

## Allylic-Type Diindium Reagents. Reactivity toward Electrophiles and Cascade Coupling Reactions with Imines<sup>†</sup>

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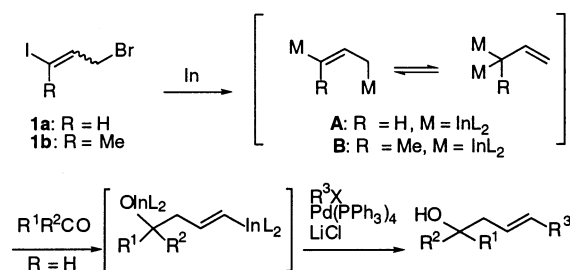
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The allylic-type diindium reagents **A** and **B** were prepared from 3-bromo-1-iodopropene (**1a**) and 4-bromo-2-iodobut-2-ene (**1b**), respectively, and their reactions with electrophiles were investigated. The diindium reagents **A** and **B** were initially reacted with imines and the resulting vinylindium compounds were then treated with organic halides in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> to give linear *N*-aryl and *N*-tosyl homoallylic amines. Diindium **A** is stable in a small amount of water in solvent, whereas **B** is easily protonated to give a crotylindium reagent. The reaction of **B** with benzaldehyde gives mainly the 1,3- and 1,5-diols via a spontaneous coupling with two molecules of the aldehyde, in contrast to **A**, which reacts with one molecule of carbonyl compounds to give the vinylindium compounds.

### Introduction

Organodimetallic compounds, which contain two metal–carbon bonds in one molecule, are attractive reagents from a viewpoint of organic synthesis.<sup>1</sup> A differentiation of the two carbon–metal bonds under cross-coupling reactions with electrophiles provides a versatile method for the formation of two types of carbon–carbon bond in a single operation. Although a number of organodimetallic compounds have been prepared, allylic-type dimetallic compounds such as **A** remain unexplored and only a few examples such as M = Li,<sup>2,3</sup> Zn,<sup>4–7</sup> and Sn<sup>8,9</sup> have been reported. During the investigation on a series of organoindium reagents, we reported the preparation of diindiopropene **A** by oxidative addition of indium to 3-bromo-1-iodopropene (**1a**).<sup>10</sup> This diindium reagent first couples with a carbonyl compound and the resulting vinylindium compound further reacts with aryl, alkenyl, or allyl halide in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> leading to linear homoallylic alcohols (Scheme 1). In light of the success of constructing two carbon–carbon bonds using carbonyl compounds as the first electrophile, we have presently examined the reaction of allylic diindium **A**

### SCHEME 1



with imines at the initial coupling in the cascade. Furthermore, to recognize electronic and steric substitution effects on diindium **A**, a new diindium reagent **B** bearing a methyl group was prepared from 4-bromo-2-iodobut-2-ene (**1b**) and its reactions with various electrophiles were investigated. It has been found that the allylic-type diindium reagents **A** and **B** show distinctive reaction behavior toward water and carbonyl compounds.

### Results and Discussion

**The Reactions of Allylic-Type Diindium Reagents with Imines.** The indium-mediated reaction of **1a** with imine **2a** was first examined (Table 1). In DMA (*N,N*-dimethylacetamide), homoallylic amine **3a** was obtained together with homoallylic alcohol **5a** (entry 1). Alcohol **5a** is considered to come from the allylation of benzaldehyde resulting from the hydrolysis of **2a** with a small amount of water in the solvent. When dry THF was used, **3a** was solely obtained (entries 2 and 3). It is known that sulfonimine **2b** is much less reactive for hydrolysis than **2a**.<sup>11</sup> Indeed, the reaction with **2b** in DMA as well as in 1,3-dimethyl-2-imidazolidinone (DMI) gave the corre-

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**TABLE 1.** Indium-mediated Reactions of **1** with Imines **2**<sup>a</sup>

**1a:** R<sup>1</sup> = H (*E:Z* = 43:57)  
**1b:** R<sup>1</sup> = Me (*E* only)  
**2a:** R<sup>2</sup> = Ph  
**2b:** R<sup>2</sup> = SO<sub>2</sub>Ph

**3a:** R<sup>1</sup> = H, R<sup>2</sup> = NHPH  
**3b:** R<sup>1</sup> = H, R<sup>2</sup> = NHSO<sub>2</sub>Ph  
**3c:** R<sup>1</sup> = Me, R<sup>2</sup> = NHSO<sub>2</sub>Ph

**4:** Me, H(D), NHSO<sub>2</sub>Ph  
**5a:** R<sup>1</sup> = H  
**5b:** R<sup>1</sup> = Me

entry	<b>1</b>	<b>2</b>	conditions	products and yields (%)	
1	<b>1a</b>	<b>2a</b>	DMA, rt, 2 h	<b>3a</b> 55	<b>5a</b> 31
2	<b>1a</b>	<b>2a</b>	THF, rt, 36 h	<b>3a</b> 74	<b>5a</b> trace
3	<b>1a</b>	<b>2a</b>	THF, 50 °C, 5 h	<b>3a</b> 75	<b>5a</b> trace
4	<b>1a</b>	<b>2b</b>	DMA, rt, 2 h	<b>3b</b> 86	<b>5a</b> 0
5	<b>1a</b>	<b>2b</b>	DMI, rt, 2 h	<b>3b</b> 93	<b>5a</b> 0
6	<b>1a</b>	<b>2b</b>	DMI-H <sub>2</sub> O (1:1), rt, 6 h	<b>3b</b> 0	<b>5a</b> 76
7	<b>1b</b>	<b>2b</b>	DMA, rt, 4 h	<b>3c</b> + <b>4</b> 43 (32:68 <sup>b</sup> )	<b>5b</b> 17 <sup>c</sup>
8	<b>1b</b>	<b>2b</b>	THF, D <sub>2</sub> O (1 drop), rt, 6 h	<b>3c</b> + <b>4</b> 82 (8:92 <sup>d,e</sup> )	<b>5b</b> 16
9	<b>1b</b>	<b>2b</b>	THF, rt, 6 h	<b>3c</b> + <b>4</b> 48 (96:4)	<b>5b</b> 0

<sup>a</sup> All reactions were carried out with **1** (0.50 mmol), **2** (0.50 mmol), and indium (1.0 mmol). <sup>b</sup> Syn:anti = 79:21. <sup>c</sup> Syn:anti = 87:13. <sup>d</sup> Syn:anti = 77:23. <sup>e</sup> Deuterium (79%) was incorporated in **4**.

sponding homoallylic amide **3b** in high yield without the formation of **5a** (entries 4 and 5); nevertheless, **2b** was completely hydrolyzed in aqueous DMI, giving **5b** exclusively (entry 6). Next, the reaction of 4-bromo-2-iodobut-2-ene (**1b**) with **2b** was examined. This coupling was found to be affected greatly by water in the solvents; in DMA a mixture of regioisomers **3c** and **4** was obtained, together with homoallylic alcohol **5b** (entry 7). The reaction in THF containing a small amount of D<sub>2</sub>O gave **4-d**, where deuterium was introduced to the allylic carbon (entry 8). This fact indicates that the organodiindium compound **B** was protonated with H<sub>2</sub>O (D<sub>2</sub>O) at the substituted carbon prior to the coupling with **2b**, then reacted with **2b** as a crotylindium reagent. Crotylindium is known to couple with sulfonimine **2b** to give the branched amide **4**.<sup>11,12</sup> The high reactivity of this reagent **B** toward water is in contrast to diindium **A**, which is not protonated by water in polar solvents such as DMA and NMP (*N*-methyl-2-pyrrolidone).<sup>10</sup> In carefully dried THF, the diindium reagent **B** coupled with sulfonimine to afford **3c** selectively (entry 9). When this reaction was quenched with diluted DCl, (*Z*)-**3c-d** (93% D) was obtained, indicating the existence of an (*E*)-vinylindium intermediate.

**The Palladium-Catalyzed Cascade Reactions of Allylic-Type Diindium Reagents with Imines and Organic Halides.** Recently, the Pd-catalyzed cross-coupling reactions of vinylindium compounds with halides have been reported.<sup>10,13–17</sup> Next the Pd-catalyzed

**TABLE 2.** The Cascade Reactions of **1** with Imines and Organic Halides<sup>a</sup>

**1**  $\xrightarrow[2) R^4X, Pd(PPh_3)_4, LiCl]{1) In, R^2CH=NR^3}$  **6a-h**

Entry	<b>1</b>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup> X	Yield (%)
1 <sup>b</sup>	<b>1a</b>	Ph	Ph	PhI	<b>6a</b> 57
2	"	Ph	SO <sub>2</sub> Ph	PhI	<b>6b</b> 77
3	"	Ph	SO <sub>2</sub> Ph		<b>6c</b> 43
4	"	Ph	SO <sub>2</sub> Ph		<b>6d</b> 31 ( <i>E:Z</i> =86:14)
5	"	<i>n</i> -Bu	SO <sub>2</sub> (Tol- <i>p</i> )	PhI	<b>6e</b> 47
6	"	<i>i</i> -Pr	SO <sub>2</sub> (Tol- <i>p</i> )	PhI	<b>6f</b> 51
7 <sup>c</sup>	<b>1b</b>	Ph	SO <sub>2</sub> Ph	PhI	<b>6g</b> 22
8 <sup>d</sup>	"	Ph	SO <sub>2</sub> Ph	PhI	" 52
9 <sup>d</sup>	"	Ph	SO <sub>2</sub> Ph		<b>6h</b> 44 ( <i>E:Z</i> =86:14)

<sup>a</sup> Unless otherwise noted, reactions were carried out in DMI with **1** (0.50 mmol), imine (0.50 mmol), and indium (1.0 mmol) at room temperature for 2 h, then halide (1.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), and LiCl (1.0 mmol) were added and heated at 110 °C for 17 h. <sup>b</sup> In DMA. <sup>c</sup> In THF at reflux. <sup>d</sup> In THF–DMI (1:2).

cascade coupling of the vinylindium intermediates with the second electrophiles was examined (Table 2). The vinylindium compound, prepared from **1a** and imine **2a**, was subjected to the coupling with iodobenzene in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> to afford the expected linear homoallylic amine **6a** in 57% yield (entry 1). It is noted that the geometry of the C=C bond of **6a** was perfectly regulated to be *E*, whereas in the case of aldehydes the products were a mixture of the *E* and *Z* isomers.<sup>10</sup> Similarly, the reaction of sulfonimine **2b** gave homoallylic amide **6b** in good yield (entry 2). Again, the *E*-selectivity was confirmed. Allyl chloride and β-bromostyrene were also coupled with the vinylindium intermediate to give the corresponding homoallylic amides **6c** and **6d** (entries 3 and 4). Sulfonimines derived from aliphatic aldehydes could equally be used in this reaction (entries 5 and 6). The vinylindium compound derived from **1b** was also examined for the Pd-catalyzed C–C bond formation. As mentioned above, dry THF was the solvent of choice for the selective formation of this vinylindium compound. However, the Pd-catalyzed coupling with iodobenzene in refluxing THF gave poor yield of **6g** (entry 7). To perform the reaction at higher temperature, DMI was added as a cosolvent and the reaction mixture was heated at 110

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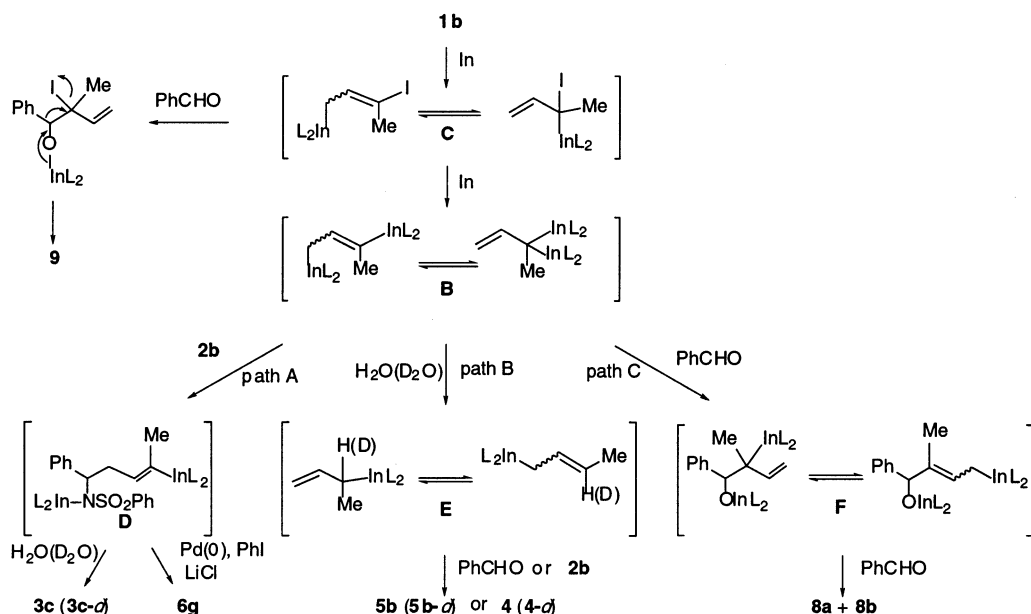
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## SCHEME 2



°C for 17 h. This reaction gave the three-component coupling product **6g** in 52% yield (entry 8).  $\beta$ -Bromostyrene was also used to furnish the corresponding linear homoallylic amide **6h** in moderate yield (entry 9).

**The Indium-Mediated Reaction of 1b with Benzaldehyde.** Although the coupling reactions of **1a** with aldehydes have been investigated by us,<sup>10</sup> the marked differences between **1a** and **1b** in the reaction with imines (Table 1, entries 1–6 vs 7–8) prompted us to investigate the indium-mediated reaction of **1b** with aldehydes. As the diindium reagent **B** was found to be highly reactive to water, the reaction was first performed in the strict absence of moisture. In contrast to the reaction of **1a** with aldehydes or imines, the indium-mediated reaction of **1b** with benzaldehyde in dry THF gave a set of mixtures composed of homoallylic alcohols **5b** and **7**, diols **8a** and **8b**, and a trace amount of aldehyde **9** (Table 3, entry 1). The expected linear homoallylic alcohol **7** was obtained in low yield. After **1b** was mixed with indium for 3 h, benzaldehyde was added to the resultant mixture. This Grignard-type reaction gave a mixture of the same products in lower combined yield (entry 2). When the same Grignard-type reaction was carried out in DMI containing a small amount of D<sub>2</sub>O, homoallylic alcohol **5b** was obtained in 91% yield with 73% D (entry 3). This fact indicates that the diindium reagent **B** was easily transformed to a crotylindium reagent, as was observed in the reaction with imine (Table 1, entry 7), and then coupled with benzaldehyde to afford **5b**. However, Barbier-type reactions, by mixing **1b**, indium, and benzaldehyde at once in aqueous THF or pure water afforded not only **5b** but also homoallylic alcohol **7** and diols **8a** and **8b** (entries 4 and 5). It is noted that diols **8a** and **8b** were obtained as a single diastereomer on the basis of <sup>13</sup>C NMR analysis.

**Reaction Mechanism.** Plausible reaction courses for the reaction of **1b** are depicted in Scheme 2. The oxidative addition of indium to **1b** produces the allylic monoindium reagent **C**, which further reacts with indium to give the allylic-type diindium reagent **B**.  $\gamma$ -Iodoallylindium **C** reacts with benzaldehyde to some extent before generat-

TABLE 3. Indium-Mediated Reaction of **1b** with Benzaldehyde<sup>a</sup>

entry	solvent	yield (%)				
		<b>5b</b> <sup>b</sup> ( <i>syn/anti</i> )	<b>7</b> <sup>b</sup> ( <i>E/Z</i> )	<b>8a</b> <sup>c</sup>	<b>8b</b> <sup>c</sup>	<b>9</b>
1 <sup>d</sup>	THF	trace	15 (9:91)	64	11	trace
2 <sup>d,e</sup>	THF	3 (39:61)	3 (20:80)	40	12	0
3 <sup>e</sup>	DMI-D <sub>2</sub> O (30:1)	91 (71:29) <sup>f</sup>	0	0	0	0
4	THF-H <sub>2</sub> O (1:1)	22 (61:39)	8 (13:87)	10	40	0
5 <sup>g</sup>	H <sub>2</sub> O	17 (64:36)	8 (14:86)	12	28	0

<sup>a</sup> Unless otherwise noted, reactions were carried out by mixing **1b** (0.50 mmol), benzaldehyde (1.0 mmol), and indium (1.0 mmol) at rt for 3 h. <sup>b</sup> The yields were estimated by <sup>1</sup>H NMR analysis of a mixture of **7** and **5b**. <sup>c</sup> Isolated yield. <sup>d</sup> PhCHO (0.50 mmol) was used. <sup>e</sup> The reaction was performed in a Grignard-type manner. <sup>f</sup> 73% D. <sup>g</sup> Reaction time 24 h.

ing diindium **B** to give **9** via an intramolecular rearrangement of the phenyl group. A similar formation of aldehyde **9** is documented in the coupling between benzaldehyde and allylstannane possessing a good leaving group such as OTf or Cl at the  $\gamma$ -position.<sup>17</sup> We previously found that the In-mediated reaction of 1,3-dibromopropene with benzaldehyde gives a mixture of vinyloxy and homoallylic alcohol.<sup>18</sup> The latter came from the diindium reagent **A** depicted in Scheme 1, whereas the former is considered to be derived from

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$\gamma$ -bromoallylindium species (*monoindium*). In the present case, we did not find the corresponding epoxide but a trace amount of aldehyde **9**. Therefore, the monoindium reagent **C** is converted to diindium **B** before reacting with benzaldehyde. The reaction of **B** with imine proceeds regioselectively at the methylene carbon to give the corresponding vinylindium **D** in dry THF (path A) and the resulted vinylindium **D** gives rise to homoallylic amine **3c** during acidic workup. In the presence of the Pd(0) catalyst, **D** couples with iodobenzene to afford **6g**. On the other hand, diindium **B** reacts with water in the solvents at the methyl-substituted carbon to give crotylindium **E** (path B), followed by the reaction with benzaldehyde or imine leading to homoallylic alcohol **5b** or homoallylic amine **4**. The higher reactivity of **B** toward water compared with **A** is considered to be owing to the electron-donating nature of the methyl group on diindium **B**. The coupling of **B** with benzaldehyde proceeds mainly at the substituted carbon to give a new allylic indium compound **F** (path C), which is further reacted with another benzaldehyde to afford diols **8a** and **8b**. Although the reason is not clear at the present stage why the different regioselectivity was observed in the coupling of **B** with aldehyde and imine, only a minor amount of benzaldehyde couples at the methylene carbon of **B** to furnish **7**. It is noted that the In-mediated reaction of 1,3-dibromopropene with aldehyde in *aqueous media* suggests a possibility of a stepwise mechanism that does not involve the diindium species **A**.<sup>19</sup> Therefore, the reaction courses and intermediates may not be the same in organic and aqueous media.

## Conclusions

The reactions of the allylic-type diindium reagents **A** and **B** with electrophiles were investigated and their reaction behavior toward water and aldehyde was found to be of marked difference. Diindium **A** is capable of reacting with both aldehyde and imine at the methylene carbon to give the corresponding vinylindium compounds even in the existence of a small amount of water. On the contrary, diindium **B** is easily protonated by water in solvent and reacts as a crotylindium reagent. In dry THF, diindium **B** couples with aldehyde at the quaternary carbon and the resulting allylic indium reacts further with another aldehyde to give the diols, whereas with imines it reacts at the methylene carbon affording the vinylindium compounds as diindium **A** does. The cascade reactions of the allylic-type diindium reagents **A** and **B** with imines provide a versatile synthetic route for linear homoallylic amines.

## Experimental Section

All reactions were performed under an argon atmosphere. THF was distilled from LiAlH<sub>4</sub> prior to use. The bromides **1a**<sup>20</sup> and **1b**<sup>21</sup> were prepared according to the reported procedures. Imine **2a** is commercially available and used as received. Imine **2b**,<sup>22</sup> 4-methyl-*N*-pentylidenebenzenesulfonamide,<sup>23</sup> and *N*-2-

methylpropylidene-4-methylbenzenesulfonamide<sup>23</sup> were prepared according to the literature.

**Indium-Mediated Reaction of 3-Bromo-1-iodopropene (1a) and Imines.** The following reaction with imine **2b** (Table 1, entry 5) represents the general procedure. A mixture of indium powder (57 mg, 0.50 mmol), 3-bromo-1-iodopropene (**1a**) (*E:Z* = 43:57, 50  $\mu$ L, 0.50 mmol), and sulfonimine **2b** (107 mg, 0.50 mmol) was stirred in DMI (2 mL) at room temperature for 2 h. The reaction mixture was quenched with 1 N hydrochloric acid and the product was extracted with diethyl ether. The extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (elution with EtOAc:hexane = 1:10 and gradually changed to 1:5 then EtOAc) to give *N*-(1-phenylbut-3-enyl)benzenesulfonamide (**3b**) (124 mg, 93%).

**Indium-Mediated Reaction of 4-Bromo-2-iodobut-2-ene (1b) and Imines.** The following reaction with imine **2b** (Table 1, entry 9) represents the general procedure. A mixture of indium powder (57 mg, 0.50 mmol), **1b** (*E* only, 50  $\mu$ L, 0.50 mmol), and sulfonimine **2b** (107 mg, 0.50 mmol) was stirred in THF (2 mL) at room temperature for 2 h. The reaction mixture was quenched with 1 N hydrochloric acid and the product was extracted with diethyl ether. The extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (elution with EtOAc:hexane 1:10 to 1:5 then EtOAc) to give a mixture of (*Z*)-*N*-(1-phenylpent-3-enyl)benzenesulfonamide (**3c**) and *N*-(1-phenyl-2-methylbut-3-enyl)benzenesulfonamide (**4**) (72 mg, 48%, **3c**:**4** 96:4). The ratio of **3c**/**4** was determined by <sup>1</sup>H NMR.

**Cascade Reaction of 3-Bromo-1-iodopropene (1a) with Imines and Halides.** The following reaction with sulfonimine **2b** (Table 2, entry 2) represents the general procedure. A mixture of indium powder (57 mg, 0.50 mmol), **1a** (50  $\mu$ L, 0.50 mmol), and sulfonimine **2b** (123 mg, 0.50 mmol) was stirred in DMI (2 mL) at room temperature for 2 h. To this mixture was added a solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg, 0.01 mmol), LiCl (65 mg, 1.5 mmol), and PhI (58  $\mu$ L, 0.50 mmol) in DMI (4 mL) premixed at room temperature for 1.5 h. The reaction was continued at 110 °C for another 17 h and quenched with 1 N hydrochloric acid. The product was extracted with diethyl ether. The extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (elution with EtOAc:hexane 1:10 gradually 1:5 then EtOAc) to give *N*-(1,4-diphenylbut-3-enyl)benzenesulfonamide (**5b**) (140 mg, 77%).

**Cascade Reaction of 4-Bromo-2-iodobut-2-ene (1b) with Imines and Halides.** The following reaction with sulfonimine **2b** (Table 2, entry 8) represents the general procedure. A mixture of indium powder (57 mg, 0.50 mmol), **1b** (50  $\mu$ L, 0.50 mmol), and sulfonimine **2b** (107 mg, 0.50 mmol) was stirred in THF (2 mL) at room temperature for 2 h. To this mixture was added a solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg, 0.01 mmol), LiCl (65 mg, 1.5 mmol), and PhI (58  $\mu$ L, 0.50 mmol) in DMI (4 mL) premixed at room temperature for 1.5 h. The reaction was continued at 110 °C for another 17 h and quenched with 1 N hydrochloric acid. The product was extracted with diethyl ether. The extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (elution with EtOAc:hexane 1:10 to 1:5 then EtOAc) to give *N*-(1,4-diphenylbut-3-enyl)benzenesulfonamide (**6g**) (98 mg, 52%).

**Indium-Mediated Reaction of 4-Bromo-2-iodobut-2-ene (1b) with Benzaldehyde (Table 3, Entry 4).** A mixture

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of indium powder (57 mg, 0.50 mmol), **1b** (50  $\mu$ L, 0.50 mmol), and benzaldehyde (103  $\mu$ L, 1.0 mmol) was stirred in distilled water (2 mL) at room temperature for 1 day. The product was extracted with diethyl ether and the extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (elution with EtOAc: hexane 1:10 to 1:5 then EtOAc) to give a mixture of **5b** and **7** (20 mg, 25%, **5b**:**7** 68:32), **8a** (8 mg, 12%), and **8b** (18 mg, 28%). The ratio of **7** and **5b** was estimated by <sup>1</sup>H NMR analysis.

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**Supporting Information Available:** Spectral and analytical data for all new compounds and <sup>1</sup>H NMR spectra for **3c**, **6a–h**, **8a**, and **8b** and <sup>13</sup>C NMR spectra for **8a** and **8b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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