56.

2-Acetoxymethyl-1-(3-acetoxypropyl)-1-allylcyclopropane (17): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.76$ (ddt, $J = 16.9$, 10.4, 6.9 Hz, 1H), 5.06 (dd, $J =$ 10.4, 1.3 Hz, 1H), 5.04 (dd, $J = 16.9$, 1.3 Hz, 1H), 4.23 (dd, $J = 11.8$, 6.9 Hz, 1H), 4.05 (dt, $J = 11.0$, 6.5 Hz, 1H), 4.02 (dt, $J = 11.0$, 6.5 Hz, 1H), 3.91 (dd, $J = 11.8$, 8.7 Hz, 1H), 2.11 – 1.85 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 1.80 – 1.65 (m, 2H), 1.43 – 1.34 (m, 2H), 1.12 – 0.97 (m, 1H), 0.64 (dd, $J = 8.8$, 5.0 Hz, 1H), 0.23 (t, $J = 5.0$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 171.1$, 135.5, 116.5, 65.1, 64.4, 41.1, 27.1, 25.8, 23.5, 21.6, 21.0, 20.9, 16.4; IR (neat): $\tilde{\nu}_{max} = 2960$, 1736, 1638, 1440, 1368, 1236, 1034, 966, 916 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{22}O_4$: C 66.11, H 8.72; found: C 65.73, H 8.88.

2-Acetoxymethyl-1-(4-acetoxybutyl)-1-allylcyclopropane (18): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.76$ (ddt, $J = 16.8$, 10.6, 6.8 Hz, 1H), 5.05 (d, $J =$ 16.8 Hz, 1H), 5.03 (d, $J = 10.6$ Hz, 1H), 4.20 (dd, $J = 11.7$, 6.9 Hz, 1H), 4.05 (t, $J = 6.5$ Hz, 2H), 3.95 (dd, $J = 11.7$, 8.6 Hz, 1H), 2.08 (dd, $J = 14.1$, 7.5 Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 1.92 (dd, $J = 14.1$, 6.8 Hz, 1H), 1.67 – 1.22 (m, 6H), 1.10 – 0.95 (m, 1H), 0.62 (dd, $J = 8.8$, 4.9 Hz, 1H), 0.22 (t, $J = 4.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 171.0$, 135.7, 116.3, 65.1, 64.3, 41.1, 30.4, 28.7, 23.8, 22.9, 21.5, 20.94, 20.86, 16.4; IR (neat): $\tilde{\nu}_{max} = 2955$, 1734, 1638, 1454, 1438, 1370, 1240, 1038, 964, 914 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{24}O_4$: C 67.13, H 9.02; found: C 66.71, H 9.09.

Allylindation of 1i with various allylindium reagents (Table 4): The reactions were conducted as described above by using allylindium sesquihalides,[9] allylindium dihalides,[17] and triallylindium[18] which were prepared according to the methods in literature.

X-ray crystallography:[19] A colorless crystal grown from $CHCl_3$ was used. All measurements were made on a CAD4-EXPRESS diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation. The structure was solved by the direct methods (SAPI91). Crystal data for **3**: $C_{11}H_{17}Cl_2InO_3$, $M_r = 382.98$, crystal size $0.2 \times 0.2 \times 0.2$ mm^3, triclinic, space group $P\bar{1}$, $a = 8.467(7)$, $b =$ 9.089(6), $c = 10.396(7)$ Å, $\alpha = 114.27(6)$, $\beta = 98.01(6)$, $\gamma = 91.50(6)^\circ$, $V =$ 719.09(10) Å^3, $Z = 2$, $\rho = 1.769$ g cm^{-3}, $F(000) = 380.00$, $\mu(Mo_{K\alpha}) =$ 20.06 cm^{-1}, $T = 295$ K. Of the 3107 reflections observed ($2\theta_{max} = 52.6^\circ$), 2196 were used ($I > 2\sigma(I)$); $R = 0.074$, $R_w = 0.094$.

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[19] Crystallographic data (excluding structure factors) for the structure **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147767. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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