Development of Activation Methods of Organotin Compounds Using Transmetalation and Their Application to Organic Synthesis

（金属交換を利用した有機スズ化合物の効率的活性化手法の開発と有機合成への展開）

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Preface and Acknowledgements

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List of Publications

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   Makoto Yasuda, Kensuke Kiyokawa, Kenji Osaki, and Akio Baba
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2. **Cyclopropylmethylation of Benzylic and Allylic Chlorides with Cyclopropylmethylstannane Catalyzed by Gallium or Indium Halide**
   Kensuke Kiyokawa, Makoto Yasuda, and Akio Baba
   Org. Lett. **2010**, *12*, 1520–1523.

3. **Synthesis of Cyclopropane-Containing Phosphorus Compounds by Radical Coupling of Butenylindium with Iodophosphorus Compounds**
   Kensuke Kiyokawa, Itaru Suzuki, Makoto Yasuda, and Akio Baba
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   Kensuke Kiyokawa, Makoto Yasuda, and Akio Baba
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5. **Direct Synthesis of Alkynylstannanes: $ZnBr_2$ Catalyst for the Reaction of Tributyltin Methoxide and Terminal Alkynes**
   Kensuke Kiyokawa, Nodoka Tachikake, Makoto Yasuda, and Akio Baba
   Angew. Chem. Int. Ed. **2011**, *50*, 10393–10396.

Contents

General Introduction 1

Coupling Reaction of Cyclopropylmethylstannane with Iodocarbonyl Compounds or Iodo Phosphorus Compounds 3

1-1. Radical Coupling of Iodocarbonyl Compounds with Butenylindium Generated by Transmetalation between Cyclopropylmethylstannane and Indium Halides 3

1-1-1. Introduction 3

1-1-2. Results and Discussion 3

1-1-3. Conclusion 11

1-1-4. Experimental Section 11

1-1-5. References 20

1-2. Substituted Butenylindium Generated by Transmetalation of Cyclopropylmethylstannane with Indium Iodide: Synthesis and Characterization of Monobutenylindium 22

1-2-1. Introduction 22

1-2-2. Results and Discussion 22

1-2-3. Conclusion 28

1-2-4. Experimental Section 28

1-2-5. References 36

1-3. Synthesis of Cyclopropane-Containing Phosphorus Compounds by Radical Coupling of Butenylindium with Iodophosphorus Compounds 39

1-3-1. Introduction 39

1-3-2. Results and Discussion 39

1-3-3. Conclusion 44

1-3-4. Experimental Section 44

1-3-5. References 57

Cyclopropylmethylation of Benzylic and Allylic Chlorides with Cyclopropylmethylstannane Catalyzed by Gallium or Indium Halide 60

2-1. Introduction 60

2-2. Results and Discussion 60

2-3. Conclusion 65

2-4. Experimental Section 65

2-5. References 74

Direct Synthesis of Alkynylstannanes: $ZnBr_2$ Catalyst for the Reaction of Tributyltin Methoxide and Terminal Alkynes 76

3-1. Introduction 76

3-2. Results and Discussion 77

3-3. Conclusion 82

3-4. Experimental Section 82

3-5. References 95

Conclusion 98

General Introduction

Organometallic compounds are fundamental reagents in organic synthesis. Organolithium or organomagnesium compounds are representative reagents, but their applications have been limited from the viewpoint of functional group tolerance. In recent years, organotin, -silicon, -boron, and -zinc compounds, which have both high functional group compatibility and reasonable reactivity, have been widely used for organic synthesis.[1] In particular, organotin compounds are one of the most useful organometallic reagents because of their comparable high availability and reactivity.[2] Development of appropriate activation methods for those organometallic compounds has led to development of novel synthetic methods. In the case of organotin compounds, transmetalation method provides efficient protocol for organic synthesis. The transmetalation using organotin compounds effectively affords the corresponding active species *in situ*, and by-products in the trasmetalation, alkyltin compounds or tin halides, does not affect the reaction system because of their low reactivity. For example, organolithium or organocopper reagents, which are readily prepared by the transmetalation of Sn-Li or Sn-Cu, respectively, have been used for many types of reactions.[3] Transmetalation with metal halides such as $SnCl_4$, $TiCl_4$, or BBr_3, is also a useful method to provide the corresponding active metal species.[4] Recently, the transmetalation with mild Lewis acids such as indium halides or tin(II) halides has been developed to generate the corresponding active nucleophiles with unique characters which have been applied to various chemo-, regio-, and stereoselective transformations.[5,6] Transmetalation between organotin compounds and appropriate metal halides is expected to be a useful tool for the development of a new synthetic methodology. In this work, the transmetalation with cyclopropylmethylstannane or tin alkoxide, which have been rarely used due to their low reactivity, was applied to organic syntheses as note in Chapters 1–3.

Chapter 1 describes that the generation of butenylindium species by the trasmetalation between cyclopropylmethylstannane and indium halides and their radical coupling reactions with α-iodocarbonyl compounds or iodo phosphorus compounds. The detail structure and reactivity of the butenylindium species were revealed.

Chapter 2 deals with the coupling reaction of cyclopropylmethylstannane with alkyl chlorides using indium or gallium halides as catalysts. It is found that the reaction proceeded in an ionic mechanism, and the unique reactivity of the butenylindium or butenylgallium species was unveiled.

Chapter 3 discloses the $ZnBr_2$-catalyzed direct synthesis of alkynylstannanes from tin methoxide and terminal alkynes. This system enabled the synthesis of various functionalized alkynylstannanes, which had been difficult to synthesis by precedent methods. Moreover, alkynylstannanes synthesized by this system were applicable to one-pot coupling reaction to give functionalized aryl alkyne compounds.

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(2) (a) *Chemistry of Tin*; Harrison, P. G., Ed.; Blackie Academic and Professional: Glasgow & London, 1989. (b) *Tin Chemistry: Fundamentals, Frontiers, and Applications*; Davies, A. G., Gielen, M., Pannell, K. H., Tiekink, E. R. T., Eds.; John Wiley & Sons: Chichester, UK, 2008.

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(4) For selected examples, see: (a) Tanigawa, Y.; Moritani, I.; Nishida, S. *J. Organomet. Chem.* **1971**, *28*, 73. (b) Keck, G. E.; Abbott, D. E. *Tetrahedron Lett.* **1984**, *25*, 1883. (c) Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927.

(5) For selected examples, see: (a) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920. (b) Yasuda, M.; Miyai, T.; Shibata, I.; Baba, A. *Tetrahedron Lett.* **1995**, *36*, 9497. (c) Yasuda, M.; Sugawa, Y.; Yamamoto, A.; Shibata, I.; Baba, A. *Tetrahedron Lett.* **1996**, *37*, 5951. (d) Yasuda, M.; Hirata, K.; Nishino, M.; Yamamoto, A.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 13442.

Chapter 1

Coupling Reaction of Cyclopropylmethylstannane with Iodocarbonyl Compounds or Iodo Phosphorus Compounds

1-1. Radical Coupling of Iodocarbonyl Compounds with Butenylindium Generated by Transmetalation between Cyclopropylmethylstannane and Indium Halides

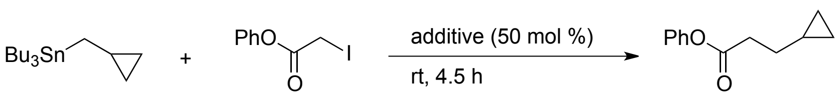
1-1-1. Introduction

Cyclopropylmethylstannane has the potential to introduce a cyclopropyl ring to organic molecules through C–C bond formation. Although some examples using cyclopropylmethylstannane were reported by Young, only ring-opening reactions took place with inorganic reagents such as SO_2, Brønstead acid, or iodine.[1] The lack of a suitable activation method creates difficulty in the control of cyclopropylmethylstannane for carbon–carbon bond formation. There are some examples of starting from a butenylmetal species instead of a cyclopropylmethyl compound to introduce cyclopropylmethyl groups in organic compounds. For example, there is the reaction of butenylstannane with acetals, acid chlorides, and aldehydes in the presence of Lewis acids to form cyclopropylmethylated products.[2,3] *In situ*-generated butenylgallium, -indium, and -aluminum from butenyl Grignard reagents with metal halides are assumed, and they couple with α-halocarbonyls in the presence of Et_3B as a radical initiator.[4] However, the reaction using cyclopropylmethylstannane for introduction of the cyclopropyl ring through C–C bond formation has never been reported as far as we know. In this paper, we report a radical coupling of cyclopropylmethylstannane with α-halocarbonyl compounds mediated by indium halides. In this system, no additional radical initiator was required. Effective transmetalation between the stannane and indium halides gives the butenylindium species, as confirmed by NMR spectroscopy and X-ray analysis. The use of the stannane is advantageous because it allows smooth and clean transmetalation, and the byproduct, halostannane, had no effect on the reaction system.

1-1-2. Results and Discussion

The reaction of cyclopropylmethylstannane **1** with phenyl 2-iodoacetate **2a** in the presence of 0.5 equiv of $InBr_3$ gave the corresponding coupling product **3a** in 73% yield in toluene and a nitrogen-flowing flask (Table 1, entry 1). Although a trace amount of the ring-opening product, which was not precisely identified,[28] was observed, the effective introduction of a cyclopropyl group was accomplished. Without additives, there was no reaction (entry 2). Some solvents, such as Et_2O or MeCN, gave lower yields, and no reaction was observed in THF, probably due to strong solvent coordination (entries 4–6). Exposure to air improved the yield of **3a** (entry 7). The other indium halides, $InCl_3$ or InI_3, gave lower yields (entries 8 and 9). $GaCl_3$ also gave a high yield of **3a** (entry 10), but $AlCl_3$ afforded phenyl 4-iodohexanoate in 41% yield with a trace amount of **3a** (entry 11). In the reaction using BF_3•OEt_2 as an additive, a low yield of **3a** was obtained and the rearranged species, butenylstannane, was confirmed after the reaction (entry 12).[1] When $ZnCl_2$, $TiCl_4$, $ZrCl_4$, $HfCl_4$, or $SnCl_2$ was used as additive, satisfactory yields were not obtained (entries 13–17). The loading of a catalytic amount of galvinoxyl suppressed the reaction (entry 18), and thus the reaction proceeds via a radical mechanism.

Table 1. Optimization of Reaction Conditions[a]



entry	additive	solvent	yield/ %
1	$InBr_3$	toluene	73
2	none	toluene	0
3	$InBr_3$	CH_2Cl_2	76
4	$InBr_3$	Et_2O	42
5	$InBr_3$	MeCN	17
6	$InBr_3$	THF	0
7[b]	$InBr_3$	toluene	79
8	$InCl_3$	toluene	50
9	InI_3	toluene	57
10	$GaCl_3$	toluene	71
11	$AlCl_3$	toluene	<5[c]
12	BF_3•OEt_2	toluene	9
13	$ZnCl_2$	toluene	0
14	$TiCl_4$	toluene	13
15	$ZrCl_4$	toluene	0
16	$HfCl_4$	toluene	0
17	$SnCl_2$	toluene	0
18[d]	$InBr_3$	toluene	<5

[a] All entries were carried out at room temperature in solvent (1 mL) with 1.0 mmol of **1**, 1.0 mmol of **2a**, and 0.5 mmol of additive. [b] Exposure to air (15 min). [c] Phenyl 4-iodohexanoate was formed (41% yield). [d] Addition of galvinoxyl (0.1 mmol).

To gain a thorough understanding of the active species, the relationship between the loading ratio of $InBr_3$/**1** and the product yield was investigated in the reaction of **1** with **2a**, and the results are shown in Figure 1. As the ratio $InBr_3$/**1** increased from 0.1 to 0.5, higher yields of **3a** were obtained, and ca. 0.5 equiv of $InBr_3$ afforded the highest yield. It was curious that ca. 0.3 equiv of $InBr_3$ also gave a relatively high yield, while the yield was reduced when 1.0 equiv of $InBr_3$ was used. These results suggest generation of different active species as a result of varying the ratio of $InBr_3$/**1**.

As confirmation of the conclusion demonstrated by the results in Figure 1, we examined the three types of mixtures of $InBr_3$ and **1** with the ratios of 1/1, 1/2, and 1/3 (= $InBr_3$/**1**) using NMR spectroscopy (Figure 2). The 1/1 mixture of $InBr_3$/**1** gave two types of butenyl-substituted species that were assumed to be butenylindium dibromide **4** and dibutenylindium bromide **5** generated by transmetalation (spectrum a). One species that is reasonable for dibutenylindium bromide **5** was observed when mixed at a ratio of 1/2 ($InBr_3$/**1**) (spectrum b). No other highly substituted species were found from the 1/3 mixture ($InBr_3$/**1**), and only dibutenylindium species **5** and unreacted **1** were observed (spectrum c). The mass spectrum of the 1/2 mixture of $InBr_3$/**1** gave the molecular ion corresponding to the dibutenylindium species [calculated for ($C_8H_{14}In$), 225.0134; found for *m/z,* 225.0134]. The dibutenyl species **5** was more reactive than **4**, as evidenced by more rapid consumption of **5** than of **4** when iodoester **2a** was added to a mixture

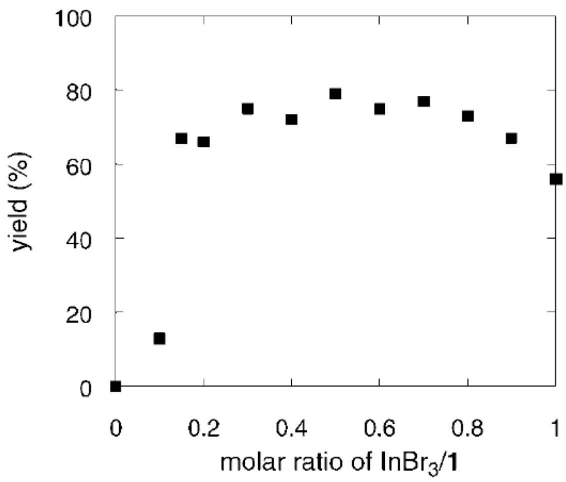


Figure 1. Relationship between amount of $InBr_3$ and the yield of **3a** in the reaction of **1** (1 mmol) with **2a** (1 mmol) at rt for 4.5 h.

that included both **4** and **5** (see the Experimental Section). The amount of **4** remained nearly constant until **5** was completely consumed. Both butenyl groups on **5** were transferred to the product prior to transfer of the butenyl group on **4**. The amount of the monobutenyl species **4** was decreased after **5** had disappeared (see the Experimental Section). The result that loading 1.0 equiv of $InBr_3$ resulted in low efficiency, as shown in Figure 1, is consistent with the greater production of the less reactive monosubstituted indium species. Transmetalation of allylic stannane or hydrostannane with indium halides is widely reported,[6,7] but this is the first example where transmetalation of cyclopropylmethylstannane results in a homoallylic building block.[8]

To investigate the effect of air on the coupling reaction shown in Table 1, the $InBr_3$-mediated reaction of **1** with **2a** was performed in a nitrogen-filled glovebox (O_2 < 5 ppm), as shown in Scheme 1. The reaction gave **3a** in 20% yield after 4.5 h (19% yield even after 10 days). On the other hand, loading 10 mL of air through a syringe into the mixture of **1**, **2a**, and $InBr_3$ prepared in the glovebox gave **3a** in 81% yield after stirring for 4.5 h. These results suggest that oxygen plays an important role in the generation of radical species like the O_2-Et_3B system.[9] In our system, use of another radical initiator is not necessary, as exposure to air is sufficient to initiate the coupling reaction. The *in situ*-generated butenylindium species acts as a radical initiator as well as an alkylating reagent. The conventional experimental bench procedure (not in a glovebox) using a nitrogen-flow system may have adequate oxygen to accelerate the reaction system.

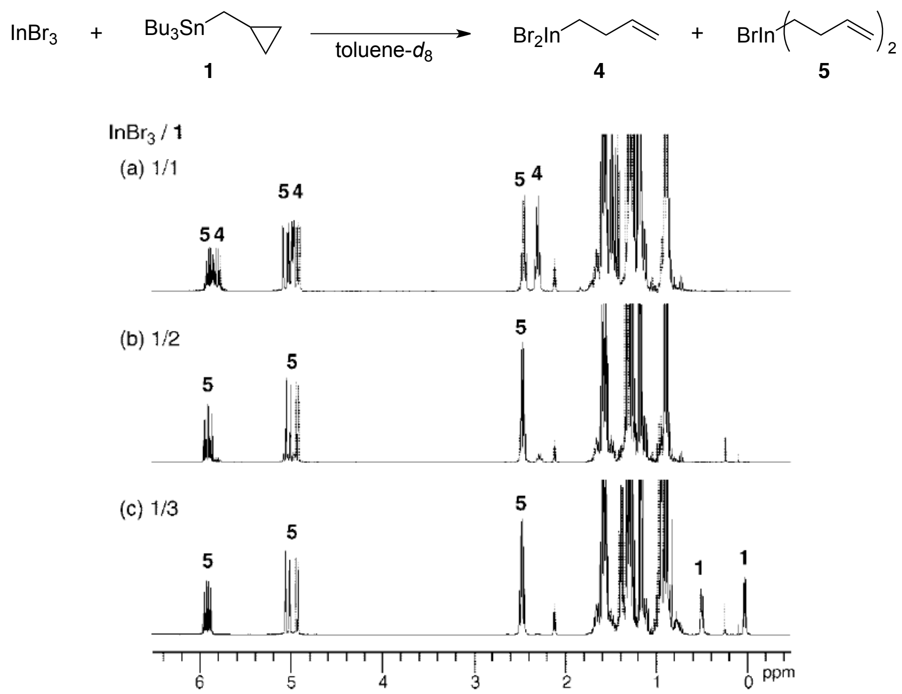
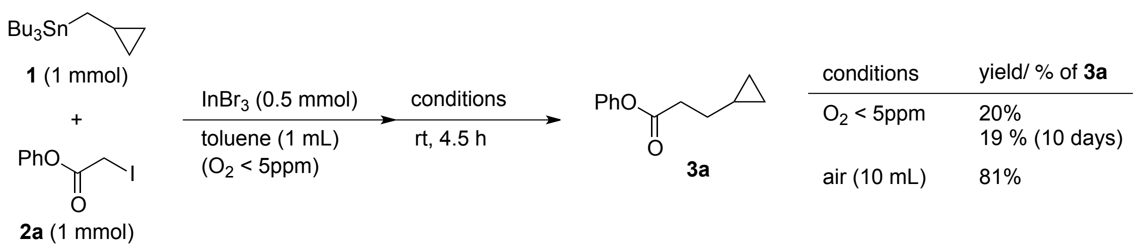


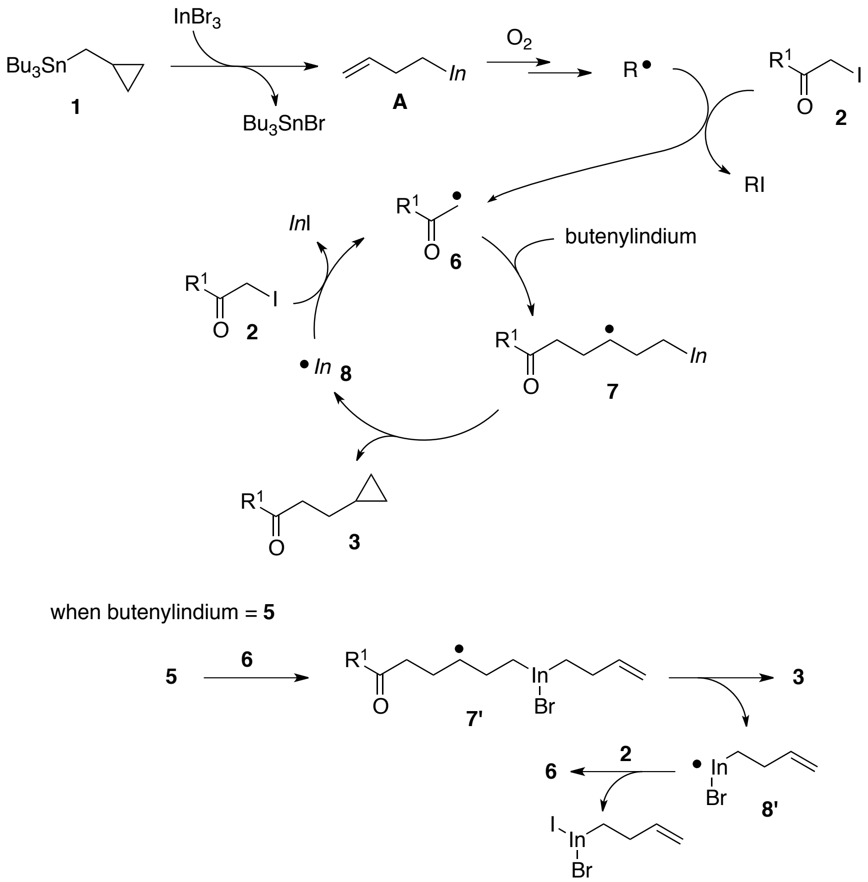
Figure 2. [1]H NMR spectra of the reaction mixtures of $InBr_3$ and **1** with (a) 1/1, (b) 1/2, and (c) 1/3 ratios in toluene-d_8.

Scheme 1. Effect of Air on the Coupling Reaction



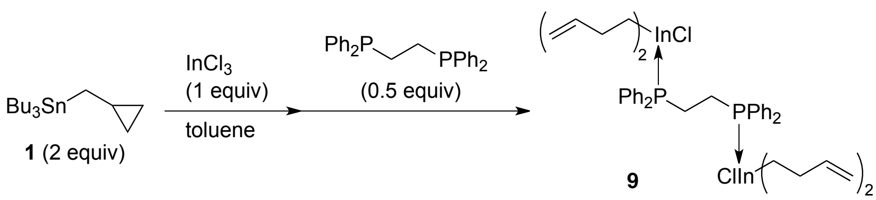
A plausible reaction mechanism is shown in Scheme 2. Transmetalation between **1** and $InBr_3$ gives butenylindium species **A** (other butenyl group and/or ligands are omitted on In). Oxygen-assisted radical initiation abstracts iodine from the iodocarobonyl compound **2**.[9] The generated acylmethyl radical **6** is trapped by butenylindium to give the radical species **7**. Species **7** cyclizes with elimination of the indium radical **8**, which abstracts iodine from **2**, and the acylmethyl radical **6** is regenerated. When the radical species **6** is trapped by dibutenylindium bromide **5**, the resulting indium radical, butenylindium(II) bromide **8′**, is generated via **7′**. The species **8′** abstracts the iodine of **2** to give **6** and butenylbromoindium(III) iodide. Because the formed butenylbromoindium(III) iodide is close to radical **6**, fast coupling between them takes place effectively.[10] This mechanism is consistent with the observation that both butenyl groups on dibutenylindium bromide **5** are preferentially consumed over the butenyl group on **4**. Species **7** could abstract an iodine from **2** to afford an iodinated compound, which then cyclizes into product **3**.[11] However, this mechanism does not explain the rate difference between the butenyl groups on **5** and **4**. Another interesting point is that the byproduct halostannane is not likely to affect the reaction system, and transmetalation starting from tin compounds is quite effective.

Scheme 2. Plausible Reaction Mechanism



Complexation of the active species in the reaction system by various ligands was examined to prove that butenylindium species were generated using X-ray analysis of isolated compounds. Among various ligands and indium sources employed, DPPE and $InCl_3$ gave a crystal of dibutenylindium complex **9** that was suitable for X-ray analysis, as shown in Scheme 3.

Scheme 3. Isolation of Butenylindium Species



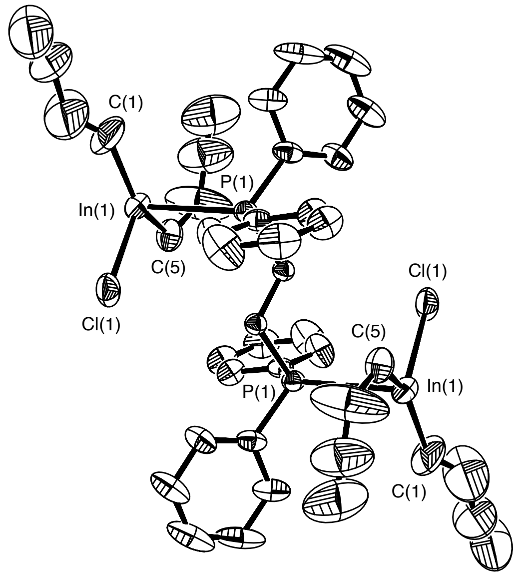


Figure 3. ORTEP drawing of molecular structure of dibutenylindium chloride–DPPE complex **9** (all hydrogens are omitted for clarity).

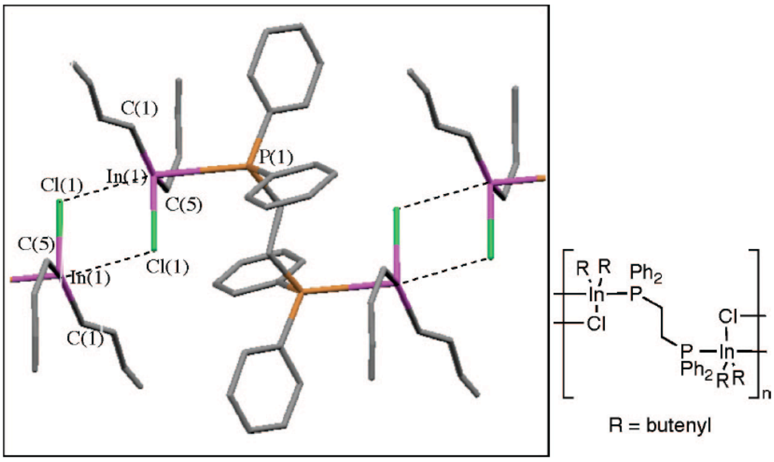


Figure 4. Molecular structure and its intermolecular contacts of dibutenylindium chloride–DPPE complex **9** (all hydrogens are omitted for clarity). Selected bond angles (deg) and lengths (Å): C(1)–In(1)–C(5) 146.6(3), C(1)–In(1)–Cl_{eq}(1) 106.5(3), C(5)–In(1)–Cl_{eq}(1) 105.93(17), P(1)–In(1)–Cl_{ax}(1) 169.95(2), P(1)–In(1)–Cl_{eq}(1) 88.73(3), In(1)–C(1) 2.145(11), In(1)–C(5) 2.148(6), In(1)–P(1) 2.9264(11), In(1)–Cl_{eq}(1) 2.5011(17), In(1)–Cl_{ax}(1) 2.9899(13).

The ORTEP drawing of the indium complex **9** and its intermolecular contacts are shown in Figures 3 and 4. The five-coordinated indium centers had two butenyl groups, a phosphorus in DPPE, and two chlorines. Each chlorine binds two indium centers by bridging.[12] Although DPPE is often used as a bidentate ligand, each phosphine moiety in **9** independently coordinates to different indium centers. The indium center exhibited a distorted trigonal bipyramidal structure with bond angles of C–In–C (146.6°)

and C–In–Cl (106.5° and 105.9°), the sum of which was 359°. P–In–Cl exhibited bond angles of 169.95° and 88.73°. The lengths of the two In–C bonds were 2.145 and 2.148 Å. The lengths of the other three bonds around the indium, In–P, In–Cl_{eq}, and In–Cl_{ax}, were 2.926, 2.501, and 2.990 Å, respectively. This is the first example of X-ray crystallographic analysis of a butenylindium species. Because two In–Cl moieties interact with each other and the phosphines in DPPE independently coordinate to indium centers, the packing structure is clearly linear with a core $(–Cl–In–Cl–In–P–C–C–P–In–)_n$, as shown in Figures 5 and 6. The unit has a length of ca. 10 Å. The view along the *c* axis of the linear structure exhibits three types of atoms (P, In, Cl) in a linear arrangement at close distances. This arrangement appears promising for new materials, although applications of this compound have not yet been investigated.

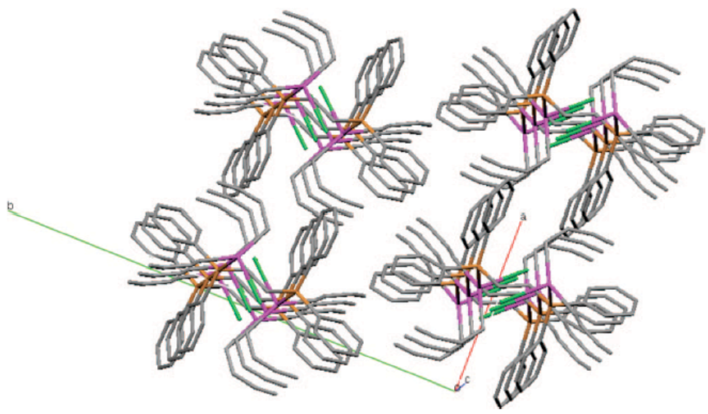


Figure 5. Packing structure of dibutenylindium chloride–DPPE complex **9** (all hydrogens are omitted for clarity).

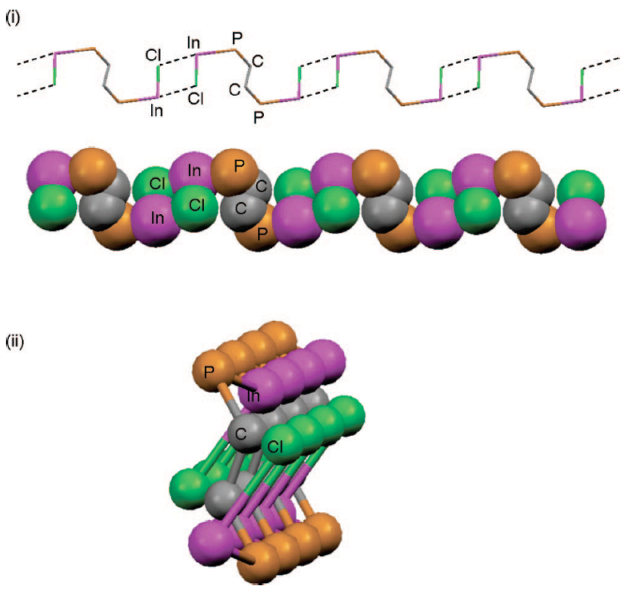
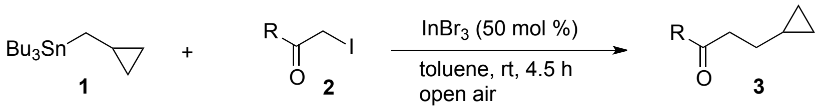
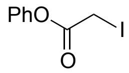
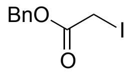
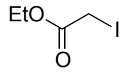
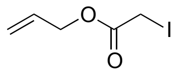
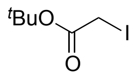
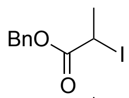
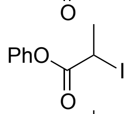
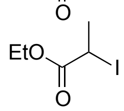
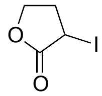
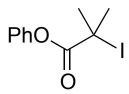
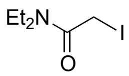
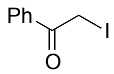


Figure 6. Part of a linear shaped structure of dibutenylindium chloride–DPPE complex **9** (In, P, and carbons of DPPE are shown only for clarity). Views along the *a* axis and *c* axis (with a slight deviation) are shown in (i) and (ii), respectively.

Table 2. Reaction of **1** with α–Iodocarbonyl Compounds **2**[a]



entry	iodocarbonyl			yield/ %	(under N_2)[c]
1		**2a**	**3a**	79	(64)
2[b]		**2b**	**3b**	71	(56)
3		**2c**	**3c**	66	(62)
4		**2d**	**3d**	68	(50)
5		**2e**	**3e**	11	(53)
6		**2f**	**3f**	48	(46)
7		**2g**	**3g**	47	(79)
8		**2h**	**3h**	65	(47)
9		**2i**	**3i**	80	(98)
10		**2j**	**3j**	<5	(<5)
11[b,d]				15	(30)
12[b,d]		**2k**	**3k**	54	(62)
13		**2l**	**3l**	71	(67)

[a] All entries were carried out at room temperature in solvent (1 mL) with 1.0 mmol of **1**, 1.0 mmol of **2**, and 0.5 mmol of $InBr_3$. Tin compound **1** was added to the mixture of **2** and $InBr_3$ in toluene. [b] Iodocarbonyl **2** was added to the mixture of **1** and $InBr_3$ in toluene that had been previously stirred at room temperature for 30 min. [c] Reactions were carried out on the bench using a nitrogen-flowing flask. [d] Reactions were carried out at 100 °C.

Table 2 shows the scope and limitations of using the reaction system for various substrates. The reactions were carried out with exposure to air through the $CaCl_2$ drying tube. Primary iodoesters **2a–d** (entries 1–4) effectively gave the corresponding coupling products, the cyclopropylethyl carbonyl compounds **3a–d**. Although the *tert*-butyl ester **2e** gave a low yield, in the absence of air, the yield increased to 53% (entry 5).[13] The coupling also proceeded with secondary substrates **2f–h** in moderate to high yields (entries 6–8). A high yield was obtained for the reaction with iodolactone **2i** (entry 9). The reaction with the tertiary iodoester **2j** resulted in a low yield (entry 11). Instead of iodoesters, iodoamide **2k** and iodoketone **2l** gave the corresponding products in satisfactory yields (entries 12 and 13). A conventional reaction procedure, which used a nitrogen-flow flask on the bench whereby a very small amount of oxygen was introduced, gave yields that were nearly identical to those obtained under air, although in some cases lower yields were obtained.

1-1-3. Conclusion

The transmetalation of cyclopropylmethylstannane with indium halides to give dibutenylindium halide and butenylindium dihalide was described. This transmetalation can be applied to the reactions with iodocarbonyls to give coupling products that bear cyclopropyl groups. This reaction does not require a radical initiator. Open air conditions sometimes accelerated the radical reaction pathway. The generated dibutenylindium species was stabilized by a phosphine ligand, and the resulting complex was analyzed using X-ray crystallography. The butenylindium species was used as an alkylating reagent without a radical initiator. Transmetalation starting from the stannane proceeded in an effective and clean manner for the synthesis of interesting cyclopropylated carbonyl compounds.

1-1-4. Experimental Section

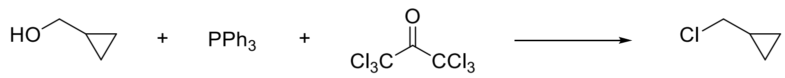
General Procedures. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a 400 and 100 MHz spectrometer, respectively, with TMS as internal standard. ^{119}Sn NMR spectra were obtained with a 150 MHz spectrometer with Me_4Sn as external standard. Mass spectra were recorded on a JEOL JMS-DS303. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (Merck C60). Recycle GPC was performed with $CHCl_3$ as the eluent. Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or ^{1}H NMR using internal standards.

Materials. Dehydrated toluene, dichloromethane, Et_2O, acetonitrile, and THF were purchased and used as obtained. The additives examined in Table 1 were also purchased from commercial sources. Cyclopropylmethylstannane **1** was prepared as previously described.**1a** All iodocarobnyls **2a–l** were prepared according to the known method.[14] The spectral data of **2d**,[15] **2e**,[16] **2g**,[17] **2h**,[14] **2i**,[18] **2k**,[19] and **2l**[20] were in excellent agreement with the reported data. The spectral data of **2c** were in an excellent agreement with those obtained for the commercially available product. The synthetic procedure and spectral data of the other iodocarbonyls **2a**, **2b**, 2**f**, and **2j** are shown below. All other reagents were commercially available.

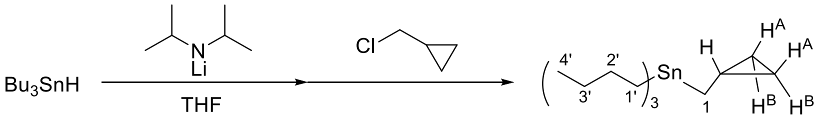
Cyclopropylmethyltributylstannane (1)[21]

$$Bu_3SnOMe \quad + \quad PMHS \longrightarrow Bu_3SnH$$

To a stirred tributyltinmethoxide (330 mmol) was added poly(methylhydrosiloxane) (330 mmol). The mixture was stirred for 8 h at room temperature, and then purified by distillation under reduced pressure to give the product (85.9 g, 89%).

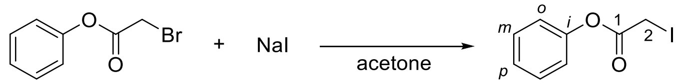


To a stirred hexachloro 2-propanone (600 mmol) at 0 °C was added triphenylphosphine (110 mmol) and the suspension was vigorously stirred for 5 min. To the suspension was added 1-cyclopropylmethanol (100 mmol) dropwaise over 25 min. The mixture was warmed to room temperature and stirred for 3 h before flash distillation to collect a volatile product (7.9 g, 88%).



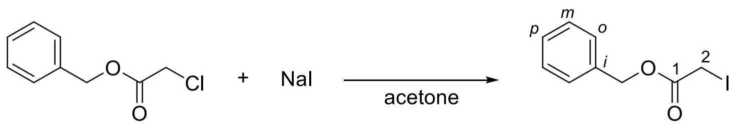
To a solution of *n*-butyllithium (1.6 M in hexane, 47 mL) in THF (80 mL) at 0 °C was slowly added diisopropylamine (75 mmol) and the mixture was stirred for 20 min. To the mixture was added tributyltinhydride (75 mmol) dropwaise within 30 min and the mixture was stirred for 15 min, and then added 1-chloro-1-cyclopropylmethane (70 mmol) dropwaise within 30 min. The mixture was warmed to room temperature and stirred for 16 h, and then quenched by KF aq (10%, 200 mL). Ethylacetate (200 mL) was added and the organic layer was washed by the saturated NaCl aq (200 mL) and H_2O (200 mL), and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (600 mL)] on silica gel and distillation under reduced pressure to give the product (9.4 g, 37%). bp: 78 °C/0.07 mmHg; IR: (neat) 2958, 2924, 1462 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 1.49 (m, 6H, 2'-H_2 x 3), 1.31 (tq, J = 7.2, 7.2 Hz, 6H, 3'-H_2 x 3), 0.96-0.69 (m, 18H, 4'-H_3 x 3, 1'-H_2 x 3, 1-H_2 and $SnCH_2CH$), 0.46 (m, 2H, H^A x 2), -0.04 (m, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 29.4 (t, C-2', d, $^2J_{Sn\text{-}C}$ = 19.7 Hz), 27.5 (t, C-3', d, $^3J_{Sn\text{-}C}$ = 52.4 Hz), 15.0 (t, C-1, d, $^1J_{119Sn\text{-}C}$ = 307.2, $^1J_{117Sn\text{-}C}$ = 293.3 Hz), 13.8 (q, C-4'), 9.2 (d, $SnCH_2CH$, d, $^2J_{Sn\text{-}C}$ = 19.7 Hz), 9.0 (t, C-1', d, $^1J_{119Sn\text{-}C}$ = 312.1, $^1J_{117Sn\text{-}C}$ = 299.0 Hz), 8.3 (t, two methylene groups in cyclopropyl ring, d, $^3J_{Sn\text{-}C}$ = 34.4 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) -15.6; MS: (EI, 70 eV) *m/z* 291 (39), 289 (86), 288 (31), 287 (59), 285 (28), 235 (57), 233 (57), 231 (37), 179 (94), 178 (29), 177 (100), 176 (34), 175 (70), 173 (22), 121 (31), 119 (24); HRMS: (EI, 70 eV) calcd for ($C_{12}H_{27}{}^{120}Sn$) 291.1135 ($M^+ - CH_2C_3H_5$) found *m/z* 291.1104, calcd for ($C_{12}H_{25}{}^{120}Sn$) 289.0978 (M^+ – Bu) found *m/z* 289.1048; Analysis: $C_{16}H_{34}Sn$ (345.15) calcd for C, 55.68; H, 9.93 Found: C, 55.47; H, 9.91.

Phenyl 2-iodoacetate (2a)



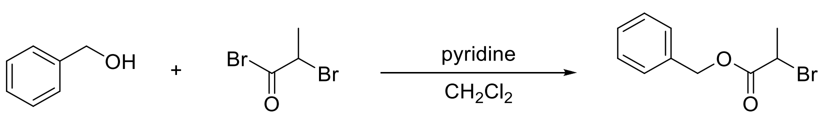
To a stirred solution of sodium iodide (135 mmol) in acetone (150 mL) was added phenyl bromoacetate (45 mmol). The mixture was stirred for 3 h, and then acetone was evaporated. Ethyl acetate (200 mL) was added and the organic layer was washed by $Na_2S_2O_3$ aq (10%, 200 mL) and water (200 mL x 2), and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by recrystallized to give the product (10.5 g, 90%). mp: 65–67 °C; IR: (KBr) 1736 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.40 (dd, J = 8.0, 8.0 Hz, 2H, *m*), 7.25 (t, J = 8.0 Hz, 1H, *p*), 7.11 (d, J = 8.0 Hz, 2H, *o*), 3.90 (s, 2H, 2-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 167.5 (s, C-1), 150.5 (s, C-*i*), 129.5 (d, C-*m*), 126.2 (d, C-*p*), 120.9 (d, C-*o*), -6.0 (t, C-2); MS: (EI, 70 eV) *m/z* 262 (M^+, 8), 94 (100); HRMS: (EI, 70 eV) calcd for ($C_8H_7IO_2$) 261.9491 (M^+) found *m/z* 261.9475; Analysis: $C_8H_7IO_2$ (262.04) Calcd: C, 36.67; H, 2.69; I, 48.43 Found: C, 36.68; H, 2.63; I, 48.70.

Benyl 2-iodoacetate (2b)

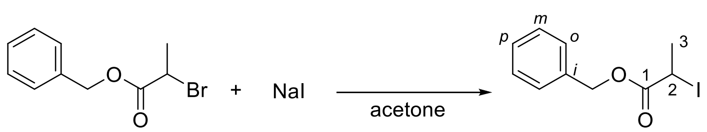


To a stirred solution of sodium iodide (30 mmol) in acetone (60 mL) was added benzyl 2-chloroacetate (30 mmol). The mixture was stirred for 3 h, and then acetone was evaporated. Ethyl acetate (200 mL) was added and the organic layer was washed by $Na_2S_2O_3$ aq (10%, 100 mL) and water (100 mL x 2) and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (6.7 g, 80%). bp: 75 °C/0.1 mmHg; IR: (neat) 1732 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.40-7.30 (m, 5H, Ar), 5.15 (s, 2H, $C_6H_5CH_2$), 3.71 (s, 2H, 2-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 168.5 (s, C-1), 135.0 (s, C-*i*), 128.5 (d), 128.4 (d, C-*p*), 128.2, (d), 67.7 (t, $C_6H_5CH_2$), -5.5 (t, C-2); MS: (EI, 70 eV) *m/z* 276 (M^+, 0.04), 149 ($C_6H_5CH_2OCOCH_2^+$, 89), 107 ($C_6H_5CH_2O^+$, 100), 91 ($C_6H_5CH_2^+$, 90); HRMS: (EI, 70 eV) calcd for ($C_9H_9IO_2$) 275.9647 (M^+) found *m/z* 275.9655; Analysis: $C_9H_9IO_2$ (276.07) Calcd: C, 39.16; H, 3.29; I, 45.97 Found: C, 39.07; H, 3.16; I, 45.96.

Benzyl 2-iodopropanoate (2f)

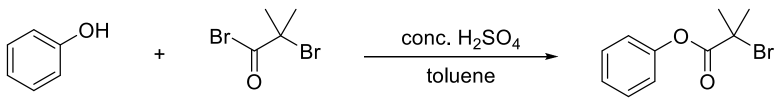


To a stirred solution of benzyl alcohol (110 mmol) and pyridine (120 mmol) in CH_2Cl_2 (80 mL) at 0 °C was added the solution of 2-bromopropionyl bromide (120 mmol) in CH_2Cl_2 (20 mL) dropwise within 25 min. The mixture was warmed to room temperature and stirred for 12 h, and then quenched by water (200 mL). Chloroform (200 mL) was added and the organic layer was washed by 1M HCl aq (200 mL) and saturated $NaHCO_3$ aq (200 mL), and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (24.0 g, 87%). bp: 78 °C/0.05 mmHg

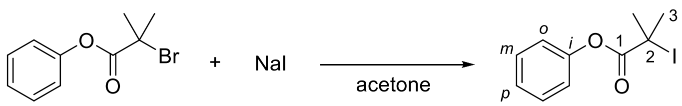


To a stirred solution of sodium iodide (100 mmol) in acetone (100 mL) was added benzyl 2-bromopropanoate (50 mmol). The mixture was stirred for 8 h, and then the solvent was evaporated. Ethyl acetate (200 mL) was added and the organic layer was washed by $Na_2S_2O_3$ aq (10%, 100 mL) and water (100 mL x 2), and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (12.4 g, 82%). bp: 84 °C/0.06 mmHg; IR: (neat) 1736 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.42-7.30 (m, 5H, Ar), 5.17 (m, 2H, $C_6H_5CH_2$), 4.51 (q, J = 7.2 Hz, 1H, 2-H), 1.97 (d, J = 7.2 Hz, 3H, 3-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 171.6 (s, C-1), 135.2 (s, *i*), 128.5 (d), 128.4 (d, *p*), 128.2 (d), 67.4 (t, $C_6H_5CH_2$), 23.2 (q, C-3), 12.8 (d, C-2); MS: (CI, 200 eV) *m/z* 291 (M^+ + 1, 13), 91 ($C_6H_5CH_2^+$, 100); HRMS: (CI, 200 eV) calcd for ($C_{10}H_{12}IO_2$) 290.9882 (M^+ + 1) found *m/z* 290.9894; Analysis: $C_{10}H_{11}IO_2$ (290.10) Calcd: C, 41.40; H, 3.82; I, 43.75 Found: C, 41.63; H, 3.78; I. 43.92.

Phenyl 2-iodo-2-methylpropanoate (2j)



To a stirred solution of phenol (110 mmol) and sulfuric acid (95%, 0.3 mL) in toluene (65 mL) was added 2-bromo-2-methylpropionyl bromide (110 mmol). The mixture was heated to reflux for 5 h, and then cooled to room temperature and quenched by water (200 mL). Ethyl acetate (200 mL) was added and the organic layer was washed by KOH aq (10%, 200 mL) and water (200 mL), and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (21.6 g, 81%). bp: 63 °C/0.04 mmHg



To a stirred solution of sodium iodide (160 mmol) in acetone (80 mL) was added phenyl 2-bromo-2-methylpropanoate (40 mmol). The mixture was heated to reflux for 14 h, and then cooled to room temperature and acetone was evaporated. Ethyl acetate (200 mL) was added and the organic layer was washed by $Na_2S_2O_3$ aq (10%, 100 mL) and water (100 mL x 2), and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (8.72 g, 75%). bp: 100 °C/0.6 mmHg; IR: (neat) 1747 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.40 (dd, J = 8.0, 8.0 Hz, 2H, *m*), 7.25 (t, J = 8.0 Hz, 1H, *p*), 7.13 (d, J = 8.0 Hz, 2H, *o*), 2.20 (s, 6H, 3-H_3 and 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 171.9 (s, C-1), 150.7 (s, *i*), 129.4 (d, *m*), 126.0 (d, *p*), 120.8 (d, *o*), 33.5 (q, C-3 and 2-Me); MS: (EI, 70 eV) *m/z* 290 (M^+, 28), 197 ($COC(CH_3)_2I^+$, 48), 169 ($C(CH_3)_2I^+$, 100), 163 ($C_6H_5OCOC(CH_3)_2^+$, 76), 135 (64), 94 (85), 70 ($COC(CH_3)_2^+$, 28), 69 (22), 41 (38); HRMS: (EI, 70 eV) calcd for ($C_{10}H_{11}IO_2$) 289.9804 (M^+) found *m/z* 289.9822; Analysis: $C_{10}H_{11}IO_2$ (290.10) Calcd: C, 41.40; H, 3.82; I, 43.75 Found: C, 41.65; H, 3.68; I, 43.59.

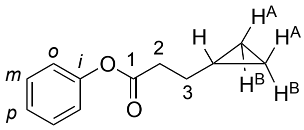
Procedure for Optimization of Coupling of Cyclopropylmethylstannane 1 and Iodocarbonyls 2 (Table 1). According to the next paragraph, the reactions were employed under the conditions noted in text.

General Procedure for $InBr_3$-Mediated Coupling of Cyclopropylmethylstannane 1 and Iodocarbonyls 2 (Table 2). To a suspension of $InBr_3$ (0.5 mmol) and iodocarbonyls **2** (1 mmol) in toluene (1 mL) was added (cyclopropylmethyl)tributylstannane **1** (1 mmol) with a $CaCl_2$ drying tube that was exposed to air. The reaction mixture was stirred at rt for 4.5 h. The mixture was quenched by addition of NH_4F(aq) (10%, 10 mL) and extracted with diethyl ether (3 × 10 mL). The collected organic layer was dried over $MgSO_4$ and concentrated *in* Vacuo. The procedures used for further purification of the new compounds are shown in the Product Data section. The reactions under nitrogen were performed using the same operation.

NMR Study of Transmetalation between 1 and 2 (Figure 2). Three mixtures with different ratios of $InBr_3$/**1** (= 1/1, 1/2, and 1/3) were prepared in toluene-d_8. After mixing for ca. 2 h, the mixtures were transferred into NMR tubes, and the resulting spectra are shown in Figure 2.

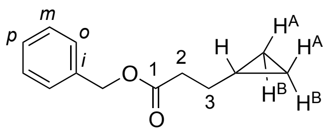
Product Data. The spectral data of **3e**,[26] **3f**,[4] **3i**,[4] **3k**,[4] and **3l**[4] were in excellent agreement with the reported data. Spectral data for the products **3a**, **3b**, **3c**, **3d**, **3g**, **3h**, and **3j** are shown below.

Phenyl 3-cyclopropylpropanoate (3a)[21]



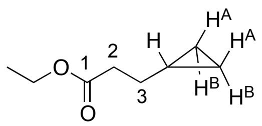
To a suspended solution of $InBr_3$ (2 mmol) in toluene (2 mL), phenyl iodoacetate (2 mmol), (cyclopropylmethyl)tributylstannane (4 mmol), and Et_3B (1.0 M in hexane, 0.5 mL) was added. The mixture was stirred and then additional Et_3B (1.0 M in hexane, 0.5 mL) was loaded after 3 h and 6 h. The mixture was stirred for 22.5 h in total, then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (400 mL) and hexane/ethyl acetate = 94/6 (400 mL)] on silica gel and distillation under reduced pressure. bp: 90 ^oC /0.07 mmHg; IR: (neat) 1759 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.38 (dd, J = 8.0, 7.2 Hz, 2H, *m*), 7.22 (t, J = 7.2 Hz, 1H, *p*), 7.08 (d, J = 8.0 Hz, 2H, *o*), 2.66 (t, J = 7.2 Hz, 2H, 2-H_2), 1.66 (dt, J = 7.2, 7.2 Hz, 2H, 3-H_2), 0.81 (ttt, J = 8.0, 7.2, 5.6 Hz, 1H, $COCH_2CH_2CH$), 0.49 (ddd, J = 8.0, 5.6, 4.8 Hz, 2H, H^A x 2), 0.13 (ddd, J = 5.6, 5.6, 4.8 Hz, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.1 (s, C-1), 150.7 (s, C-*i*), 129.3 (d, C-*m*), 125.7 (d, C-*p*), 121.5 (d, C-*o*), 34.5 (t, C-2), 30.0 (t, C-3), 10.4 (d, $COCH_2CH_2CH$), 4.5 (t, two methylene groups in cyclopropyl ring); MS: (EI, 70 eV) *m*/*z* 190 (M^+, 37), 97 ($COCH_2CH_2C_3H_5^+$, 34), 94 (100), 69 ($CH_2CH_2C_3H_5^+$, 44), 55 ($CH_2C_3H_5^+$, 24); HRMS: (EI, 70 eV) calcd for ($C_{12}H_{14}O_2$) 190.0994 (M^+) found *m*/*z* 190.1000.

Benzyl 3-cyclopropylpropanoate (3b)[21]



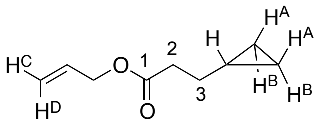
To a suspended solution of $InBr_3$ (5 mmol) in toluene (5 mL), benzyl iodoacetate (5 mmol), (cyclopropylmethyl)tributylstannane (7.5 mmol), and Et_3B (1.0 M in hexane, 0.5 mL) was added. The mixture was stirred for 4.5 h and then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (400 mL) and hexane/ethyl acetate = 95/5 (400 mL)] on silica gel and distillation under reduced pressure. bp: 77 ^oC /0.2 mmHg; IR: (neat) 1736 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.41-7.28 (m, 5H, Ar), 5.12 (s, 2H, $C_6H_5CH_2$), 2.46 (t, J = 7.2 Hz, 2H, 2-H_2), 1.54 (dt, J = 7.2, 7.2 Hz, 2H, 3-H_2), 0.70 (ttt, J = 8.0, 5.6, 7.2 Hz, 1H, $COCH_2CH_2CH$), 0.40 (ddd, J = 8.0, 5.6, 4.0 Hz, 2H, H^A x 2), 0.05 (ddd, J = 5.6, 5.6, 4.0 Hz, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.5 (s, C-1), 136.1 (s, C-*i*), 128.5 (d), 128.2 (d), 128.1 (d, C-*p*), 66.1 (t, $C_6H_5CH_2$), 34.4 (t, C-2), 30.4 (t, C-3), 10.4 (d, $COCH_2CH_2CH$), 4.4 (t, two methylene groups in cyclopropyl ring); MS: (EI, 70 eV) *m/z* 204 (M^+, 0.71), 104 (61), 91 ($C_6H_5CH_2^+$, 100); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{16}O_2$) 204.1150 (M^+) found *m/z* 204.1139; Analysis: $C_{13}H_{16}O_2$ (204.26) Calcd: C, 76.44; H, 7.90 Found: C, 76.52; H, 7.71.

Ethyl 3-cyclopropylpropanoate (3c)[21]



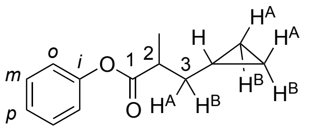
To a suspended solution of $InBr_3$ (2 mmol) in toluene (2 mL), ethyl iodoacetate (2 mmol), (cyclopropylmethyl)tributylstannane (4 mmol), and Et_3B (1.0 M in hexane, 0.5 mL) was added. The mixture was stirred and then additional Et_3B (1.0 M in hexane, 0.5 mL) was loaded after 5.5 h and 10 h. The mixture was stirred for 18.5 h in total, then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (400 mL) and hexane/ethyl acetate = 94/6 (400 mL)] on silica gel and distillation under reduced pressure. bp: 90 ^oC /20 mmHg; IR: (neat) 1739 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 4.13 (q, J = 7.2 Hz, 2H, CH_3CH_2OCO), 2.39 (t, J = 7.2 Hz, 2H, 2-H_2), 1.53 (dt, J = 7.2, 7.2 Hz, 2H, 3-H_2), 1.26 (t, J = 7.2 Hz, 3H, CH_3CH_2OCO), 0.71 (m, 1H, $COCH_2CH_2CH$), 0.43 (ddd, J = 8.0, 5.6, 4.0 Hz, 2H, H^A x 2), 0.05 (m, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.7 (s, C-1), 60.1 (t, CH_3CH_2OCO), 34.5 (t, C-2), 30.1 (t, C-3), 14.2 (q, CH_3CH_2OCO), 10.4 (d, $COCH_2CH_2CH$), 4.3 (t, two methylene groups in cyclopropyl ring); MS: (EI, 70 eV) *m/z* 142 (M^+, 15), 114 ($CH_3CH_2OCOCH_2CH_2CH^+$, 70), 113 ($OCOCH_2CH_2C_3H_5^+$, 20), 99 ($CH_2OCOCH_2CH_2C_3H_5^+$, 32), 97 ($COCH_2CH_2C_3H_5^+$, 64), 96 (21), 88 (96), 73 ($CH_3CH_2OCO^+$, 42), 71 (27), 70 (32), 69 ($CH_2CH_2C_3H_5^+$, 100), 68 (88), 67 (22), 61 (36), 60 (88), 55($CH_2C_3H_5^+$, 71), 54 (27), 42 (22), 41 ($C_3H_5^+$, 74), 39 (31); HRMS: (EI, 70 eV) calcd for ($C_8H_{14}O_2$) 142.0994 (M^+) found *m/z* 142.1010.

Allyl 3-cyclopropylpropanoate (3d)[21]



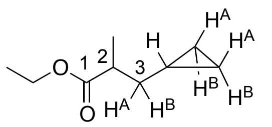
To a suspended solution of $InBr_3$ (2.5 mmol) in toluene (3 mL), allyl iodoacetate (3 mmol), (cyclopropylmethyl)tributylstannane (5 mmol), and Et_3B (1.0 M in hexane, 0.5 mL) was added. The mixture was stirred for 22.5 h and then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (400 mL) and hexane/ethyl acetate = 94/6 (400 mL)] on silica gel and distillation under reduced pressure. bp: 120 ^{o}C /30 mmHg; IR: (neat) 1739 (C=O), 1651 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 5.93 (ddt, J = 17.6, 10.4, 5.6 Hz, 1H, $CH_2C\mathit{H}CH_2OCO$), 5.32 (ddd, J = 17.6, 3.2, 1.6 Hz, 1H, H^D), 5.24 (ddd, J = 10.4, 3.2, 1.6 Hz, 1H, H^C), 4.58 (ddd, J = 5.6, 1.6, 1.6 Hz, 2H, $CH_2CHC\mathit{H}_2OCO$), 2.44 (t, J = 7.2 Hz, 2H, 2-H_2), 1.63 (dt, J = 7.2, 7.2 Hz, 2H, 3-H_2), 0.72 (ttt, J = 8.0, 5.6, 7.2 Hz, 1H, $COCH_2CH_2C\mathit{H}$), 0.43 (ddd, J = 8.0, 5.6, 4.0 Hz, 2H, H^A x 2), 0.06 (ddd, J = 5.6, 5.6, 4.0 Hz, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.4 (s, C-1), 132.3 (d, $CH_2\mathit{C}HCH_2OCO$), 118.1 (t, $\mathit{C}H_2CHCH_2OCO$), 65.0 (t, $CH_2CH\mathit{C}H_2OCO$), 34.4 (t, C-2), 30.1 (t, C-3), 10.5 (d, $COCH_2CH_2\mathit{C}H$), 4.4 (t, two methylene groups in cyclopropyl ring); MS: (CI, 200 eV) m/z 155 (M^+ + 1, 100); HRMS: (CI, 200 eV) calcd for ($C_9H_{15}O_2$) 155.1072 (M^+ + 1) found m/z 155.1080.

Phenyl 3-cyclopropyl-2-methylpropanoate (3g)[21]



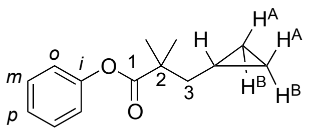
To a suspended solution of $InBr_3$ (1.5 mmol) in toluene (2 mL), phenyl 2-iodopropanoate (2 mmol), (cyclopropylmethyl)tributylstannane (3 mmol), and Et_3B (1.0 M in hexane, 0.2 mL) was added. The mixture was stirred and then additional Et_3B (1.0 M in hexane, 0.2 mL) was loaded after 13 h and 17 h. The mixture was stirred for 20 h in total, then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (400 mL) and hexane/ethyl acetate = 94/6 (400 mL)] on silica gel and distillation under reduced pressure. bp: 95 ^{o}C /0.15 mmHg; IR: (neat) 1759 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.38 (dd, J = 8.0, 7.2 Hz, 2H, *m*), 7.22 (t, J = 7.2 Hz, 1H, *p*), 7.08 (d, J = 8.0 Hz, 2H, *o*), 2.81 (tq, J = 7.2, 7.2 Hz, 1H, 2-H), 1.69 (ddd, J = 14.4, 7.2, 7.2 Hz, 1H, 3-H^A), 1.53 (ddd, J = 14.4, 7.2, 7.2 Hz, 1H, 3-H^B), 1.34 (d, J = 7.2 Hz, 3H, 2-Me), 0.82 (m, 1H, $COCH(CH_3)CH_2C\mathit{H}$), 0.50 (m, 2H, H^A x 2), 0.13 (m, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 175.1 (s, C-1), 150.7 (s, *i*), 129.3 (d, *m*), 125.5 (d, *p*), 121.4 (d, *o*), 40.2 (d, C-2), 38.6 (t, C-3), 16.9 (q, 2-Me), 8.8 (d, $COCH(CH_3)CH_2\mathit{C}H$), 4.6 (t, $COCH(CH_3)CH_2CH\mathit{C}^AH_2$), 4.4 (t, $COCH(CH_3)CH_2CH\mathit{C}^BH_2$); MS: (EI, 70 eV) m/z 204 (M^+, 28), 111 ($COCH(CH_3)CH_2C_3H_5^+$, 54), 94 (88), 83 ($CH(CH_3)CH_2C_3H_5^+$, 70), 55 ($CH_2C_3H_5^+$, 100); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{16}O_2$) 204.1150 (M^+) found m/z 204.1145; Analysis: $C_{13}H_{16}O_2$ (204.26) Calcd: C, 76.44; H, 7.90 Found: C, 76.15; H, 7.74.

Ethyl 3-cyclopropyl-2-methylpropanoate (3h)[21]



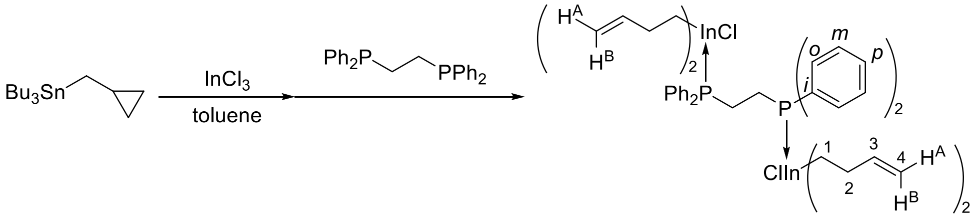
To a suspended solution of $InBr_3$ (1.5 mmol) in toluene (2 mL), ethyl 2-iodopropanoate (2 mmol), (cyclopropylmethyl)tributylstannane (3 mmol), and Et_3B (1.0 M in hexane, 0.2 mL) was added. The mixture was stirred and then additional Et_3B (1.0 M in hexane, 0.2 mL) was loaded after 5 h and 15.5 h. The mixture was stirred for 21 h in total, then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (400 mL) and hexane/ethyl acetate = 94/6 (400 mL)] on silica gel and distillation under reduced pressure. bp: 100 ^oC /10 mmHg; IR: (neat) 1736 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 4.13 (q, J = 7.2 Hz, 2H, CH_3CH_2OCO), 2.53 (tq, J = 7.2, 7.2 Hz, 1H, 2-H), 1.53 (ddd, J = 14.4, 7.2, 7.2 Hz, 1H, 3-H^A), 1.37 (ddd, J = 14.4, 7.2, 7.2 Hz, 1H, 3-H^B), 1.26 (t, J = 7.2 Hz, 3H, CH_3CH_2OCO), 1.18 (d, J = 7.2 Hz, 3H, 2-Me), 0.69 (m, 1H, $COCH_2CH_2CH$), 0.43 (m, 2H, H^A x 2), 0.04 (m, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 176.8 (s, C-1), 60.1 (t, CH_3CH_2OCO), 40.1 (d, C-2), 38.7 (t, C-3), 17.0 (q, 2-Me), 14.2 (q, CH_3CH_2OCO), 8.9 (d, $COCH(CH_3)CH_2CH$), 4.5 (t, $COCH(CH_3)CH_2CHC^AH_2$), 4.2 (t, $COCH(CH_3)CH_2CHC^BH_2$); MS: (EI, 70 eV) m/z 156 (M^+, 14), 128 ($CH_3CH_2OCOCH(CH_3)CH_2CH^+$, 70), 102 (65), 87 (36), 83 ($CH(CH_3)CH_2C_3H_5^+$, 48), 74 (100), 55 ($CH_2C_3H_5^+$, 91), 41 ($C_3H_5^+$, 25); HRMS: (EI, 70 eV) calcd for ($C_9H_{16}O_2$) 156.1150 (M^+) found m/z 156.1139.

Phenyl 3-cyclopropyl-2,2-dimethylpropanoate (3j)[21]



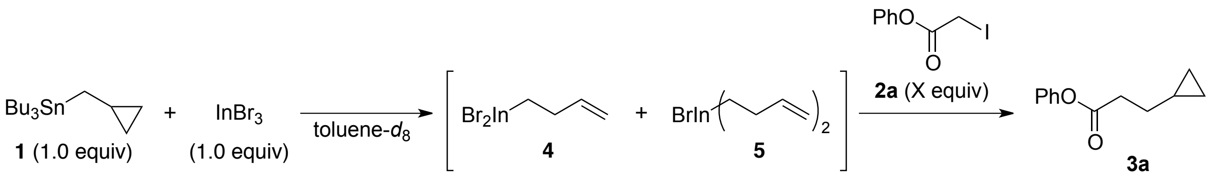
To a suspended solution of $InBr_3$ (0.5 mmol) in toluene (1 mL), (cyclopropylmethyl)tributylstannane (1 mmol) was added. The mixture was stirred for 30 min, and then phenyl 2-iodo-2-methylpropanoate (1 mmol) was added. The mixture was stirred for 4.5 h at 100 ^oC, and then cooled to room temperature and quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography [solvent; hexane (100 mL) and hexane/ethyl acetate = 94/6 (250 mL)] on silica gel and gel permeation chromatography [solvent; chloroform]. IR: (neat) 1751 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.38 (dd, J = 8.0, 7.2 Hz, 2H, *m*), 7.22 (t, J = 7.2 Hz, 1H, *p*), 7.08 (d, J = 8.0 Hz, 2H, *o*), 1.63 (d, J = 7.2 Hz, 2H, 3-H_2), 1.36 (s, 6H, 2-Me_2), 0.79 (ttt, J = 8.0, 7.2, 4.8 Hz, 1H, $COC(CH_3)_2CH_2CH$), 0.50 (ddd, J = 8.0, 5.6, 4.0 Hz, 2H, H^A x 2), 0.13 (ddd, J = 5.6, 4.8, 4.0 Hz, 2H, H^B x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 176.5 (s, C-1), 151.0 (s, *i*), 129.3 (d, *m*), 125.5 (d, *p*), 121.4 (d, *o*), 45.4 (t, C-3), 43.4 (s, C-2), 25.3 (q, 2-Me_2), 7.0 (d, $COC(CH_3)_2CH_2CH$), 4.5 (t, two methylene groups in cyclopropyl ring); MS: (EI, 70 eV) m/z 218 (M^+, 3), 125 ($COC(CH_3)_2CH_2C_3H_5^+$, 50), 97 ($C(CH_3)_2CH_2C_3H_5^+$, 84), 96 (28), 94 (84), 81 (30), 55 ($CH_2C_3H_5^+$, 100); HRMS: (EI, 70 eV) calcd for ($C_{14}H_{18}O_2$) 218.1307 (M^+) found m/z 218.1367.

Dibutenylindium chloride-dppe complex (9)



In a glove box, to a suspended solution of $InCl_3$ (0.5 mmol) in toluene (1 mL) was added (cyclopropylmethyl)tributylstannane (1 mmol) at rt. The mixture was stirred for 2 h, and then 1,2-bis(diphenylphosphino)ethane (0.25 mmol) was loaded. The mixture was stirred for 1 h, and then the volatiles were evaporated to give a viscous liquid, which was then washed by hexane to give the product as a white solid (95mg, 42%). The product was recrystallized from dichloromethane/hexane for X-ray analysis. The data obtained from the measurement is really good and the analysis is completed to optimize the structure. Although some level A alerts still remain, this structure should be justified because of the excellent level of the data and structure refinement. ^{1}H NMR: (400 MHz, $CDCl_3$) 7.47-7.31 (m, 20H, Ar), 5.89 (ddt, J = 16.8, 9.6, 6.4 Hz, 4H, 3-H x 4), 4.95 (dd, J = 16.8, 1.6 Hz, 4H, H^B x 4), 4.88 (dd, J = 9.6, 1.6 Hz, 4H, H^A x 4), 2.38 (dt, J = 7.2, 6.4 Hz, 8H, 2-H_2 x 4), 2.36 (m, 4H, PCH_2CH_2P), 1.11 (t, J = 7.2 Hz, 8H, 1-H_2 x 4); ^{13}C NMR: (100 MHz, $CDCl_3$) 142.7 (C-3), 132.8 (*o*, d, $^2J_{P\text{-}C}$ = 15.6 Hz), 132.3 (*i*), 130.2 (*p*), 129.0 (*m*, d, $^3J_{P\text{-}C}$ = 8.2 Hz), 113.1 (C-4), 30.9 (C-2), 21.9 (PCH_2CH_2P, d, $^1J_{P\text{-}C}$ = 9.8 Hz), 20.4 (C-1).

Observation of the Reaction of Generated butenylindium species. A mixture of $InBr_3$/**1** (= 1/1 molar ratio) was prepared in toluene-d_8 to generate the butenylindium spcecies **4** and **5** (Figure A, iodoester **2a**; 0 equiv). To the mixture was added phenyl 2-iodoacetate **2a** by small portions in several times from 0 to *ca.* 0.9 equiv. ^{1}H NMR integrations of the butenyl groups on **5** and **4** are shown in Figure A. The ^{1}H NMR integration of **3a** based on cyclopropyl group is also included in Figure A.



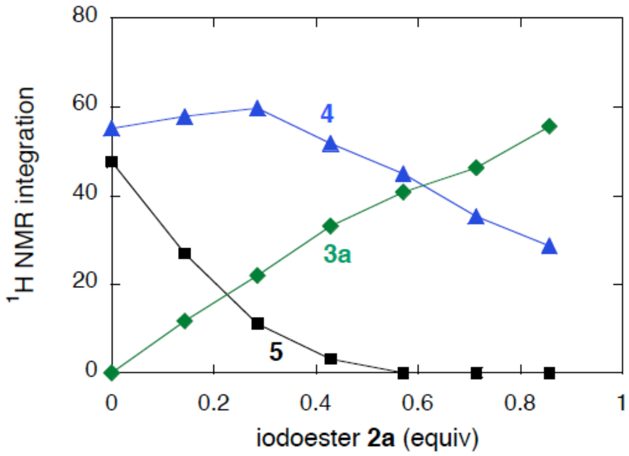


Figure A. ^{1}H NMR integration of butenyl groups on **5** and **4**, and the integration of **3a** based on cyclopropyl group; loading of iodoester **2a** to the mixture of $InBr_3$ and **1** with 1/1 ratios in toluene-d_8.

1-1-5. References

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(10) It might also be explainable that the iodoindium species has a high reactivity toward the carbonyl compound. The halogens on the indium center dramatically affect the reactivity of oxy-functionalized compounds; for example: Nishimoto, Y.; Yasuda, M.; Baba, A. *Org. Lett.* **2007**, *9,* 4931– 4934. The iodine might supply high reactivity in this case.

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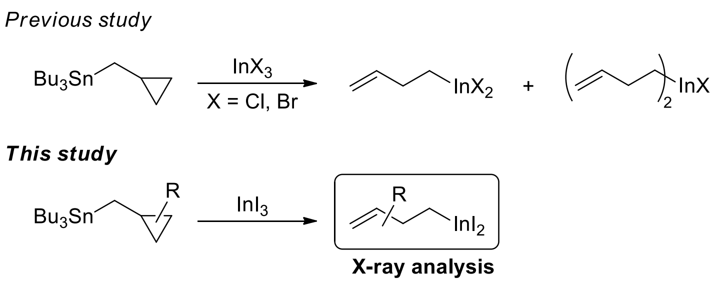
1-2. Substituted Butenylindium Generated by Transmetalation of Cyclopropylmethylstannane with Indium Iodide: Synthesis and Characterization of Monobutenylindium

1-2-1. Introduction

Organoindium compounds are recognized as an important class of organometallic reagents in organic synthesis because of their characteristics: ease of handling, moisture stability, excellent functional group tolerance, etc.[1] In particular, allylic indiums have been widely used for carboncarbon bond formations such as the allylation of carbonyl compounds.[1,2] In addition, various types of other organoindium compounds (alkenyl, alkynyl, aryl, etc.) are also applicable to transition-metal-catalyzed cross- coupling reactions.3 Although the synthetic applications of organoindium compounds have been extensively studied, the structure of the active species is virtually unknown, and the nature of most organoindiums is still undefined.[2f,4] To solve these problems, our group has recently studied organoindium compounds such as alkenylindium[5] (2-carbon unit) and allylindium6 (3-carbon unit). In addition, the higher homologue, the butenylindium (4-carbon unit) species, was investigated for radical and ionic reactivity, particularly dibutenylindium.[7,8] However, the more basic monobutenyl derivative has not been investigated.[9] Herein, we focus on the synthesis of the mono- butenylindium species. Fortunately, the employment of substi- tuted cyclopropylmethylstannanes selectively afforded the monobutenylindium species, as determined by NMR spectros- copy and X-ray structural analysis (Scheme 1). A monobuteny- lindium species had not previously been isolated, while our group has previously reported the isolation of monobutenylgallium.[8] Furthermore, the radical coupling between the substituted butenylindium species with an α-iodoester elucidated the importance of steric hindrance and the β-effect of indium.

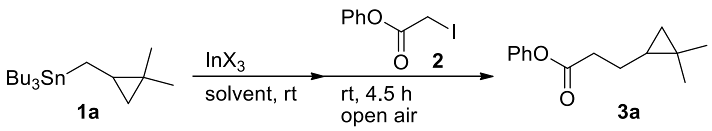
Scheme 1. Synthesis of Monobutenylindium Species by Transmetalation between Substituted Cyclopropylmethylstannanes and InI_3



1-2-2. Results and Discussion

Initially, the reaction of 2,2-dimethylcyclopropylmethyltributylstannane (**1a**) and phenyl 2-iodoacetate (**2**) was conducted to investigate the effect of indium sources and solvents, in which the generation of the butenylindium species was followed by a reaction with **2** (Table 1). The treatment of $InCl_3$ in toluene under open air conditions resulted in a low yield, and unreacted stannane **1a** was recovered (entry 1). This result indicates that the transmetalation between $InCl_3$ and **1a** was not effective. When using $InBr_3$, stannane **1a** was completely consumed, and the yield of the desired product **3a** was improved by as much as 56% (entry 2). Finally, InI_3 was found to be the best choice to afford **3a** (entry 3).[10] In the presence of a radical inhibitor, the coupling reaction was inhibited, indicating that the reaction proceeds in a radical manner (entry 4). The reaction performed in hexane gave a slightly lower yield than that in toluene (entries 3 and 5). Coordinating solvents significantly suppressed the reactions (entries 6–8). Notably, no transmetalation proceeded in THF. Gratifyingly, the addition of a catalytic amount of Et_3B as a radical initiator drastically improved the yield to 94% (entry 9). The reaction in the absence of InI_3 did not give the coupling product (entry 10).

Table 1. Effect of Indium Sources and Solvents[a]



entry	InX_3	solvent	yield/ %[b]	recovery of **1a**/ %[b]
1	$InCl_3$	toluene	25	44
2	$InBr_3$	toluene	56	0
3	InI_3	toluene	64	0
4[c]	InI_3	toluene	0	6
5	InI_3	toluene	54	0
6	InI_3	Et_2O	14	12
7	InI_3	MeCN	0	40
8	InI_3	THF	0	95
9[d]	InI_3	toluene	94	0
10[d]	none	toluene	0	89

[a] Using 1.5 mmol of **1a**, 1.0 mmol of **2**, and 0.75 mmol of indium halide. [b] Determined by ^1H NMR. [c] Galvinoxyl (0.1 mmol) was added. [d] Et_3B (0.1 mmol) was added, and the reaction was carried out under N_2.

To confirm the generation of the butenylindium species, the transmetalation between **1a** and InI_3 was monitored by ^1H NMR spectroscopy (Figure 1). The mixture of **1a** and InI_3 (**1a**/InI_3 = 1:1) in toluene-d_8 immediately produced a single product (**4a**) with a doublet of doublet signal at δ 5.74 for the internal olefin proton, two doublets at δ 4.94 and 4.82 for terminal olefin protons, a singlet at δ 1.91 for methylene protons, and a singlet at δ 0.98 for methyl protons (Figure 1i). **4a** was most certainly a monobutenylindium diiodide, because using two equivalents of **1a** provided two types of butenylindium species, perhaps mono-**4a** and dibutenylindium **5a**, with a small amount of starting material **1a** remaining (Figure 1ii). After the reaction mixture was stirred for a long enough period (13 h), stannane **1a** was almost consumed, and dibutenylindium **5a** was preferentially observed (Figure 1iii). These results show that the first transmetalation between **1a** and InI_3, giving monobutenylindium **4a**, was quite fast, while the second transme- talation, giving dibutenylindium **5a**, was relatively slow probably because of the steric hindrance between butenyl substituents on the indium atom. This is the reason for the selective synthesis of monobutenylindium **4a** from equimolar amounts of **1a** and InI_3. This tendency is quite different from the transmetalation of non-substituted cyclopropylmethylstannane and $InBr_3$, in which the dibutenylindium was readily generated even before the complete consumption of the starting stannane.[7]

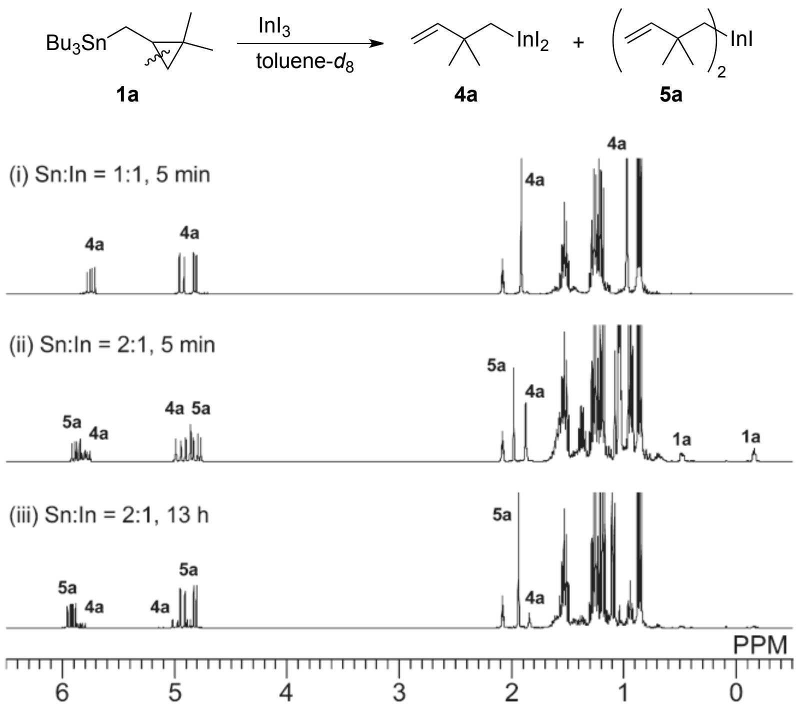
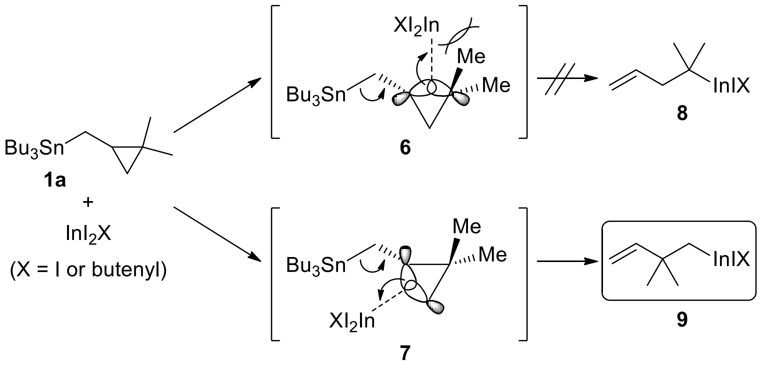


Figure 1. ^{1}H NMR spectra of the reaction mixture of **1a** and InI_3 with (i) 1/1 (5 min), (ii) 2/1 (5 min), and (iii) 2/1 (13 h) ratios in toluene-d_8.

An investigation into the structure of the generated buteny- lindium **4a** (**5a**) provided some insight into the mechanism of transmetalation. For efficient transmetalation, the π-Lewis acidity of indium halide provides an important interaction with the carboncarbon bond of the cyclopropyl ring, which has a much higher p character than a normal carboncarbon σ bond.[11] Since butenylindium **4a** (**5a**) has two methyl groups at the β-position, the selective ring cleavage takes place at the less hindered carbon-carbon bond of **1a** (**6** vs **7**) to produce butenylindium **9**, rather than **8**, as shown in Scheme 2. This proposed mechanism is supported by the fact that InI_3, which is a softer Lewis acid by comparison with either $InCl_3$ or $InBr_3$, gave the best results (see Table 1). In addition, suppression of the transmetalation in coordinating solvents by lowering the Lewis acidity of indium halide can be explained.

Next, to confirm the generation of a monobutenylindium species, isolation by complex formation was attempted using various combinations of stannanes (**1a–d**) (Figure 2) and phosphine ligands.[7,8] Although some stable complexes were isolated, only the combination of stannane **1d** and PPh_3 gave a colorless single crystal that was suitable for X-ray structural analysis (Scheme 3).[12,13]

Scheme 2. Plausible Mechanism for Transmetalation between **1a** and Indium Iodide



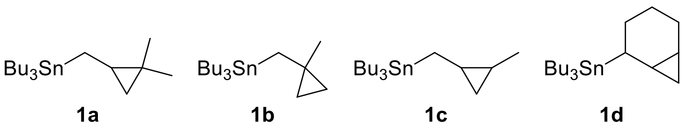
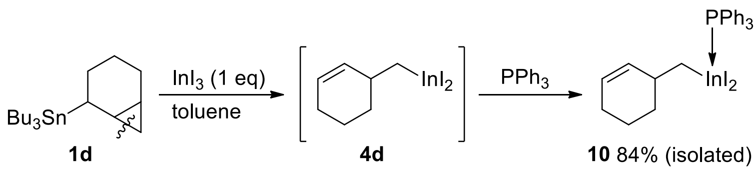


Figure 2. Substituted cyclopropylmethylstannanes.

Scheme 3. Isolation of 2-Cyclohexen-1-ylmethylindium Diiodide–PPh_3 Complex **10**



The ORTEP drawing of 2-cyclohexen-1-ylmethylindium diiodide–PPh_3 complex **10** is shown in Figure 3.[14] As far as can be ascertained, this is the first example of the X-ray structural analysis of a monobutenylindium species.[15] The coordination of one PPh_3 constructed a distorted tetrahedral structure with a four-coordinated indium center. In this complex, there was no intermolecular interaction through bridging by halogen atoms. The In1–C1 length at 2.165(9) Å was slightly shorter than the sum of the individual covalent radii ($d_{In–C}$ = 2.18 Å).[16] The In–C bond is comparable to a previously reported one in the dibutenylindium complex.[7] The C3–C4 length of 1.33(2) Å indicates a double bond. Bond lengths of In1–I1 (2.7189(8) Å), In1–I2 (2.7252(8) Å), and In1–P1 (2.6341(14) Å) and bond angles between substituents at the indium atom were reasonable and were comparable to those reported for the InI_3–PPh_3 complex.[17]

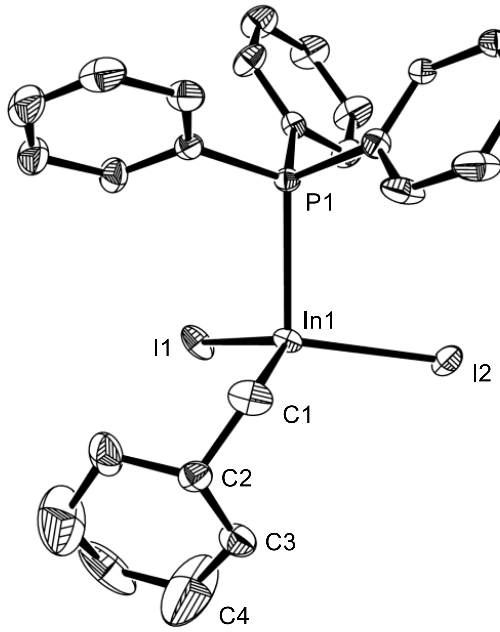


Figure 3. ORTEP drawing of 2-cyclohexen-1-ylmethylindium diiodide–PPh_3 complex **10** (30% thermal ellipsoids. All hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): In1–C1 = 2.165(9), In1–I1 = 2.7189(8), In1–I2 = 2.7252(8), In1–P1 = 2.6341(14), C1–C2 = 1.484(11), C2–C3 = 1.51(10), C3–C4 = 1.33(2); I1–In1–I2 = 107.00(3), I1–In1–C1 = 124.8(3), I2–In1–C1 = 116.5(3), P1–In1–C1 = 106.03(18).

Scheme 4 shows a plausible mechanism for the radical coupling reaction of a butenylindium species with iodoester **2**. First, monobutenylindium **4a** is generated from the transmetalation between stannane **1a** and InI_3, and further transmetalation partly provides dibutenylindium **5a**. The radical initiation step may be different from the case of an unsubstituted butenylindium species,[7] because the present case needs the addition of Et_3B (see Table 1). Therefore, two possibilities are proposed: (i) radical species **11** is generated from **2** assisted by Et_3B with O_2; or (ii) butenylindium **4a** or **5a** works as a radical initiator in the presence of a small amount of O_2 (or O_2/Et_3B), and the resultant radical species abstracts the iodo radical from **2** to produce the corresponding radical **11**. The trap of **11** by the butenylindium species is followed by the cyclization of **12** into cyclopropyl product **3a** along with an indium radical (other butenyl group and/or ligands are omitted on In). Finally, the generated indium radical abstracts the iodine from **2** to regenerate **11**.

In order to investigate the reactivity of the substituted butenylindium species for radical coupling, the reactions of various cyclopropylmethylstannanes **1** and iodoester **2** mediated by InI_3 were conducted, as shown in Table 2. The corresponding cyclopropylmethylated product **3a** was afforded in high yield with no byproduct (entry 1) when using 2,2-dimethylbutenylindium **13a** from **1a**. Other stannanes **1b**, **1c**, and **1e** gave varying amounts of olefins. Among them, **1b**, which generates 3-methylbutenylindium by transmetalation, gave the alkene product **14b** predominantly (**3b**/**14b** = 32/68) (entry 2).[18] This is probably because the cyclization of intermediate **15** is disturbed by the steric hindrance of the tertiary radical (Scheme 5). In addition, the β-effect of indium stabilizes radical intermediate **16** to accelerate the isomerization from **15** to **16** through H-shift to give alkene **14b**.[8,19] Scheme 5 would also be a reasonable explanation for why mono- and nonsubstituted cyclopropylmethylstannanes **1c** and **1e** gave moderate (20%) and small (7%) selectivities of alkenes **14c** and **14e** along with major products of desired cyclopropyls **3c** and **3e**, respectively (entries 3 and 4).[20] No β-hydrogen for an H-shift in intermediate **12** (Scheme 4) is perhaps the reason there was no alkene formation from dimethyl-substituted stannane **1a** (entry 1). Unfortunately, the reaction of cyclic butenylindium **13d** did not proceed due to steric hindrance at the reaction site (entry 5).

Scheme 4. Plausible Reaction Mechanism

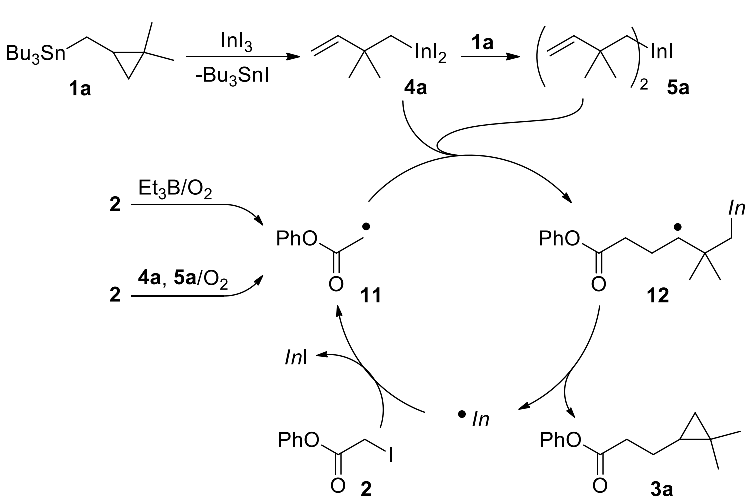
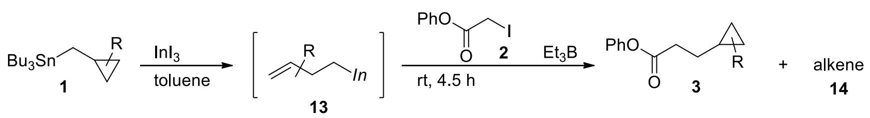


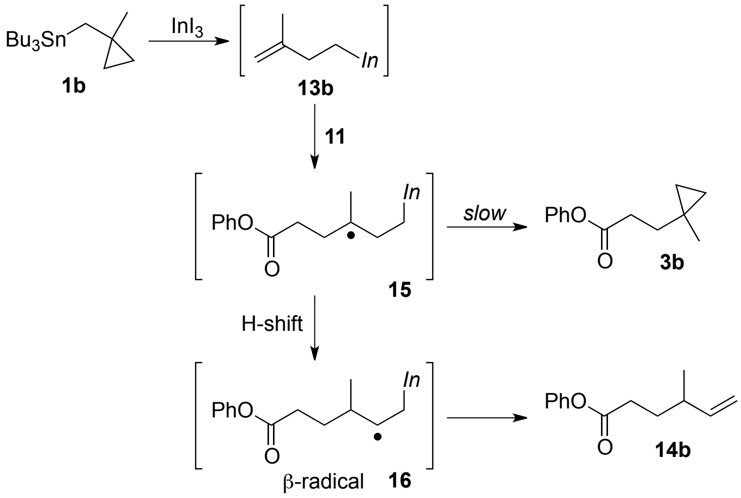
Table 2. Reactions of Cyclopropylmethylstannanes **1** with Iodoester **2**[a]



entry	stannane **1**	butenylindium **13**	product **3**	alkene **14**		**3**/**14**[b]	yield/ %[c]
1	**1a**	**13a**	**3a**	n.d.	**14a**	**3a/14a** (100/0)	81 (94)
2	**1b**	**13b**	**3b**		**14b**	**3b/14b** (32/68)	72 (86)
3[d,e]	**1c**	**13c**	**3c**		**14c**	**3c/14c** (80/20)	45 (56)
4[d]	**1e**	**13e**	**3e**		**14e**	**3e/14e** (93/7)	77 (98)
5[d,e]	**1d**	**13d**	n.d.	n.d.			0

[a] Using 1.5 mmol of **1**, 1.0 mmol of **2**, 0.75 mmol of InI_3, and 0.1 mmol of Et_3B. [b] Determined by ^{1}H NMR. [c] Isolated yields (combined yields of **3** and **14**). Values in parentheses are NMR-determined yields. [d] Et_3B was not added. [e] Open air.

Scheme 5. Plausible Mechanism for Alkene Formation



1-2-3. Conclusion

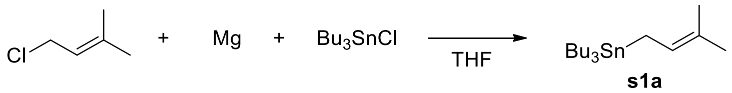
In conclusion, we have reported the facile preparation of substituted butenylindium species from substituted cyclopropyl- methylstannanes and InI_3. The selective generation of monobutenylindium species was also confirmed by NMR spectroscopy and X-ray structural analysis. In transmetalation, the π-Lewis acidity of indium halide and the steric hindrance of the cyclo- propyl ring are important factors for the effective and selective synthesis of monobutenylindium species. Substituted butenylindium species easily coupled with an iodoester to give the corresponding cyclopropane products and alkenes. The results of this radical coupling revealed a dependence on the substituent for the change in reactivity of the butenylindium species.

1-2-4. Experimental Section

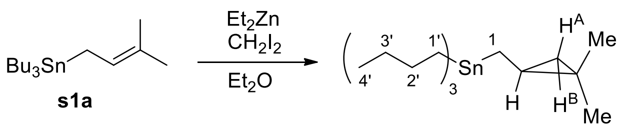
General. New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance techniques, HMQC, HMBC, IR, MS, HRMS, and elemental analysis. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS as internal standard. ^{119}Sn (150 MHz) spectra were obtained with Me_4Sn as external standard. ^{31}P (160 MHz) spectra were obtained with 85 wt% D_3PO_4 in D_2O as external standard. IR spectra were recorded as thin films or solids in KBr pellets. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (MERK C60 or Fuji Silysia FL100DX). Recycle GPC was performed with $CHCl_3$ as the eluent. Bulb-to-Bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. Yields were determined by ^{1}H NMR using internal standard.

Materials. Dehydrated hexane, toluene, acetonitrile, dirthyl ether, and tetrahydrofuran were purchased and used as obtained. Indium halides examined in Table 1 were also purchased from commercial sources. Cyclopropylmethylstannanes **1b**[8] and **1e**[7,8] was prepared by known method and these compounds were reported. Cyclopropylmethylstannanes **1a**, **1c**, and **1d** were prepared by known method.[8] Iodoester **2** was prepared by known method and this compound was reported.[7] All other reagents were commercially available.

Preparation of 2,2-Dimethylcyclopropylmethyltributylstannane (1a)[8]

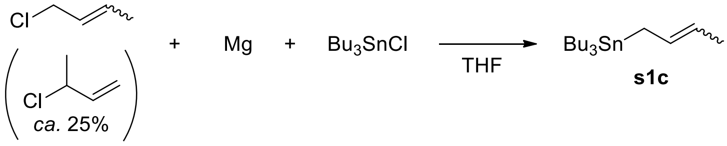


To a flask containing magnesium (4.38 g, 180 mmol) in THF (150 mL), Bu_3SnCl (49.45 g, 152 mmol) was added. The reaction mixture was cooled to 0 ºC, and then 1-chloro-3-methyl-2-butene (18.88 g, 181 mmol) was added. The reaction mixture was irradiated with ultrasound at 0 ºC for 2 h and stirred at room temperature for 10 h, and then quenched by water (200 mL) at 0 ºC. Hexane (200 mL) was added, and the organic layer was washed by water (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane] to give the product **s1a** (51.09 g, 94%).

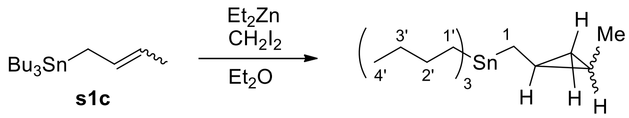


To a solution of **s1a** (10.67 g, 30 mmol) in diethyl ether (40 mL), diethylzinc (1.0 M in hexane, 45 mL) was added. To the reaction mixture, the solution of diiodomethane (26.16 g, 98 mmol) in diethylether (30 mL) was added dropwise within 30 min. The reaction mixture was stirred for 3 h at room temperature, and then quenched by saturated NH_4Cl aq (100 mL). Hexane (200 mL) was added, and the organic layer was washed by saturated NH_4Cl aq (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane] to give the product **1a** (10.83 g, 98% yield, >99% purity (a small portion was analyzed by ^{1}H NMR using an internal standard)). IR: (neat) 2927 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 1.59-1.39 (m, 6H, 2'-H_2 x 3), 1.36-1.25 (m, 6H, 3'-H_2 x 3), 1.02 (s, 3H, Me^A), 1.01 (s, 3H, Me^B), 0.95-0.67 (m, 17H, 4'-H_3 x 3, 1'-H_2 x 3, and 1-H_2), 0.66-0.54 (m, 1H, $SnCH_2C\mathit{H}$), 0.40 (dd, J = 8.0, 4.8 Hz, 1H, H^B), 0.25 (dd, J = 4.8, 4.8 Hz, 1H, H^A); ^{13}C NMR: (100 MHz, $CDCl_3$) 29.3 (t, C-2', d by $^2J_{Sn\text{–}C}$ = 19.6 Hz), 27.5 (t, C-3', d by $^3J_{Sn\text{–}C}$ = 52.4 Hz), 27.4 (q, Me^A), 22.9 (d, $SnCH_2\mathit{C}H$, d by $^2J_{Sn\text{–}C}$ = 19.6 Hz), 22.5 (t, $CH_2CH\mathit{C}H_2$, d by $^3J_{Sn\text{–}C}$ = 27.8 Hz), 19.5 (q, Me^B), 17.1 (s, 14.8, $CH_2CH\mathit{C}Me_2$), 13.7 (q, C-4'), 9.0 (t, C-1, d by $^1J_{119Sn\text{–}C}$ = 304.8, $^1J_{117Sn\text{–}C}$ = 292.5 Hz), 8.9 (t, C-1', d by $^1J_{119Sn\text{–}C}$ = 310.5, $^1J_{117Sn\text{–}C}$ = 297.4 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –14.1; MS: (EI, 70 eV) *m/z* 317 ($Bu_3{}^{120}SnC_6H_{11}{}^+$ – Bu, 15), 291 (63), 290 (22), 289 (48), 287 (28), 235 (68), 234 (23), 233 (52), 231 (31), 179 (100), 178 (29), 177 (92), 176 (31), 175 (60), 121 (25); HRMS: (EI, 70 eV) calcd for ($C_{14}H_{29}{}^{120}Sn$) 317.1291 (M^+ – Bu) found *m/z* 317.1292; Analysis: $C_{18}H_{38}Sn$ (373.20) Calcd: C, 57.93; H, 10.26 Found: C, 57.78; H, 10.16.

Preparation of 2-Methylcyclopropylmethyltributylstannane (1c)[8]

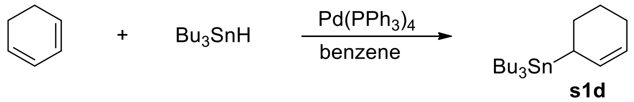


To a flask containing magnesium (4.38 g, 180 mmol) in THF (150 mL), Bu_3SnCl (48.34 g, 149 mmol) was added. The reaction mixture was cooled to 0 ºC, and then crotyl chloride (*cis*- and *trans*- mixture, contains *ca.* 25% 3-chloro-1-butene) (15.91 g, 176 mmol) was added. The reaction mixture was irradiated with ultrasound at 0 ºC for 2 h and stirred at room temperature for 2 h, and then quenched by water (200 mL) at 0 ºC. Hexane (200 mL) was added, and the organic layer was washed using water (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane] to give the product **s1c** (34.30 g, 67%).

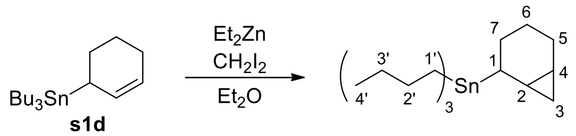


To a solution of **s1c** (10.80 g, 31 mmol) in diethyl ether (40 mL), diethylzinc (1.0 M in hexane, 45 mL) was added. To the reaction mixture, the solution of diiodomethane (25.39 g, 95 mmol) in diethylether (30 mL) was added dropwise within 30 min. The reaction mixture was stirred for 6 h at room temperature, and then quenched by saturated NH_4Cl aq (100 mL). Hexane (200 mL) was added, and the organic layer was washed using saturated NH_4Cl aq (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane] to give the product **1c** (*ca.* 60:40 mixture of *cis* and *trans* isomer) (10.96 g, 97% yield, 99% purity (a small portion was analyzed by ^{1}H NMR using an internal standard)). IR: (neat) 3059, 2908 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 1.60-1.39 (m, 2'-H_2), 1.37-1.24 (m, 3'-H_2), 1.02 (d, J = 5.6 Hz, Me), 1.00 (d, J = 5.6 Hz, Me'), 0.95-0.60 (m, 4'-H_3, 1'-H_2, and 1-H_2), 0.50-0.39 (m), 0.50-0.39 (m), 0.29-0.23 (m), 0.15-0.07 (m), 0.41-0.50 (m); ^{13}C NMR: (100 MHz, $CDCl_3$) 29.3 (t, d by $J_{Sn\text{–}C}$ = 19.7 Hz), 27.5 (t, d by $J_{Sn\text{–}C}$ = 52.4 Hz), 19.0 (q), 18.1 (d, d by $J_{Sn\text{–}C}$ = 19.7 Hz), 16.9 (t, d by $J_{Sn\text{–}C}$ = 37.7 Hz), 16.3 (d, d by $J_{Sn\text{–}C}$ = 32.8 Hz), 14.8 (t, d by $J_{Sn\text{–}C}$ = 25.4 Hz), 14.5 (t, d by $J_{119Sn\text{–}C}$ = 305.5, $J_{117Sn\text{–}C}$ = 293.3 Hz), 13.74 (q), 13.71 (t), 12.7 (q), 11.4 (d, d by $J_{Sn\text{–}C}$ = 38.5 Hz), 9.0 (t), 8.9 (t), 7.4 (t); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –12.3, –16.5; MS: (EI, 70 eV) *m/z* 303 ($Bu_3{}^{120}SnC_5H_9{}^+$ – Bu, 53), 301 (40), 299 (23), 291 (51), 289 (39), 287 (23), 235 (71), 234 (24), 233 (55), 231 (32), 179 (100), 178 (30), 177 (96), 176 (31), 175 (61), 121 (27), 119 (21); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{27}{}^{120}Sn$) 303.1135 (M^+ – Bu) found *m/z* 303.1137; Analysis: $C_{17}H_{36}Sn$ (359.18) Calcd: C, 56.85; H, 10.10 Found: C, 56.58; H, 10.30.

Preparation of (2-Tributylstannyl)bicyclo[4.1.0]heptane (1d)[8]



To a solution of $Pd(PPh_3)_4$ (3.51 g, 3 mmol) in benzene (250 mL), 1,3-cyclohexadiene (12.83 g, 160 mmol) was added. To the reaction mixture, the solution of Bu_3SnH (30.16 g, 104 mmol) in benzene (50 mL) was added dropwise within 1 h. After the reaction mixture was stirred for 3 h at room temperature, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane/diethyl ether = 85/15] to give the product **s1d** (34.15 g, 89%).



To a solution of **s1d** (3.83 g, 10 mmol) in diethyl ether (20 mL), diethylzinc (1.0 M in hexane, 20 mL) was added. To the reaction mixture, the solution of diiodomethane (10.82 g, 40 mmol) in diethylether (10 mL) was added dropwise within 30 min. The reaction mixture was stirred for 2 h at room temperature, and then quenched by saturated NH_4Cl aq (50 mL). Hexane (100 mL) was added, and the organic layer was washed using saturated NH_4Cl aq (50 mL), saturated NaCl aq (50 mL), and NH_4F aq (10%, 50 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product **1d** (3.531 g, 76% yield, 85% purity (a small portion was analyzed by ^{1}H NMR using an internal standard)). Further purification by distillation under reduced pressure improved the purity of **1d** to 99%. IR: (neat) 2927 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 1.88-1.71 (m, 2H), 1.62-1.41 (m, 8H), 1.40-1.22 (m, 8H), 1.15-1.02 (m, 1H), 0.96-0.72 (m, 17H), 0.58 (ddd, J = 8.8, 8.8, 4.8 Hz, 1H, 3-H^A), 0.08 (ddd, J = 4.8, 4.8, 4.8 Hz, 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 29.3 (t, C-2', d by $^2J_{Sn-C}$ = 19.7 Hz), 27.5 (t, C-3', d by $^3J_{Sn-C}$ = 51.6 Hz), 26.7 (t, C-7, d by $^2J_{Sn-C}$ = 16.4 Hz), 23.7 (t, C-5), 23.0 (t, C-6, d by $^3J_{Sn-C}$ = 52.4 Hz), 22.7 (d, C-1, d by $^1J_{119Sn-C}$ = 339.2 Hz, $^1J_{117Sn-C}$ = 323.6 Hz), 13.7 (q, C-4'), 13.5 (d, d by J_{Sn-C} = 7.4 Hz), 13.1 (t, C-3, d by $^3J_{Sn-C}$ = 36.1 Hz), 10.7 (d), 8.4 (t, C-1', d by $^1J_{119Sn-C}$ = 299.9 Hz, $^1J_{117Sn-C}$ = 286.7 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) -14.7; MS: (EI, 70 eV) m/z 329 ($Bu_3{}^{120}SnC_7H_{11}{}^+$ – Bu, 50), 327 (37), 325 (22), 291 (32), 289 (24), 235 (91), 234 (30), 233 (68), 232 (25), 231 (39), 179 (100), 178 (29), 177 (86), 176 (29), 175 (53), 121 (22), 95 (34); HRMS: (EI, 70 eV) calcd for ($C_{15}H_{29}{}^{120}Sn$) 329.1291 (M^+ – Bu) found m/z 329.1292.

Typical procedure for the reaction of cyclopropylmethylstannane 1a with iodoacetate 2 (Table 1). To a suspended solution of InX_3 (0.75 mmol) in toluene (1 mL), 2,2-dimethylcyclopropylmethyltributylstannane (**1a**) (99% purity) (1.50 mmol) was added. The mixture was stirred for 20 min. Then phenyl iodoacetate (**2**) (1.00 mmol) was added. The reaction mixture was stirred for 4.5 h, and then quenched by NH_4F aq (10%, 10 mL). The obtained white precipitate was filtered off and the filtrate was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR. The detail of further purification was described in Product Data.

NMR study of transmetalation between cyclopropylmethylstannane 1 and InI_3. The mixture of cyclopropylmethylstannane **1** and InI_3 (**1**/InI_3 = 1:1 or 2:1) was prepared in toluene-d_8 in a nitrogen-filled glove box. After mixing at room temperature, the mixture was transferred into NMR tube, and the resulting spectra are shown.

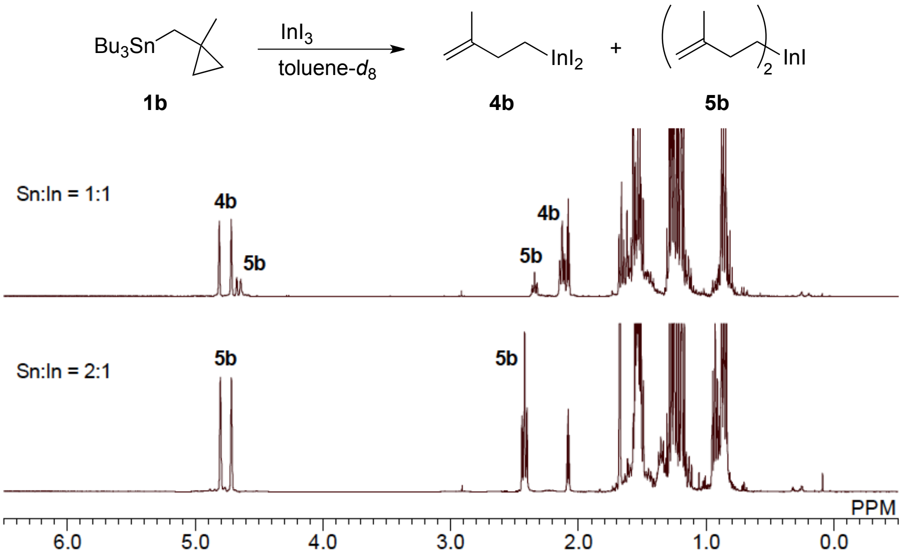


Figure S1. ¹H NMR spectra of the reaction mixtures of InI_3 and **1b** in toluene-d_8.

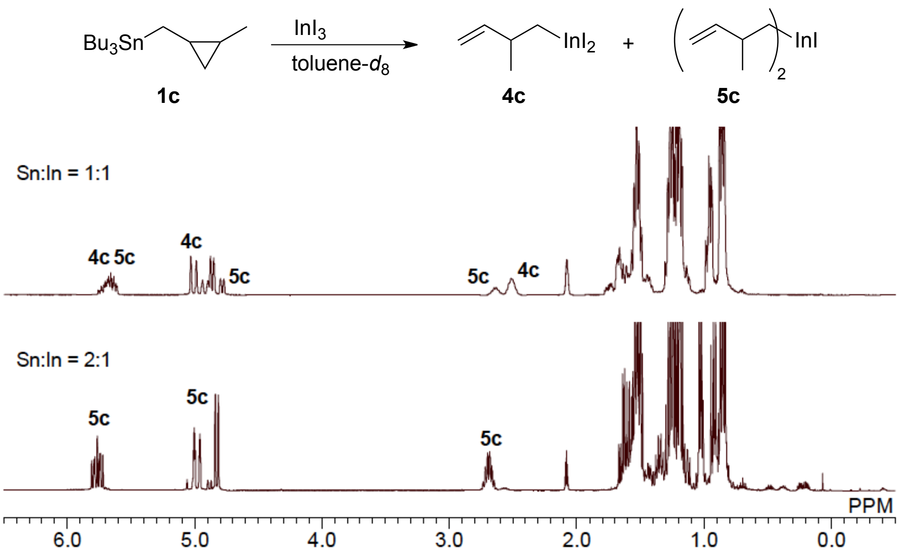


Figure S2. ¹H NMR spectra of the reaction mixtures of InI_3 and **1c** in toluene-d_8.

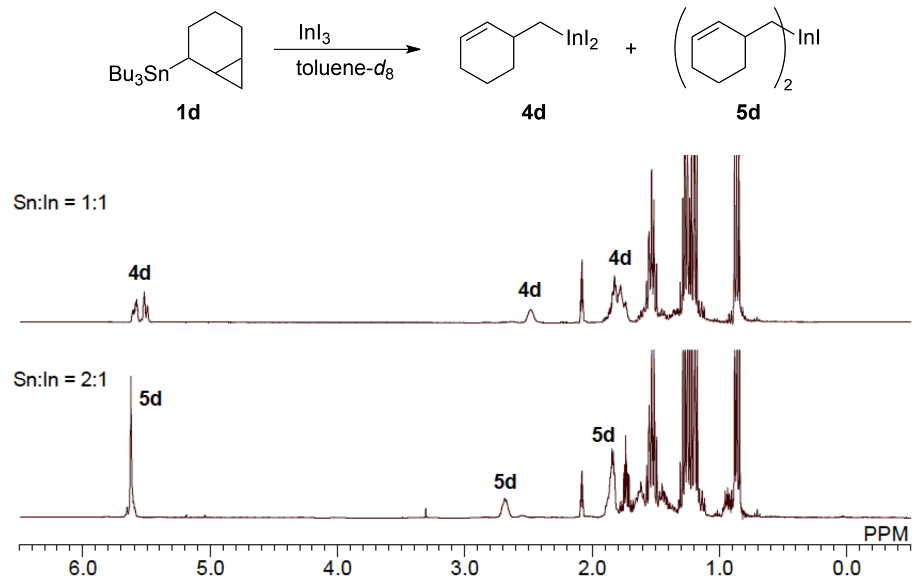
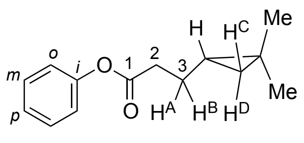


Figure S3. ^{1}H NMR spectra of the reaction mixtures of InI_3 and **1d** in toluene-d_8.

Experimental procedure of the isolation of butenylindium complex 10 (Scheme 3). In a nitrogen-filled glove box, to a suspended solution of InI_3 (0.102 g, 0.21 mmol) in toluene (1 mL), (2-tributylstannyl)bicyclo[4.1.0]heptane (**1d**) (99% purity) (0.079 g, 0.21 mmol) was added at room temperature. The mixture was stirred for 20 min, and then triphenylphosphine (0.053 g, 0.20 mmol) was loaded. The mixture was stirred for 10 min, and then the volatiles were evaporated to give a viscous liquid, which was then washed by hexane to give the product as a white solid (0.125 g, 84%). The product was recrystallized from dichloromethane/hexane to give the suitable crystal for X-ray analysis.

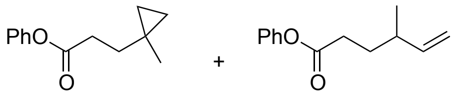
Product data

Phenyl 3-(2,2-dimethylcyclopropyl)propanoate (3a)



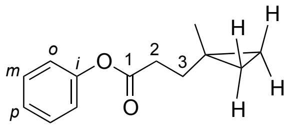
According to the typical procedure, InI_3 (0.371 g, 0.75 mmol), 2,2-dimethylcyclopropylmethyltributylstannane (**1a**) (99% purity) (0.567 g, 1.52 mmol), phenyl iodoacetate (**2**) (0.260 g, 0.99 mmol), and Et_3B (1.0 M in hexane, 0.1 mL) gave the crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 95/5, column length; 11 cm] gave the product **3a** (0.175 g, 81%). Further purification was performed by distillation under reduced pressure to give the product **3a** (0.150 g, 69%). bp: 115 °C /0.18 mmHg; IR: (neat) 1759 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.39 (dd, J = 8.0, 8.0 Hz, 2H, *m*), 7.23 (t, J = 8.0 Hz, 1H, *p*), 7.11 (d, J = 8.0 Hz, 2H, *o*), 2.65 (dd, J = 8.0, 8.0 Hz, 2H, 2-H_2), 1.86 (ddt, J = 14.4, 6.4, 6.4 Hz, 1H, 3-H^A), 1.71 (ddt, J = 14.4, 6.4, 6.4 Hz, 1H, 3-H^B), 1.11 (s, 3H, Me^A), 1.08 (s, 3H, Me^B), 0.62 (dddd, J = 8.0, 6.4, 6.4, 4.8 Hz, 1H, $COCH_2CH_2CH$), 0.47 (dd, J = 8.0, 4.8 Hz, 1H, H^C), –0.02 (dd, J = 4.8, 4.8 Hz, 1H, H^D); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.1 (s, C-1), 150.7 (s, C-*i*), 129.3 (d, C-*m*), 125.6 (d, C-*p*), 121.5 (d, C-*o*), 34.9 (t, C-2), 27.4 (q, Me), 25.3 (t, C-3), 23.8 (d, $COCH_2CH_2$*C*H), 19.8 (q, Me), 19.6 (t, $COCH_2CH_2CH$*C*H_2), 15.6 (s, $COCH_2CH_2CH$*C*Me_2); MS: (EI, 70 eV) *m*/*z* 218 (M^+, 2), 125 (M^+ – OPh, 48), 94 (100), 83 (M^+ – $PhOCOCH_2$, 20), 55 (44); HRMS: (EI, 70 eV) calcd for ($C_{14}H_{18}O_2$) 218.1307 (M^+) found *m*/*z* 218.1299; Analysis: $C_{14}H_{18}O_2$ (218.29) Calcd: C, 77.03; H, 8.31 Found: C, 76.87; H, 8.24

Phenyl 3-(1-methylcyclopropyl)propanoate (3b) and Phenyl 4-methyl-5-hexanoate (14b)



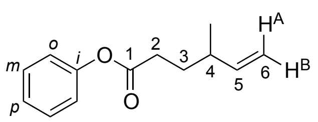
According to the typical procedure, InI_3 (0.376 g, 0.76 mmol), 1-methylcyclopropylmethyltributylstannane (**1b**) (91% purity) (0.602 g, 1.53 mmol), phenyl iodoacetate (**2**) (0.262 g, 1.00 mmol), and Et_3B (1.0 M in hexane, 0.1 mL) gave the crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 95/5, column length; 11 cm] gave the mixture of **3b** and **14b** (0.148 g, 72%, **3b**:**14b** = 32:68). Further purification was performed by gel permeation chromatography [solvent; chloroform] to give products (**3b** and **14b**).

Phenyl 3-(1-methylcyclopropyl)propanoate (3b)



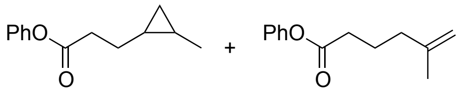
IR: (neat) 1759 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.37 (dd, *J* = 7.2, 7.2 Hz, 2H, *m*), 7.22 (t, *J* = 7.2 Hz, 1H, *p*), 7.08 (d, *J* = 7.2 Hz, 2H, *o*), 2.68-2.61 (m, 2H, 2-H_2), 1.74-1.67 (m, 2H, 3-H_2), 1.09 (s, 3H, Me), 0.39-0.28 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.4 (s, C-1), 150.7 (s, C-*i*), 129.4 (d, C-*m*), 125.7 (d, C-*p*), 121.5 (d, C-*o*), 34.6 (t, C-3), 32.3 (t, C-2), 22.3 (q, Me), 15.0 (s, $COCH_2CH_2$*C*) 13.0 (t, two methylene groups in cyclopropyl ring); MS: (EI, 70 eV) *m*/*z* 204 (M^+, 17), 111 (M^+ – OPh, 56), 94 (100), 69 (M^+ – $PhOCOCH_2$, 24), 55 (M^+ – $PhOCOCH_2CH_2$, 30); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{16}O_2$) 204.1150 (M^+) found *m*/*z* 204.1148.

Phenyl 4-methyl-5-hexanoate (14b)



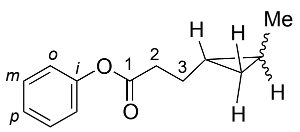
IR: (neat) 1763 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.38 (dd, *J* = 7.2, 7.2 Hz, 2H, *m*), 7.22 (t, *J* = 7.2 Hz, 1H, *p*), 7.07 (d, *J* = 7.2 Hz, 2H, *o*), 5.69 (ddd, *J* = 17.6, 10.4, 7.2 Hz, 1H, 5-H), 5.04 (d, *J* = 17.6 Hz, 1H, 6-H^A), 5.01 (d, *J* = 10.4 Hz, 1H, 6-H^B), 2.63-2.48 (m, 2H, 2-H_2), 2.24 (qtd, *J* = 7.2, 7.2, 7.2 Hz, 1H, 4-H), 1.86-1.67 (m, 2H, 3-H_2), 1.07 (d, 3H, Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.3 (s, C-1), 150.7 (s, C-*i*), 143.3 (d, C-5), 129.4 (d, C-*m*), 125.7 (d, C-*p*), 121.5 (d, C-*o*), 113.9 (t, C-6), 37.6 (d, C-4), 32.3 (t, C-2), 31.3 (t, C-3), 20.2 (q, Me); MS: (EI, 70 eV) *m*/*z* 204 (M^+, 4), 111 (M^+ – OPh, 49), 94 (100), 69 (M^+ – $PhOCOCH_2$, 21), 55 (M^+ – $PhOCOCH_2CH_2$, 59); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{16}O_2$) 204.1150 (M^+) found *m*/*z* 204.1149.

Phenyl 3-(2-methylcyclopropyl)propanoate (3c) and Phenyl 5-methyl-5-hexcanoate (14c)



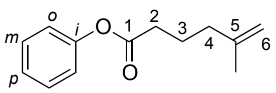
According to the typical procedure, InI_3 (0.372 g, 0.75 mmol), 2-methylcyclopropylmethyltributylstannane (**1c**) (99% purity) (0.539 g, 1.50 mmol), and phenyl iodoacetate (**2**) (0.260 g, 0.99 mmol) gave the crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 95/5, column length; 11 cm] gave the mixture of **3c** (50:50 mixture of *cis* and *trans* isomer) and **14c** (0.092 g, 45%, **3c**/**14c** = 80/20). Further purification was performed by gel permeation chromatography [solvent; chloroform] to give products (**3c** (59:41 mixture of *cis* and *trans* isomer) and **14c**).

Phenyl 3-(2-methylcyclopropyl)propanoate (3c)



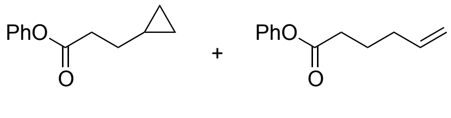
IR: (neat) 1759 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.37-7.06 (m, Ar), 7.37-7.06 (m, Ar'), 2.71-2.58 (m, 2-H_2), 2.71-2.58 (m, 2'-H_2), 1.87-1.55 (m, 3-H_2), 1.87-1.55 (m, 3'-H_2), 1.07 (d, J = 6.4 Hz, Me), 1.04 (d, J = 6.4 Hz, Me'), 0.89-0.73 (m, $COCH_2CH_2C\mathit{H}$ and C*H*Me), 0.67 (ddd, J = 8.0, 8.0, 4.0 Hz, $COCH_2CH_2CHC\mathit{H}H$), 0.58-0.46 (m, $COCH_2CH_2C\mathit{H}'$ and C*H*'Me), 0.28 (ddd, J = 8.0, 4.0, 4.0 Hz, $COCH_2CH_2CHC\mathit{H}'H$), 0.22 (ddd, J = 8.0, 4.0, 4.0 Hz, $COCH_2CH_2CHCH\mathit{H}'$), –0.21 (ddd, J = 4.8, 4.8, 4.0 Hz, $COCH_2CH_2CHCH\mathit{H}$); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.2 (s, C-1), 150.7 (s, C-*i*), 129.4 (d, C-*m*), 125.7 (d, C-*p*), 121.6 (d, C-*o*), 34.9 (t, C-2), 34.6 (t, C-2'), 29.6 (t, C-3'), 24.1 (t, C-3), 19.2 (d, $COCH_2CH_2\mathit{C}H$), 18.9 (q, Me'), 15.0 (d, $COCH_2CH_2\mathit{C}'H$), 13.1 (q, Me), 13.0 (t, $COCH_2CH_2CH\mathit{C}'H_2$), 12.8 (d, *C*'Me), 11.9 (t, $COCH_2CH_2CHCH_2$), 9.6 (d, *C*Me); Two mass spectra were obtained from the mixture of *cis* and *trans* isomer. MS: (EI, 70 eV) *m/z* 204 (M^+, 27), 111 (M^+ – OPh, 41), 94 (100), 69 (M^+ – $PhOCOCH_2$, 28), 55 (M^+ – $PhOCOCH_2CH_2$, 39); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{16}O_2$) 204.1150 (M^+) found *m/z* 204.1140; MS: (EI, 70 eV) *m/z* 204 (M^+, 23), 111 (M^+ – OPh, 40), 94 (100), 69 (M^+ – $PhOCOCH_2$, 26), 55 (M^+ – $PhOCOCH_2CH_2$, 39); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{16}O_2$) 204.1150 (M^+) found *m/z* 204.1153.

Phenyl 5-methyl-5-hexenoate (14c)



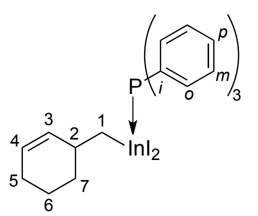
^{1}H NMR: (400 MHz, $CDCl_3$) 7.38 (dd, J = 7.2, 7.2 Hz, 2H, *m*), 7.23 (t, J = 7.2 Hz, 1H, *p*), 7.08 (d, J = 7.2 Hz, 2H, *o*), 4.81-4.76 (m, 1H, 6-H^A), 4.76-4.72 (m, 1H, 6-H^B), 2.57 (t, J = 7.2 Hz, 2H, 2-H_2), 2.15 (t, J = 7.2 Hz, 2H, 4-H_2), 1.91 (tt, J = 7.2, 7.2 Hz, 2H, 3-H_2), 1.75 (s, 3H, Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.1 (s, C-1), 150.7 (s, C-*i*), 144.6 (s, C-5), 129.4 (d, C-*m*), 125.7 (d, C-*p*), 121.5 (d, C-*o*), 110.9 (t, C-6), 37.0 (t, C-4), 33.7 (t, C-2), 22.7 (t, C-3), 22.2 (q, Me); MS: (CI, 200 eV) *m/z* 205 (M^+ + 1, 100); HRMS: (CI, 200 eV) calcd for ($C_{13}H_{17}O_2$) 205.1229 (M + 1) found *m/z* 205.1222.

Phenyl 3-cyclopropylpropanoate (3e) and Phenyl 5-hexenoate (14e)



According to the typical procedure, InI_3 (0.372 g, 0.75 mmol), cyclopropylmethyltributylstannane (**1e**) (92% purity) (0.570 g, 1.51 mmol), and phenyl iodoacetate (**2**) (0.261 g, 1.00 mmol) gave the crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 95/5, column length; 11 cm] gave the mixture of **3e** and **14e** (0.146 g, 77%, **3e**/**14e** = 93/7). Further purification was performed by distillation under reduced pressure to give the mixture of **3e** and **14e** (0.144 g, 76%, **3e**/**14e** = 93/7). The analytical data for these compounds were in excellent agreement with the reported data.[7,21] The GC mass spectrum of the mixture gave the two signals corresponding to the **3e** and **14e** [calculated for ($C_{12}H_{14}O_2$), 190.0994; found for *m*/*z* 190.0990 (**3e**) and 190.0991 (**14e**)]. Analysis: $C_{12}H_{14}O_2$ (190.24) Calcd: C, 75.76; H, 7.42 Found: C, 75.58; H, 7.27.

Cyclohexenylmethylindium diiodide triphenylphosphine complex (10)



^{1}H NMR: (400 MHz, $CDCl_3$) 7.63-7.44 (m, 15H, Ar), 5.58-5.51 (m, 1H, 4-H), 5.51-5.43 (m, 1H, 3-H), 2.59-2.43 (m, 1H, 2-H), 1.94-1.15 (m, 8H, 1-H_2, 5-H_2, 6-H_2, and 7-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 133.8 (d, d by $J_{P\text{-}C}$ = 12.2 Hz), 133.5 (d, C-3), 132.0 (d, C-*p*, d by $^{4}J_{P\text{-}C}$ = 1.7 Hz), 129.5 (d, d by $J_{P\text{-}C}$ = 10.7 Hz), 126.9 (d, C-4), 125.7 (s, C-*i*, d by $^{1}J_{P\text{-}C}$ = 38.5 Hz), 34.5 (d, C-2), 33.2 (t), 30.0 (t, C-1), 25.0 (t), 21.4 (t); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) -2.33.

1-2-5. References

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(11) Wong, H. N. C.; Hon, M.-Y.; Tse, C. W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165–198.

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small amount of dibutenylindium. The second transmetalation could be relatively fast because the steric hindrance of substituents of **1b** (**1c**) are smaller than those of **1a** and **1d**.

(13) The generation of **4d** as a single product was observed by NMR spectroscopy.

(14) The data obtained from the measurement was good, and the analysis was completed to optimize the structure. Although some level A alerts still remain, this structure should be justified because of the excellent level of the data and structure refinement.

(15) Monoalkylindiums from the reaction of alkenes, $InBr_3$, and ketene silyl acetals were isolated, see: Nishimoto, Y.; Ueda, H.; Inamoto, Y.; Yasuda, M.; Baba, A. *Org. Lett.* **2010**, *12*, 3390–3393.

(16) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

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(18) The reaction of **1b** with **2** was examined at 0 ºC and gave the products in 86% yield and ratio of **3b**/**14b** = 37/63. This result indicates that the ratio of **3**/**14** does not depend on a reaction temperature.

(19) (a) Sakurai, H.; Imai, T.; Hosomi, A. *Tetrahedron Lett.* **1977**, *18*, 4045–4048. (b) Sugawara, M.; Yoshida, J. *Tetrahedron* **2000**, *56*, 4683–4689. (c) Ogasawara, M.; Okada, A.; Murakami, H.; Watanabe, S.; Ge, Y.; Takahashi, T. *Org. Let.* **2009**, *11*, 4240–4243.

(20) We assume that butenylindiums **13a**–**c** with substituents are relatively stable to oxygen, so a radical initiator (Et_3B) or an open air condition is required in a radical initiation step to facilitate the efficient reaction. On the contrary, because nonsubstituted **13e** easily generates a radical species (not fully determined) assisted by oxygen, an additional radical initiator is not required.

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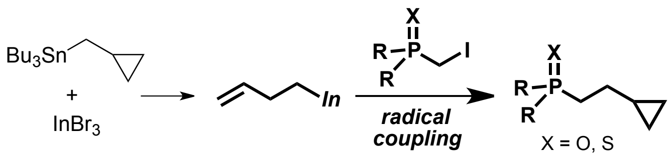
1-3. Synthesis of Cyclopropane-Containing Phosphorus Compounds by Radical Coupling of Butenylindium with Iodophosphorus Compounds

1-3-1. Introduction

Phosphonates have been recognized as highly valuable compounds in medicinal chemistry because of their potential biological activities.[1] Moreover, in the field of organic synthesis, they are widely used as important intermediates in the Horner–Wadsworth–Emmons (HWE) reaction.[2–4] Therefore, development of a synthetic method for more functionalized phosphonates is an important subject. An α-iodo phosphonate is a good functionalized candidate for radical coupling with an organometallic species.[5] However, its synthetic applications have been restricted to radical addition to alkenes or alkynes,[6] and no example of radical coupling reactions for α-iodo phosphonates with organometallic reagents has been reported, as far as we know. To develop this type of reaction, a new type of organometallic species is required. Recently, we found that a butenylindium species generated from the transmetalation between a (cyclopropylmethyl)stannane[7] and an indium halide was a useful reagent for radical coupling with α-iodocarbonyl compounds to afford cyclopropylmethylated carbonyl compounds.[8] Herein, we report the unprecedented radical coupling of the butenylindium species with iodo phosphoruscompounds such as iodo phosphonate, iodo phosphane oxide, or iodo phosphonothioate (Scheme 1). This is also a useful route to produce phosphorus compounds bearing a cyclopropyl ring,[9,10] which has the potential for pharmacological utility.[11]

Scheme1. Radical Coupling of Iodophosphorus Compound with Butenylindium Generated by Tin-Indium Transmetalation

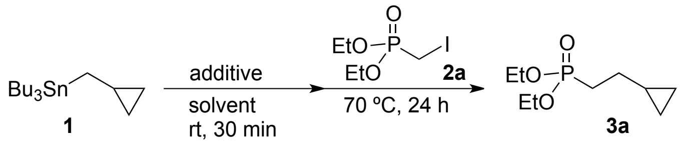


1-3-2. Results and Discussion

To optimize reaction conditions, the effects of additives and solvents were investigated by employing the reaction of cyclopropylmethylstannane **1** and diethyl iodomethylphosphonate (**2a**) in a nitrogen-flowing flask (Table 1). First, we examined a coupling reaction using $InBr_3$ in toluene at room temperature, which are considered the optimal conditions for radical coupling with α-iodocarbonyl compounds,[8] but the yield was low (entry 1). Raising the reaction temperature improved the yield to 48% (entry 2). When hexane was used instead of toluene, the best results were obtained, furnishing **3a** in a 74% yield (entry 3).[12,13] Unfortunately, a catalytic amount of $InBr_3$ gave only a trace amount of **3a** (entry 4). The reactions in 1,2-dichloroethane or acetonitrile decreased the yields (entries 5 and 6). The use of InI_3 instead of $InBr_3$ resulted in a lower yield (entry 7). In the reaction with alkyl chlorides, gallium trichloride was a good catalyst,[14] but it was less effective for this coupling (entry 8). Other group 13

Lewis acids (BF_3•OEt_2 and $AlCl_3$) were not effective at all (entries 9 and 10). The loading of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as a radical inhibitor completely suppressed the coupling (entry 11). When the reaction was carried out under severely resticted conditions — free of oxygen — in a nitrogen-filled glovebox (O_2 < 0.1 ppm), the coupling was significantly depressed (entry 12). These results indicate that this reaction proceeded in a radical mechanism and was promoted by a considerably small amount of O_2. It is assumed that the *in situ*-generated butenylindium species acts as a radical initiator as well as an alkylating reagent.

Table 1. Reaction of Cyclopropylmethylstannane **1** with Diethyl Iodomethylphosphonate (**2a**)[a]



entry	additive	solvent	yield/ %[b]
1[c]	$InBr_3$	toluene	18
2[d]	$InBr_3$	toluene	48
3	$InBr_3$	hexane	74
4[e]	$InBr_3$	hexane	<5
5	$InBr_3$	$ClCH_2CH_2Cl$	57
6	$InBr_3$	MeCN	15
7	InI_3	hexane	57
8	$GaCl_3$	hexane	28
9	BF_3•OEt_2	hexane	0
10	$AlCl_3$	hexane	0
11[f]	$InBr_3$	hexane	0
12[g]	$InBr_3$	hexane	8

[a] Unless otherwise noted, reactions were carried out in a nitrogen-flowing flask using 1.6 mmol of **1**, 0.8 mmol of **2a**, and 0.8 mmol of additive. [b] Determined by ^{1}H NMR. [c] At room temperature. [d] At 80 °C. [e] $InBr_3$ (0.08 mmol) was used. [f] TEMPO (0.08 mmol) was added. [g] In a nitrogen-filled glovebox (O_2 < 0.1 ppm).

Oshima et al. have reported a radical reaction of α-halo carbonyl compounds with the butenylindium species pre- pared by transmetalation between 3-butenylmagnesium bromide (**4**) and indium halide.[15] However, application to the coupling with **2a** failed, and most of the unreacted **2a** was recovered (Scheme 2). The low yield was probably caused by the magnesium salt ($MgBr_2$) generated in situ. In fact, the addition of $MgBr_2$ to the optimized tin/indium system (Table 1, Entry 3) decreased the yield from 74 to 8%.[16] The preparation of a butenylindium species by tin/indium transmetalation, where the by-product Bu_3SnBr is inert to the reaction system due to its low Lewis acidity, is essential for successful coupling with α-iodo phosphonates.

Scheme 2. Reaction of Butenylindium Species Prepared by Grignard Reagent and $InBr_3$

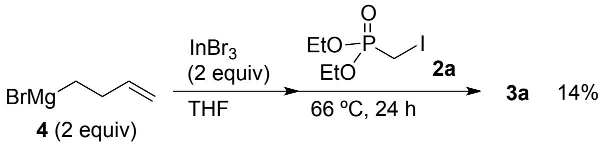
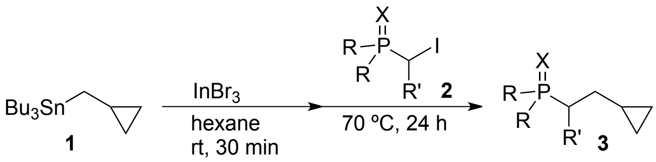
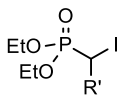
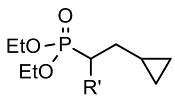
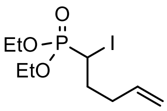
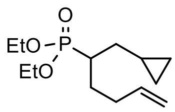
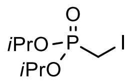
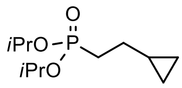
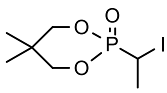
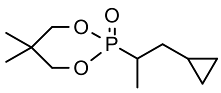
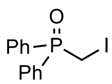
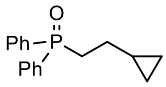
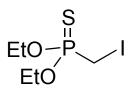
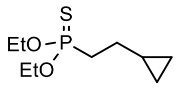


Table 2. Cyclopropylmethylation of Iodophosphorus Compounds[a]



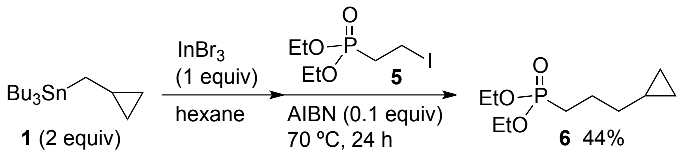
entry	iodophosphorus compound			product		yield/ %[b]
1		R' = H	**2a**		**3a**	74 (60)
2		Me	**2b**		**3b**	68 (50)
3		Et	**2c**		**3c**	57 (32)
4			**2d**		**3d**	35 (22)
5			**2e**		**3e**	78 (68)
6			**2f**		**3f**	67 (58)
7			**2g**		**3g**	75 (52)
8			**2h**		**3h**	31 (21)

[a] All entries were carried out in a nitrogen-flowing flask using 1.6 mmol of **1**, 0.8 mmol of **2**, and 0.8 mmol of $InBr_3$.
[b] Determined by ^1H NMR. Values in parentheses indicate isolated yields after column chromatography.

With the optimized system in hand, couplings with various types of iodo phosphorus compounds succeeded (Table 2).[17] Methyl- and ethyl-substituted secondary iodo phosphonates **2b** and **2c** effectively gave the corresponding products **3b** and **3c**, respectively (Entries 2 and 3). In the case of iodo phosphonate **2d**, which contains an olefin moiety, the coupling reaction selectively proceeded at the iodo site to afford the desired product **3d** (Entry 4). The coupling with butenylindium overcame the difficulty of the selective synthesis of **3d**, for instance, by a sequential allylation/cyclopropanation route to **2d**. This coupling reaction was hardly affected by the alkoxy groups on the phosphorus atom. For example, sterically demanding isopropyl-substituted phosphonate **2e** furnished the product **3e** in high yield (Entry 5). In addition, phosphonate **3f**, bearing a cyclic alkoxy moiety, was also obtained (Entry 6). Iodo phosphane oxide **2g** and iodo phosphonothioate **2h** were both viable reagents (Entries 7 and 8).

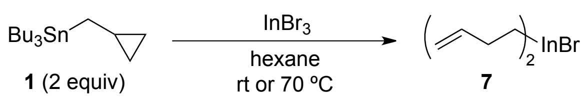
Interestingly, cyclopropylmethylation occurred even with β-iodo phosphonate **5** to give the corresponding product **6**, although a radical initiator was required as shown in Scheme 3.[18,19] This result expands the scope of the synthesis of cyclopropane-containing phosphorus compounds. When 1-iodoundecane was used instead of **5**, no product was obtained. This result indicates that the phosphonate moiety of **5** is involved in the stabilization of the β-radical.

Scheme 3. Cyclopropylmethylation of β-Iodophosphonate **5**



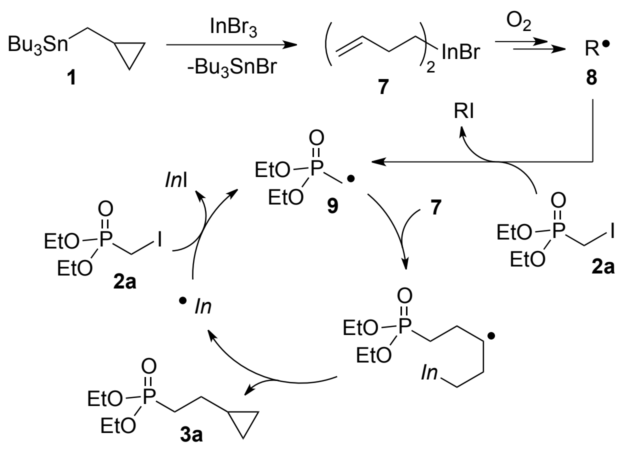
In order to investigate the transmetalation step under optimal conditions, a mixture of **1** and $InBr_3$ (**1**/$InBr_3$ = 2:1) in hexane was monitored by NMR spectroscopy (Scheme 4, see the Experimental Section). When the transmetalation was carried out at room temperature for 30min, small signals corresponding to dibutenylindium bromide (**7**) appeared as a single product, and most of **1** did not react.[20] This result strongly indicates a predominant formation of the dibutenylindium species over the monobutenylindium species. Meanwhile, transmetalation at 70 °C was completed within 30 min to give **7** quantitatively. Dibutenylindium **7** was stable enough under the reaction conditions (70 °C), and with no decomposition it should contribute to the radical coupling.

Scheme 4. Transmetalation between **1** and $InBr_3$



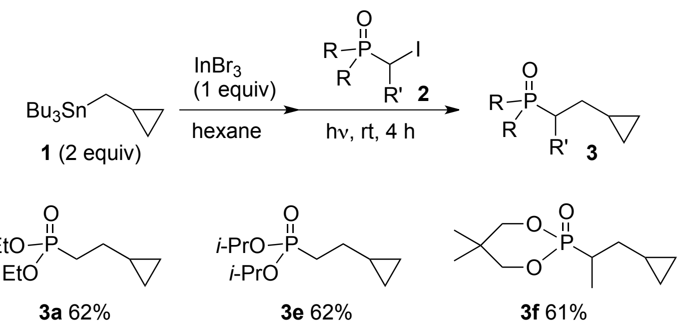
A plausible reaction mechanism is shown in Scheme 5. Transmetalation between (cyclopropylmethyl)stannane **1** and $InBr_3$ affords dibutenylindium bromide (**7**). In the radical initiation step, a small amount of radical species **8** (structure not fully determined) generated from **7** with O_2 abstracts an iodo radical from iodo phosphonate **2a** to produce the α-phosphonyl radical **9**.[21,22] The fast trapping of **9** by dibutenylindium compound **7** is followed by intramolecular cyclization to give cyclopropylmethylated product **3a** along with the eliminated indium radical. This indium radical reacts with **2a** to regenerate the phosphonyl radical **9**, which completes the radical chain reaction. Decomposition of the indium species generated in the final step may be the reason for the catalytic cycle not being achieved (see Table 1, Entry 4).[23] In addition, the effective trapping of the unstable radical **9** requires the participation of the reactive dibutenylindium species, but not of the monobutenyl species.[21,24]

Scheme 5. Plausible Reaction Mechanism



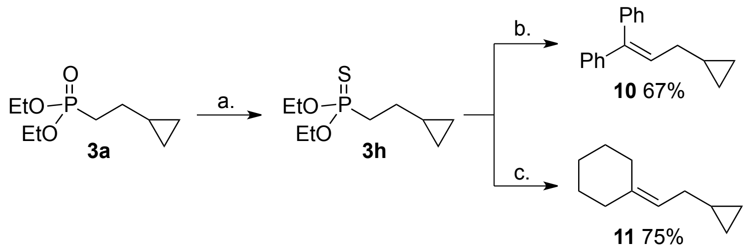
For this radical coupling reaction, we successfully applied a photochemical method (Scheme 6). UV irradiation of **1** with iodo phosphonate **2a** at room temperature afforded **3a** in a 62% yield, and the coupling reaction was completed within 4 h. Isopropyl-substituted **3e** and cyclic phosphonate **3f** were also obtained in satisfactory yields in a shorter reaction period compared with reactions under heating conditions.

Scheme 6. Photochemical Cyclopropylmethylation



Finally, the synthetic use of cyclopropylmethylated phosphonate **3a** as a precursor of functionalized olefins is demonstrated in Scheme 7. Phosphonate **3a** was treated with Lawesson's reagent, and the resulting phosphonothioate **3h** underwent Horner–Wadsworth–Emmons-type reactions.[25,26] The deprotonation of **3h** with *s*BuLi was followed by a reaction with benzophenone to produce trisubstituted alkene **10** without cleavage of the cyclopropyl ring. The aliphatic ketone cyclohexanone was also converted into the corresponding alkene **11** in 75% yield. This is a useful and reliable method for the synthesis of alkenes bearing a cyclopropane moiety, which can be easily transformed to further functionalized compounds.

Scheme 7. Synthesis of Alkenes by HWE-type Reaction[a]



[a] Reaction conditions: (a) Lawesson's reagent, toluene, reflux. (b) *s*-BuLi, PhCOPh, THF, -78 °C to rt. (c) *s*-BuLi, cyclohexanone, THF, -78 °C to rt.

1-3-3. Conclusion

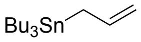
We have developed a radical coupling reaction of the butenylindium species with α- or β-iodo phosphorus compounds to give the corresponding cyclopropylmethylated products, which are an important class of functionalized compounds for pharmaceutics, biological chemistry, and organic synthesis. To promote this radical coupling, tin/indium transmetalation is indispensable for the preparation of the butenylindium species.

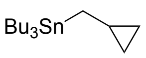
1-3-4. Experimental Section

General. New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance techniques, HMQC, HMBC, IR, MS, HRMS, and elemental analysis. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS as internal standard. ^{119}Sn (150 MHz) spectra were obtained with Me_4Sn as external standard. ^{31}P (160 MHz) spectra were obtained with 85 wt% D_3PO_4 in D_2O as external standard. IR spectra were recorded as thin films or solids in KBr pellets. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (MERK C60 or Fuji Silysia FL100DX). Bulb-to-Bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. Yields were determined by ^{1}H NMR using internal standard.

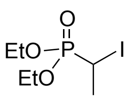
Materials. Dehydrated hexane, toluene, acetonitrile, and tetrahydrofuran were purchased and used as obtained. 1,2-Dichloroethane was distilled from P_2O_5. The additives examined in Table 1 were also purchased from commercial sources. Cyclopropylmethylstannane **1**[8,14] was prepared by known method and this compound was reported. Starting iodophosphorus compounds **2b**,[27] **2e**,[6b] **2g**,[6b] and **5**[6b] were prepared by known methods and these compounds were reported. Iodophosphorus compounds **2c**,[27] **2d**,[27] **2f**,[27] and **2h**[28] were prepared by known methods. Diethyl iodomethylphosphonate (**2a**), benzophenone, and cyclohexanone are commercially available. All other reagents were commercially available.

Preparation of cyclopropylmethyltributylstannane (1)[31]

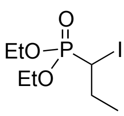

To a flask containing magnesium (230 mmol) in THF (150 mL) was added Bu_3SnCl (200 mmol). The mixture was cooled to 0 ^{o}C, and then allyl chloride (230 mmol) was added. The mixture was irradiated with ultrasound at 0 ^{o}C for 1 h and stirred. After 2 h, the reaction was quenched by water (200 mL), and then organic layer was separated. Hexane (200 mL) was added, and the organic layer was washed using water (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane] on silica gel to give the product (57.2 g, 86% yield).


To a solution of tributylallylstannane (30 mmol) in diethyl ether (40 mL), diethylzinc (1.0 M in hexane, 43 mL) was added. To the mixture was added the solution of diiodomethane (90 mmol) in diethylether (30 mL) dropwise within 1 h. The reaction mixture was stirred for 4 h at room temperature, and then quenched by saturated NH_4Cl aq (100 mL). Hexane (200 mL) was added, and the organic layer was washed using saturated NH_4Cl aq (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane] on silica gel to give the product (9.63 g, 85% yield, 84% purity (a small portion was analyzed by ^{1}H NMR using an internal standard)), which was used in the cyclopropylmethylation reaction without further purification. The analytical data for this compound matched that previously reported.

Diethyl (1-iodoethyl)phosphonate (2b)[27]

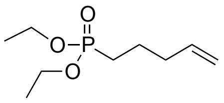

To the mixture of diisopropylamine (25.2 mmol, 2.56 g) and THF (40 mL) at -78 °C was slowly added *n*-BuLi (1.6 M in hexane, 15.2 mL). After stirring for 5 min, diethyl ethylphosphonate (10.0 mmol, 1.67 g) in THF (20 mL) was added over 15 min and Me_3SiCl (11 mmol, 1.19 g) in THF (20 mL) was rapidly added. The mixture was allowed to warm slowly to room temperature, which was stirred for 15 min and cooled again to -78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was then added slowly to the mixture and left to warm to 0 °C. After stirring for 15 min, EtOLi (1.0 M in ethanol, 20 mL) was added to the reaction mixture, which was quenched by HCl aq (1.0 M, 20 mL). The reaction mixture was extracted with ethyl acetate (3 x 30 mL) and the collected organic layer was washed with brine (2 x 30 mL) and water (2 x 30 mL), then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column cholomatography [hexane/ethyl acetate = 70/30], giving the pure product as a yellow liquid (1.60g, 54%). The analytical data for this compound matched that previously reported.

Diethyl (1-iodopropyl)phosphonate (2c)

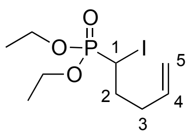

To the mixture of diisopropylamine (26 mmol, 2.62 g) and THF (40 mL) at -78 °C was slowly added *n*-BuLi (1.6 M in hexane, 15 mL). After stirring for 5 min, diethyl propylphosphonate (9.6 mmol, 1.79 g) in THF (20 mL) was added over 15 min and

Me_3SiCl (12.8 mmol, 1.40 g) in THF (20 mL) was rapidly added. The mixture was allowed to warm slowly to room temperature, which was stirred for 15 min and cooled again to -78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was then added slowly to the mixture and left to warm to 0 °C. After stirring for 15 min, EtOLi (1.0 M in ethanol, 20 mL) was added to the reaction mixture, which was quenched by HCl aq (1.0 M, 20 mL). The reaction mixture was extracted with ethyl acetate (3 x 30 mL) and the collected organic layer was washed with brine (2 x 30 mL) and water (2 x 30 mL), then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column cholomatography [hexane/ethyl acetate = 70/30], giving the pure product as a yellow liquid (2.5g, 82%). IR (neat): 1254 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.25-4.17 (m, 4H, CH_2OP x 2), 3.72 (ddd, $^{2}J_{PH}$ = 10.5 Hz, J = 10.5, 4.0 Hz, 1H, PCH), 2.06-1.92 (m, 1H, PCHICH^{A}), 1.90-1.78 (m, 1H, PCHICH^{B}), 1.36 (t, J = 7.0 Hz, 6H, C$H_3$$CH_2$O x 2), 1.10 (t, J = 7.0 Hz, 3H, PCHCH_2CH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 63.5 (t, $(CH_3\mathit{C}H_2O)^{A}$P, d by $^{2}J_{CP}$ = 6.5 Hz), 63.4 (t, $(CH_3\mathit{C}H_2O)^{B}$P, d by $^{2}J_{CP}$ = 6.6 Hz), 26.9 (t, PCHI$\mathit{C}H_2$, d by $^{2}J_{CP}$ = 2.5 Hz), 20.3 (d, PCH, d by $^{1}J_{CP}$ = 154 Hz), 16.3 (q, $\mathit{C}H_3CH_2O$, d by $^{2}J_{CP}$ = 5.8 Hz), 15.0 (q, PCH$CH_2\mathit{C}H_3$, d by $^{3}J_{CP}$ = 13.2 Hz); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 36.4; MS: (EI, 70 eV) m/z 306 (M^+, 15), 179 (M^+ – I, 65), 151 (27), 123 (100), 109 (52), 81 (31); HRMS: (EI, 70 eV) calcd for ($C_7H_{16}O_3PI$) 303.9882 (M^+) found m/z 303.9885.

Preparation of diethyl (1-iodopent-4-enyl)phosphonate (2d)



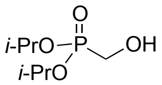
The mixture of 5-bromo-1-pentene (29 mmol, 4.32 g) and $P(OEt)_3$ (31 mmol, 5.17 g) was heated to 150 °C and stirred for 21 h. The volatiles were evaporated and the residue was purified by distillation under reduced pressure to give the product s2 (2.86 g, 48 %). bp: 120 °C /0.20 mmHg. The analytical data for this compound matched that previously reported.[6]



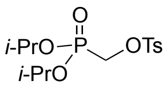
To the mixture of diisopropylamine (27 mmol, 2.75 g) and THF (40 mL) at -78 °C was slowly added *n*-BuLi (1.6 M in hexane, 16 mL). After stirring for 5 min, diethyl pent-4-enylphosphonate s2 (10.4 mmol, 2.16 g) in THF (20 mL) was added over 15 min and Me_3SiCl (12.8 mmol, 1.40 g) in THF (20 mL) was rapidly added. The mixture was allowed to warm slowly to room temperature, which was stirred for 30 min and cooled again to -78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was then added slowly to the mixture and left to warm to 0 °C. After stirring for 1 h, EtOLi (1.0 M in ethanol, 20 mL) was added to the reaction mixture, which was quenched by sodium thiosulfate aq (20 mL). The reaction mixture was extracted with ethyl acetate (3 x 30 mL) and the collected organic layer was washed with brine (2 x 30 mL) and water (2 x 30 mL), then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column cholomatography [hexane/ethyl acetate = 50/50]. Further purification was conducted by distillation under reduced pressure to give the product as a yellow liquid (2.09 g, 63%). bp: 110 °C /0.20 mmHg; IR (neat): 1245 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 5.73 (m, 1H, $\mathit{H}C=CH_2$), 5.13-5.05 (d, J = 17 Hz, 1H, HC=CHH), 5.02-5.00 (d, J = 10 Hz, 1H, HC=CHH), 4.24-4.16 (m, 4H, CH_2OP x 2), 3.77 (ddd, J = 10, 5 Hz, $^{2}J_{PH}$ = 5

Hz, 1H, PCH), 2.45-2.37 (m, 1H, PCHCH$_2$C*H*H), 2.20-2.11 (m, 1H, PCHCH$_2$CH*H*), 2.05-1.88 (m, 2H, PCHC*H*$_2$), 1.36 (t, 6H, CH$_3$ x 2); ^{13}C NMR: (100 MHz, CDCl$_3$) 135.9 (d, H*C*=CH$_2$), 116.6 (t, HC=*C*H$_2$), 63.6 (t, (CH$_3$*C*H$_2$O)^{A}P, d by $^2J_{CP}$ = 6.6 Hz), 63.5 (t, (CH$_3$*C*H$_2$O)^{B}P, d by $^2J_{CP}$ = 7.4 Hz), 33.5 (t, PCHCH$_2$*C*H$_2$, d by $^3J_{CP}$ = 11 Hz), 32.0 (t, PCH*C*H$_2$, d by $^2J_{CP}$ = 1.7 Hz), 17.1 (d, PCH, d by $^1J_{CP}$ = 154 Hz), 16.3 (q, CH$_3$, d by $^3J_{CP}$ = 5.7 Hz); ^{31}P NMR: (160 MHz, CDCl$_3$, external standard = 85 wt% D$_3$PO$_4$ in D$_2$O) 36.7; MS: (EI, 70 eV) *m/z* 332 (M$^+$, 9), 205 (M$^+$ – I, 100), 177 (22), 165 (21), 149 (81), 109 (40), 81 (20), 67 (44); HRMS: (EI, 70 eV) calcd for (C$_9$H$_{18}$O$_3$PI) 332.0038 (M$^+$) found *m/z* 332.0036.

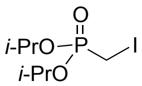
Preparation of diisopropyl (1-iodoethyl)phosphonate (2e)[30]



To a mixture of diisopropyl phosphite (3.32 g, 20.0 mmol) and paraformaldehyde (0.65 g, 22 mmol) was added triethylamine (0.23 g, 2.3 mmol). The mixture was heated to 110 °C for 4 h and evaporated to give the product (3.68 g, 94%).[31] The analytical data for this compound matched that previously reported.[30]

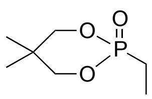


To a solution of diisopropyl hydroxymethanephosphonate (3.68g, 18.8 mmol) in pyridine (10 mL) was added *p*-toluenesulfonyl chloride (4.13g, 20.0 mmol) at 0 °C over 1 h. The mixture was allowed to warm to room temperature and stirred for 10 h, which was quenched by HCl aq (1M, 50 mL) and extracted with ethyl acetate (3 x 30 mL). The collected organic layer was dried (MgSO$_4$) and the solvent was evaporated to give the product (4.99 g, 76%). The analytical data for this compound matched that previously reported.[30]

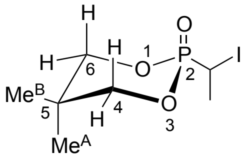


To a solution of diisopropyl {(*p*-toluenesulfonyl)oxy}methanephosphonate (4.99 g, 14.2 mmol) in acetone (60 mL) was added sodium iodide (8.65 g, 57.7 mmol). The mixture was heated to 75 °C for 24 h and then quenched by saturated sodium thiosulfate aq (100 mL), which was extracted with ethyl acetate (3 x 100 mL). The collected organic layer was dried (MgSO$_4$) and evaporated. The crude product was purified by distillation under reduced pressure to give the pure product as a colorless liquid (2.6 g, 59%). The analytical data for this compound matched that previously reported.

Preparation of 2-(1-iodoethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (2f)

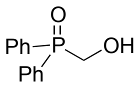


The mixture of ethyl phosphonic dichloride (19.9 mmol, 2.93 g) and 2,2-dimethyl-1,3-propanediol (20.4 mmol, 2.12 g) was stirred for 15 min at room temperature and heated at 50 ºC for 1 h. Then saturated NaHCO$_3$ aq (100 mL) was added to the mixture, which was extracted with dichloromethane (3 x 100 mL). The collected organic layer was dried (MgSO$_4$) and the solvent was evaporated to give the product as a white solid (2.95 g, 83%).[32] The analytical data for this compound matched that previously reported.[33]

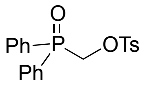


To a solution of *sec*-BuLi (1.0 M in hexane, 10 mL) in THF (60 mL) was slowly added 2-ethyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (1.76 g, 10 mmol) in THF (30 mL). After 30 min, Me_3SiCl (2.72 g, 11.3 mmol) in THF (20 mL) was rapidly added. Then, the mixture was allowed to warm slowly to room temperature, which was stirred for 30 min and cooled again to -78 °C. Iodine (2.80 g, 11 mmol) in THF (20 mL) was then added slowly to the mixture and left to warm to 0 °C. After stirring for 1 h, EtOLi (1.0 M in ethanol, 20 mL) was added to the reaction mixture, which was quenched by saturated sodium thiosulfate aq (20 mL). The reaction mixture was extracted with ethyl acetate (3 x 30 mL) and the collected organic layer was washed with brine (2 x 30 mL) and water (2 x 30 mL), then dried ($MgSO_4$). The solvent was evaporated and the residue was washed with diethyl ether, which gave the pure product as a white solid (0.59 g, 20%). mp: 200-202 °C; IR (KBr): 1265 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.28-4.22 (m, 2H, two protons of 4-H and/or 6-H), 4.03-3.94 (m, 3H, two protons of 4-H and/or 6-H and PC*H*), 2.06 (dd, 3H, J = 7.7 Hz, $^3J_{PH}$ = 17 Hz, PCHC*H*$_3$), 1.15 (s, 3H, 5-Me^B), 1.07 (s, 3H, 5-Me^A); ^{13}C NMR: (100 MHz, $CDCl_3$) 76.9 (t, 4-C or 6-C, d by $^2J_{CP}$ = 5.6 Hz), 76.8 (t, 4-C or 6-C, d by $^2J_{CP}$ = 6.6 Hz), 33.1 (s, 5-C, d by $^3J_{CP}$ = 6.5 Hz), 22.0 (q, 5-Me), 21.8 (q, PCH*C*H$_3$, d by $^2J_{CP}$ = 4.1 Hz), 21.7 (q, 5-Me), 4.6 (d, PCH, d by $^1J_{CP}$ = 153 Hz); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 32.7; MS: (EI, 70 eV) *m*/*z* 304 (M^+, 39), 177 (M^+ – I, 100), 149 (M^+ – $CHICH_3$, 48), 109 (52), 69 (91), 56 (26), 41 (38); HRMS: (EI, 70 eV) calcd for ($C_7H_{14}O_3PI$) 303.9725 (M^+) found *m*/*z* 303.9712; Analysis: $C_7H_{14}O_3PI$ (304.06) Calcd: C, 27.65; H, 4.64; I, 41.74; O, 15.79; P, 10.19 Found: C, 27.82; H, 4.35; I, 41.46.

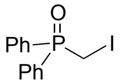
Preparation of diphenyl iodomethyl phosphine oxide (2g)[34]



To a mixture of HCl (37.8 mL) and aqueous formaldehyde (37.8 mL, 37 wt%) was added diphenyl chlorophosphine (21.0 mmol, 4.61 g). The reaction mixture was heated to 100 °C for 18 h, which was neutralized with aqueous $NaHCO_3$, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 ml). The collected organic layer was dried ($MgSO_4$) and the solvent was evaporated to give the crude product, which was washed with hexane to obtain the pure product as a white solid (3.50 g, 71%).[35] The analytical data for this compound matched that previously reported.[35]

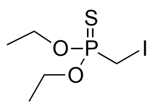


To a solution of diphenyl (hydroxymethyl)phosphine oxide (14.4 mmol, 3.35 g) in CH_2Cl_2 (50 mL) was slowly added triethylamine (16.6 mmol, 1.68 g) at 0 °C. The reaction mixture was stirred for 30 min at room temperature and cooled again to 0 °C. Then, *p*-tosyl chloride (16.0 mmol, 3.30 g) was added. The reaction mixture was kept at 0 °C for 30 min and stirred for 4 h at room temperature, which was quenched by water (50 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The collected organic layer was dried ($MgSO_4$) and the solvent was evaporated. The crude product was recrystallized (CH_2Cl_2/Et_2O, 1:9) to give the pure product as a white solid (3.93 g, 71%).[36] The analytical data for this compound matched that previously reported.[36]



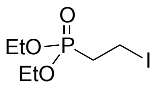
To a solution of diphenylphosphinoylmethyl *p*-toluenesulfonate (10.0 mmol, 3.86 g) in acetone (200 mL) was added sodium iodide (40.0 mmol, 5.99 g). The mixture was heated to 75 °C for 24 h and then quenched by saturated sodium thiosulfate aq (100 mL), which was extracted with ethyl acetate (3 x 100 mL). The collected organic layer was dried ($MgSO_4$) and the solvent was evaporated. The crude product was washed with hexane to give the pure product as a white solid (3.0 g, 88%). The analytical data for this compound matched that previously reported.

***O,O'*-Diethyl iodomethylphosphonothioate (2h)**



To a mixture of diethyl iodomethylphosphonate (2.99 mmol, 0.832 g) and toluene (15 mL) was added Lawesson's reagent (1.75 mmol, 0.707 g), and the reaction mixture was stirred at 120 °C for 8 h. The solvent was evaporated to give the crude product. It was purified by distillation under reduced pressure to give the product as a colorless liquid (0.70 g, 80%). bp: 100 °C /0.14 mmHg; IR (neat): 1022 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.25-4.09 (m, 4H, CH_2OP x 2), 3.34 (d, $^{2}J_{PH}$ = 7.5 Hz, 2H, PCH_2), 1.35 (t, 6H, CH_3 x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 63.9 (t, *C*H_2OP, d by $^{2}J_{CP}$ = 7 Hz), 16.0 (q, CH_3, d by $^{3}J_{CP}$ = 6 Hz), -3.8 (t, P*C*H_2, d by $^{1}J_{CP}$ = 119 Hz); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 99.2; MS: (EI, 70 eV) *m*/*z* 294 (M^+, 17), 167 ($(CH_3CH_2O)_2PSCH_2^+$, 100), 111 (41); HRMS: (EI, 70 eV) calcd for ($C_5H_{11}O_2PSI$) 293.9340 (M^+) found *m*/*z* 293.9337; Analysis: $C_5H_{12}O_2PSI$ (294.09) Calcd: C, 20.42; H 4.11 Found: C, 20.48; H, 3.93.

Diethyl (2-iodoethyl)phosphonate (5)[6b]

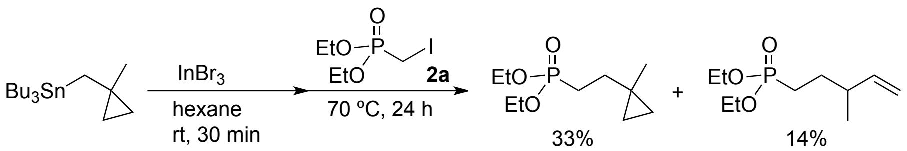


To a solution of diethyl (2-bromoethyl)phosphonate (2.45 g, 10.0 mmol) in acetone (160 mL) was added sodium iodide (6.01 g, 40.1 mmol). The mixture was heated to 75 °C for 24 h and then quenched by saturated sodium thiosulfate aq (100 mL), which was extracted with ethyl acetate (3 x 100 mL). The collected organic layer was dried ($MgSO_4$) and evaporated to give the product as a colorless liquid (2.86 g, 98%). The analytical data for this compound matched that previously reported.

Typical procedure for the reaction of cyclopropylmethylstannane 1 and diethyl iodomethylphosphonate 2a (Table 1, entry 3). To a suspended solution of $InBr_3$ (0.8 mmol) and hexane (1 mL) was added cyclopropylmethylstannane **1** (1.6 mmol) and the mixture was stirred for 30 min at room temperature. Iodophosphonate **2a** (0.8 mmol) was added with heating at 70 °C. After stirring for 24 h, NH_4F aq (10%, 20 mL) was added to the reaction mixture, which was extracted with diethyl ether (3 x 20 mL). The collected organic layers were dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR. The detail of further purification was described in Product Data.

Experimental procedure for the reaction of cyclopropylmethylstannane 1 and diethyl iodomethylphosphonate 2a under the oxygen free condition (Table 1, entry 12). A side-necked sealable tube was brought into the nitrogen-filled glove box, along with a screw-cap. In the glovebox, cyclopropylmethylstannane **1** (1.6 mmol) was added to a suspended solution of $InBr_3$ (0.8 mmol) and hexane (1 mL), and the mixture was stirred at room temperature. After stirring for 30 min, iodophosphonate **2a** (0.8 mmol) was added to the reaction mixture. The reaction tube was sealed with a screw-cap. Outside the glovebox, the sealed reaction tube was heated to 70 °C. After stirring for 24 h, NH_4F aq (10%, 20 mL) was added to the reaction mixture, which was extracted with diethyl ether (3 x 20 mL). The collected organic layer was dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR.

Experimental procedure for the reaction of (1-methylcyclopropyl)methyltributylstannane and diethyl iodomethylphosphonate 2a. According to the typical procedure, $InBr_3$ (0.8 mmol, 0.284 g), (1-methylcyclopropyl)methyltributylstannane[2] (91% purity) (1.6 mmol, 0.630 g), and diethyl iodomethylphosphonate **2a** (0.8 mmol, 0.228 g) gave the crude product which was analyzed by NMR as shown below.



Experimental procedure for the reaction of butenylindium species prepared by Grignard reagent and $InBr_3$ (Scheme 2). Butenylmagnesium bromide (1.0 M in THF) was prepared by mixing magnesium (4 mmol) and 4-bromo-1-butene (4 mmol) in THF (4 mL) at room temperature for 30 min. To a solution of $InBr_3$ (1.6 mmol) and THF (1 mL) was added butenylmagnesium bromide (**4**) (1.6 mmol) and the mixture was stirred for 30 min at room temperature. Iodophosphonate **2a** (0.8 mmol) was added with heating at 66 °C. After stirring for 24 h, water was added to the reaction mixture, which was extracted with diethyl ether (3 x 20 mL). The collected organic layer was dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR.

NMR study of transmetalation between cyclopropylmethylstannane 1 and $InBr_3$ (Scheme 4). The mixture of cyclopropylmethylstannane **1** and $InBr_3$ (the ratio of **1**/$InBr_3$ = 2:1) was prepared in hexane in nitrogen-flowing flask. After mixing at room temperature or 70 °C, the mixture was transferred into NMR tube (benzene-d_6 as an external standard), and the resulting spectra is shown below (Figure S1). The spectra were referenced against *n*-hexane, 0.89 ppm (t, CH_3) for ^1H NMR spectroscopy, and 14.32 ppm (CH_3) for ^{13}C NMR spectroscopy.

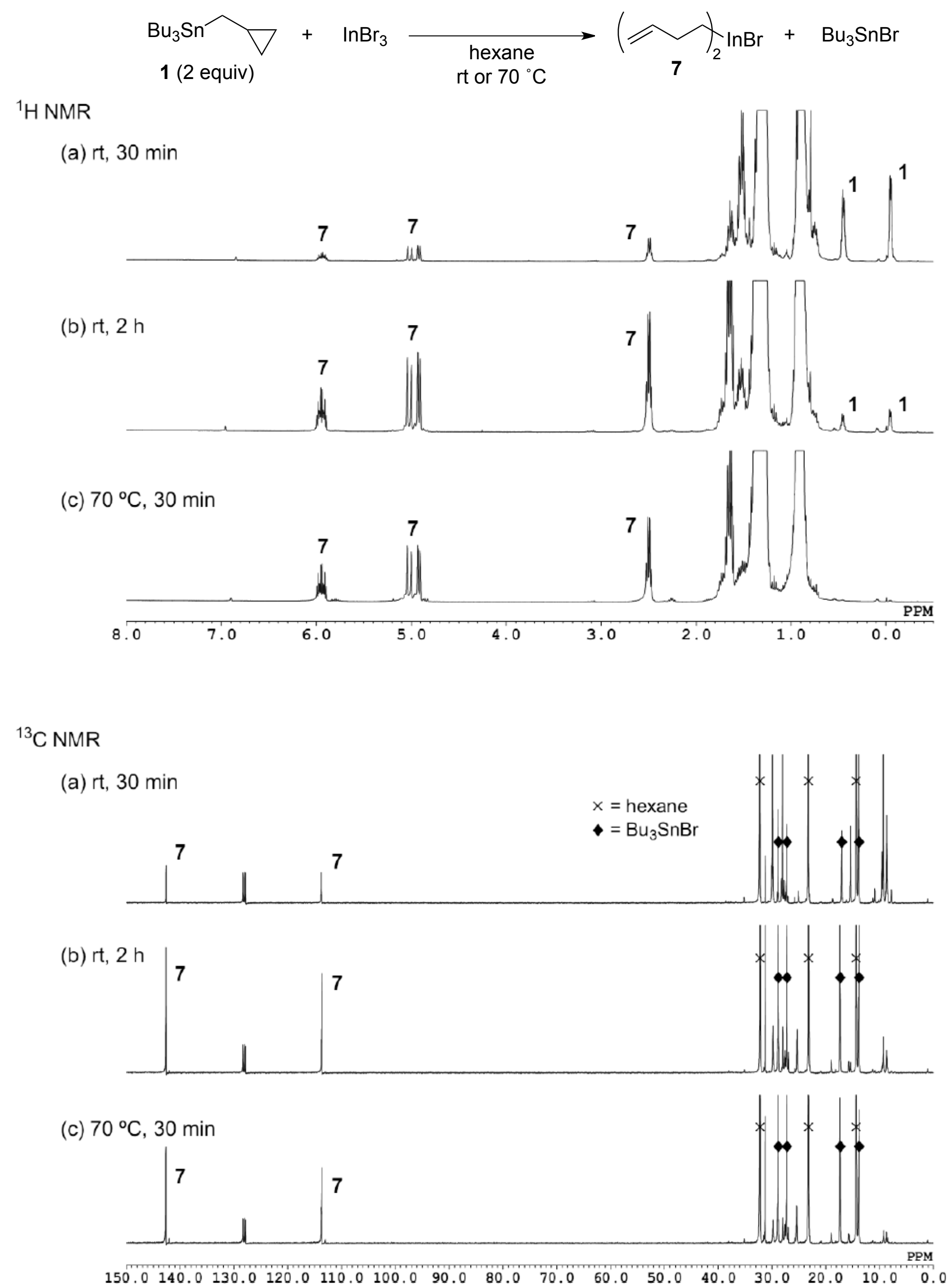


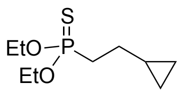
Figure S1. ^{1}H and ^{13}C NMR spectra of the reaction mixtures of $InBr_3$ and **1** in hexane for (a) 30 min (rt), (b) 2 h (rt), and 30min (70 ˚C).

The NMR spectra of **7** after replacing hexane with toluene-d_8 matched that previously reported.[31] When the transmetalation was carried out at 70 °C, 1 was completely consumed within 30 min and **7** was produced in 96% yield (determined by NMR spectroscopy using bromoform as an internal standard) (Very small amount of monobutenylindium dibromide was detected.).

Experimental procedure for the reaction of cyclopropylmethylstannane 1 and diethyl iodomethylphosphonate 2a under UV irradiation condition (Scheme 6). To a suspended solution of $InBr_3$ (0.8 mmol) and hexane (1 mL) was added cyclopropylmethylstannane **1** (1.6 mmol) and the mixture was stirred for 2 h at room temperature. Diethyl iodomethylphosphonate **2a** (0.8 mmol) was added to the mixture and placed at a distance of ~10 cm from a 300 W high-pressure mercury lamp for 4 h. NH_4F aq (10%, 20 mL) was then added to the reaction mixture, which was extracted with diethyl ether (3 x 20 mL). The collected organic layer was dried ($MgSO_4$) and evaporated to give the crude product which was analyzed by NMR. Purification by column chromatography [hexane/ethyl acetate = 70/30] gave the product **3a**.

Typical procedure for the synthesis of alkene by Horner-Wadsworth-Emmons (HWE)-type reaction (Scheme 7). To a solution of *O,O'*-diethyl (2-cyclopropylethyl)phosphonothioate **3h** (0.23 mmol) in THF (2 mL) was slowly added *s*-BuLi (1.0 M in hexane, 0.30 mL) at -78 °C and the mixture was stirred for 15 min. Benzophenone (0.24 mmol) in THF (2 mL) was slowly added to the mixture, which was allowed to warm to room temperature and stirred for 18 h. Then, saturated NH_4Cl aq (10 mL) was added and the reaction mixture was extracted with diethyl ether (3 x 10 mL). The reaction mixture was dried ($MgSO_4$) and the solvent was evaporated to give the crude product, which was purified by column chromatography [hexane (200 mL)], giving the product **10**.

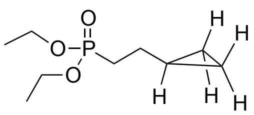
Preparation of *O,O'*-Diethyl (2-cyclopropylethyl)phosphonothioate (3h) with Lawesson's reagent (Scheme 7).



To a mixture of diethyl (2-cyclopropylethyl)phosphonate **3a** (0.66 mmol, 0.136 g) and toluene (3 mL) was added Lawesson's reagent (0.39 mmol, 0.157 g), and the reaction mixture was stirred at 125 °C for 4 h. The solvent was evaporated to give the crude product. It was purified by distillation under reduced pressure to give the product 3h as a colorless liquid (0.077 g, 53%).

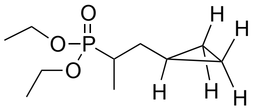
Product Data.

Diethyl 2-cyclopropylethylphosphonate (3a)



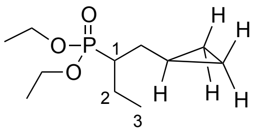
According to the typical procedure, $InBr_3$ (0.80 mmol, 0.283 g), cyclopropylmethylstannane **1** (84% purity) (1.55 mmol, 0.637 g), and diethyl iodomethylphosphonate **2a** (0.80 mmol, 0.224 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 70/30] gave the product **3a** (0.100 g, 60%). Further purification was performed by distillation under reduced pressure. bp: 90 °C /0.2 mmHg; IR (neat): 1250 (P=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 4.16-4.02 (m, 4H, CH_2OP x 2), 1.89-1.80 (m including $^2J_{PH}$ = 18 Hz, 2H, PCH_2), 1.54-1.45 (m, 2H, PCH_2CH_2), 1.32 (t, J = 7.2 Hz, 6H, CH_3 x 2), 0.81-0.71 (m, 1H, PCH_2CH_2CH), 0.47-0.42 (m, 2H), 0.08-0.05 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 61.2 (t, CH_2OP, d by $^2J_{CP}$ = 7 Hz), 27.5 (t, PCH_2CH_2, d by $^2J_{CP}$ = 5 Hz), 25.5 (t, PCH_2, d by $^1J_{CP}$ = 140 Hz), 16.3 (q, CH_3, d by $^2J_{CP}$ = 6 Hz), 11.6 (d, PCH_2CH_2CH, d by $^3J_{CP}$ = 20 Hz), 4.4 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 46.8; MS: (EI, 70 eV) m/z 206 (M^+, 10), 191 (M^+ - CH_3, 60), 179 (32), 178 (M^+ – C_2H_4, 52), 165 (M$^+$ – C_3H_5, 24), 163 (40), 152 (69), 151 (M$^+$ - $CH_2C_3H_5$, 42), 150 (41), 149 (34), 138 (67), 137 (M$^+$ – $CH_2CH_2C_3H_5$, 31), 135 (79), 134 (32), 133 (48), 125 (95), 124 (38), 123 (21), 111 (52), 110 (23), 109 (100), 108 (26), 97 (99), 96 (53), 93 (21), 82 (39), 81 (61), 80 (21), 69 ($CH_2CH_2C_3H_5^+$, 26), 68 (38), 67 (40), 65 (28), 41 ($C_3H_5^+$, 41); HRMS: (EI, 70 eV) calcd for ($C_9H_{19}O_3P$) 206.1072 found *m/z* 206.1067.

Diethyl {1-(cyclopropymethyl)ethyl}phosphonate (3b)



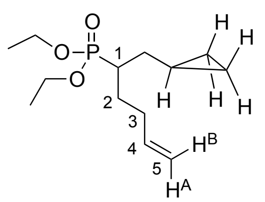
According to the typical procedure, $InBr_3$ (0.80mmol, 0.282 g), cyclopropylmethylstannane **1** (99% purity) (1.59 mmol, 0.555 g), and diethyl (1-iodoethyl)phosphonate **2b** (0.74 mmol, 0.216 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 50/50] gave the product **3b** (0.082 g, 50%). Further purification was performed by distillation under reduced pressure to give the product **3b** as a colorless liquid (0.050 g, 31 %). bp: 75 °C /0.22 mmHg; IR (neat): 1238 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.14-4.05 (m, 4H, CH_2OP x 2), 2.04-1.88 (m, 2H, PC*H*$_2$), 1.62-1.52 (m, 1H, PCH_2C*H*H), 1.47-1.35 (m, 1H, PCHCH*H*), 1.32 (t, 6H, C*H*$_3CH_2OP$ x 2), 1.25 (dd, J = 18 Hz, J = 7.0 Hz, 3H, PCHC*H*$_3$), 0.85-0.75 (m, 1H, $PCHCH_2$C*H*), 0.55-0.38 (m, 2H), 0.15- -0.01 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 61.4 (t, (CH_3*C*H_2O)^{A}P , d by $^2J_{CP}$ = 6.6 Hz), 61.3 (t, (CH_3*C*H_2O)^{B}P , d by $^2J_{CP}$ = 6.6 Hz) 35.1 (d, PCH*C*H_2, d by $^2J_{CP}$ = 3.3 Hz), 31.6 (d, P*C*H , d by $^1J_{CP}$ = 141 Hz), 16.5 (q, *C*H_3CH_2OP, d by $^3J_{CP}$ = 5.7 Hz), 13.3 (q, PCH*C*H_3, d by $^2J_{CP}$ = 5.7 Hz), 9.2 (d, $PCHCH_2$*C*H, d by $^3J_{CP}$ = 16 Hz), 5.7 (t, two methylene groups in the cyclopropyl ring), 3.8 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 49.4; MS: (EI, 70 eV) *m/z* 220 (M$^+$, 47), 205 (M$^+$ – CH_3, 43), 192 (M$^+$ – CH_3CH, 25), 179 (M$^+$ – C3H5, 30), 177 (27), 166 (68), 165 (M$^+$ – $CH_2C_3H_5$, 35), 152 (28), 149 (46), 147 (25), 139 (50), 138 (($CH_3CH_2O)_2PO^+$, 96), 123 (29), 111 (100), 110 (37), 109 (60), 82 (M$^+$ - $(CH_3CH_2O)_2PO^+$, 54), 81 (36), 67 (31), 65 (24), 55 ($CH_2C_3H_5$, 40), 41 (C_3H_5, 24); HRMS: (EI, 70 eV) calcd for ($C_{10}H_{21}O_3P$): 220.1228 (M$^+$) found *m/z* 220.1217.

Diethyl {1-(cyclopropylmethyl)propyl}phosphonate (3c)



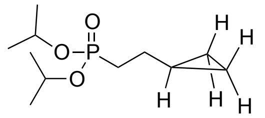
According to the typical procedure, $InBr_3$ (0.80 mmol, 0.285 g), cyclopropylmethylstannane **1** (88% purity) (1.64 mmol, 0.645 g), and diethyl (1-iodopropyl)phosphonate **2c** (0.80 mmol, 0.245 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 70/30] gave the product **3c** (0.060 g, 32%). Further purification was performed by distillation under reduced pressure to give the product **3c** as a colorless liquid (0.040 g, 21 %). bp: 85 °C /0.2 mmHg; IR (neat): 1238 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.16-4.03 (m, 4H, CH_2OP x 2), 1.89-1.72 (m, 1H, 1-H), 1.89-1.61 (m, 2H, 2-H_2), 1.61-1.36 (m, 2H, PCHC*H*$_2$), 1.31 (t, J = 7.3 Hz, 6H, C*H*$_3CH_2OP$ x 2), 1.03 (t, J = 7.2 Hz, 3H, 3-H_3), 0.92-0.82 (m, 1H, $PCHCH_2$C*H*), 0.52-0.41 (m, 2H), 0.12-0.030 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 61.3 (t, (CH_3*C*H_2O)^{A}P , d by $^2J_{CP}$ = 7 Hz), 61.2 (t, (CH_3*C*H_2O)^{B}P , d by $^2J_{CP}$ = 6 Hz), 38.2 (d, C-1, d by $^1J_{CP}$ = 137 Hz), 32.9 (t, PCH*C*H_2 , d by $^2J_{CP}$ = 3 Hz), 21.2 (t, C-2, d by $^3J_{CP}$ = 5 Hz), 16.4 (q, *C*H_3CH_2OP, d by $^3J_{CP}$ = 6 Hz), 12.2 (q, C-3, d by $^3J_{CP}$ = 9 Hz), 9.5 (d, $PCHCH_2$*C*H, d by $^3J_{CP}$ = 13 Hz), 5.3 (t, two methylene groups in the cyclopropyl ring), 4.6 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 49.3; MS: (EI, 70 eV) *m*/*z* 234 (M^+, 20), 219 (M^+ – CH_3, 100), 205 (M^+ – CH_2CH_3, 28), 193 (M^+ – C_3H_5, 12), 191 (35), 180 (22), 179 (M^+ – $CH_2C_3H_5$, 75), 177 (26), 165 (44), 163 (36), 138 (47), 137 ($(CH_3CH_2O)_2PO^+$, 32), 111 (36), 109 (36), 81 (22), 55 ($CH_2C_3H_5$, 32), 41 (C_3H_5, 16); HRMS: (EI, 70 eV) calcd for ($C_{11}H_{23}O_3P$) 234.1385 (M^+) found *m*/*z* 234.1382.

Diethyl {1-(cyclopropymethyl)pent-4-enyl}phosphonate (3d)



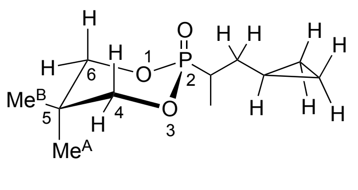
According to the typical procedure, $InBr_3$ (0.80 mmol, 0.283 g), cyclopropylmethylstannane **1** (88% purity) (1.59 mmol, 0.623 g), and diethyl (1-iodopent-4-enyl)phosphonate **2d** (0.85 mmol, 0.282 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 70/30] gave the product **3d** (0.061 g, 22%). Further purification was performed by distillation under reduced pressure to give the product **3d** as a colorless liquid (0.022 g, 8%). bp: 100 °C /0.30 mmHg; IR (neat): 1261 (P=O), 1643 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 5.79 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H, 4-H), 5.08-5.01 (m, including $^3J_{HH}$ = 17.0 Hz, 1H, 5-H^B), 5.01-4.97 (m, including $^3J_{HH}$ = 10.0 Hz, 1H, 5-H^A), 4.14-4.05 (m, 2H, 3-H_2), 1.95-1.76 (m, 2H, 1-H and PCHCH*H*), 1.72-1.54 (m, 2H, 2-H^A and PCHC*H*H), 1.48-1.34 (m, 1H, 2-H^B), 1.32 (t, J = 7.0 Hz, 6H, CH_3 x 2), 0.95-0.82 (m, 1H, $PCHCH_2C$*H*), 0.53-0.42 (m, 2H), 0.12-0.033 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 138.1 (d, C-4), 115.0 (t, 5-C), 61.3 (t, CH_2OP, d by $^2J_{CP}$ = 6 Hz), 35.9 (d, P*C*H, d by $^1J_{CP}$ = 138 Hz), 33.5 (t, C-2, d by $^2J_{CP}$ = 3.3 Hz), 31.7 (t, C-3, d by $^3J_{CP}$ = 9.1 Hz), 27.5 (t, PCH*C*H_2, d by $^3J_{CP}$ = 4 Hz), 16.5 (q, CH_3, d by $^3J_{CP}$ = 6 Hz), 9.4 (d, $PCHCH_2$*C*H, d by $^3J_{CP}$ = 12 Hz), 5.41 (t, two methylene groups in the cyclopropyl ring), 4.67 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 49.0; MS: (EI, 70 eV) *m*/*z* 260 (M^+, 5), 219 (M^+ – C_3H_5, 100), 206 (33), 205 (M^+ – $CH_2C_3H_5$, 30), 191 (27), 165 (39), 163 (38), 149 (20), 109 (36), 81 (22); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{25}O_3P$) 260.1541 (M^+) found *m*/*z* 260.1539.

Diisopropyl (2-cyclopropylethyl)phosphonate (3e)



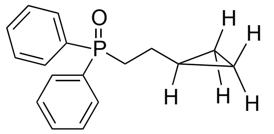
According to the typical procedure, $InBr_3$ (0.81 mmol, 0.287 g), cyclopropylmethylstannane **1** (84% purity) (1.54 mmol, 0.632 g), and diisopropyl iodomethylphosphonate **2e** (0.81 mmol, 0.251 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 70/30] gave the product **3e** (0.130 g, 68%). Further purification was performed by distillation under reduced pressure to give the product **3e** as a colorless liquid. bp: 85 °C /0.25 mmHg; IR (neat): 1250 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.69-4.58 (m, 2H, $(CH_3)_2C$*H* x 2), 1.83-1.74 (m including $^2J_{PH}$ = 18 Hz, 2H, PCH_2), 1.50-1.42 (m, PCH_2CH_2), 1.32 (dd, J = 8.2 Hz, $^4J_{PH}$ = 1.9 Hz, 12H, (CH_3)$_2$CH x 2), 0.81-0.71 (m, 1H, PCH_2CH_2C*H*), 0.46-0.42 (m, 2H), 0.08-0.04 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 69.6 (d, $(CH_3)_2$*C*H, d by $^2J_{CP}$ = 6.6 Hz), 27.7 (t, PCH_2*C*H_2, d by $^2J_{CP}$ = 5 Hz), 26.9 (t, P*C*H_2CH_2, d by $^1J_{CP}$ = 143 Hz), 23.9 (q, (*C*H_3)$_2$CH, d by $^3J_{CP}$ = 6 Hz), 11.6 (d, PCH_2CH_2CH, d by $^3J_{CP}$ = 21 Hz), 4.5 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 44.8; MS: (CI, 200 eV) *m/z* 235 (M^+ + 1, 100), 193 (M^+ – 41, 6), 191 (M^+ – 43, 1); HRMS: (CI, 200 eV); calcd for ($C_{11}H_{24}O_3P$) 235.1463 (M^+ + 1) found *m/z* 235.1456; Analysis: $C_{11}H_{23}O_3P$ (234.27) Calcd: C, 56.39; H, 9.90; O, 20.49; P, 13.22 Found: C, 56.12; H, 9.61.

2-(1-Methyl-2-cyclopropylethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (3f)



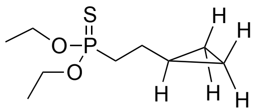
According to the typical procedure, $InBr_3$ (0.80 mmol, 0.283 g), cyclopropylmethylstannane **1** (75% purity) (1.62 mmol, 0.748 g), and 2-(1-iodoethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one **2f** (0.80 mmol, 0.243 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 70/30] gave the product **3f** (0.130 g, 58%). Further purification was performed by distillation under reduced pressure to give the product **3f** as a colorless liquid (0.070 g, 38%). bp: 130 °C/0.47 mmHg; IR (neat): 1268 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.21 (dd, J = 11 Hz, $^3J_{PH}$ = 6 Hz, 2H, two protons of 4-H and/or 6-H), 3.67 (dd, $^3J_{PH}$ = 17 Hz, J = 11 Hz, 2H, two protons of 4-H and/or 6-H), 2.08-1.95 (m, 1H, PC*H*), 1.64-1.54 (m, 1H, PCHCH*H*), 1.43-1.33 (m, 1H, PCHC*H*H), 1.25 (dd, $^3J_{PH}$ = 19 Hz, J = 7.5 Hz, 3H, PCHCH_3), 1.11 (s, 5-Me), 0.87 (s, 5-Me), 0.82-0.71 (m, 1H, $PCHCH_2CH$), 0.50-0.33 (m, 2H), 0.11- -0.06 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 73.9 (t, 4-C or 6-C, d by $^2J_{CP}$ = 5.8 Hz), 73.8 (t, 4-C or 6-C, d by $^2J_{CP}$ = 5.8 Hz), 34.5 (t, $PCHCH_2$, d by $^2J_{CP}$ = 3.3 Hz), 32.6 (s, 5-C, d by $^3J_{CP}$ = 5.7 Hz), 30.3 (d, PCH, d by $^1J_{CP}$ = 137 Hz), 21.8 (q, 5-Me), 21.2 (q, 5-Me), 12.8 (q, $PCHCH_3$, d by $^2J_{CP}$ = 5.8 Hz), 9.0 (d, $PCHCH_2CH$, d by $^3J_{CP}$ = 17 Hz), 5.4 (t, cyclopropyl methylene), 3.7 (t, cyclopropyl methylene); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 110.5; MS: (EI, 70 eV) *m/z* 232 (M^+, 55), 217 (M^+ – CH_3, 51), 191 (M^+ – C_3H_5, 48), 178 (59), 177 (M^+ – $CH_2C_3H_5$, 37), 164 (31), 163 (36), 150 (39), 149 (M^+ – $CH_3CHCH_2C_3H_5$, 67), 147 (46), 136 (23), 123 (51), 111 (82), 110 (36), 109 (28), 97 (21), 83 ($CH_3CHCH_2C_3H_5$, 34), 82 (99), 81 (50), 71 (27), 69 (98), 68 (71), 67 (56), 57 (40), 56 (52), 55 ($CH_2C_3H_5$, 78), 43 (20), 41 (C_3H_5, 100); HRMS: (EI, 70 eV) calcd for ($C_{11}H_{21}O_3P$) 232.1228 (M^+) found *m/z* 232.1225.

(2-Cyclopropylethyl)diphenylphosphine oxide (3g)



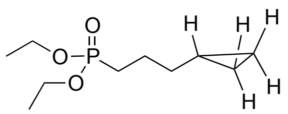
According to the typical procedure, $InBr_3$ (0.80 mmol, 0.285 g), cyclopropylmethylstannane **1** (84% purity) (1.61 mmol, 0.660 g), and diphenyl iodomethylphosphine oxide **2g** (0.80 mmol, 0.272 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 60/40] gave the product **3g** as a white solid (0.140 g, 52%). mp: 95 °C; IR (KBr): 1438, 1172, 698 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.76-7.71 (m, 4H, *o*), 7.53-7.43 (m, 6H, *m* and *p*), 2.42-2.35 (m including $^2J_{PH}$ = 11 Hz, 2H, PCH_2), 1.56-1.48 (m, 2H, PCH_2CH_2), 0.79-0.69 (m, 1H, PCH_2CH_2CH), 0.43-0.38 (m, 2H), 0.049-0.012 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 133.05 (d, C-*i*, d by $^1J_{CP}$ = 98 Hz), 131.5 (d, C-*p*, d by $^4J_{CP}$ = 2.5 Hz), 130.6 (d, C-*o*, d by $^3J_{CP}$ = 9 Hz), 128.4 (d, C-*m*, d by $^2J_{CP}$ = 11 Hz), 29.6 (t, PCH_2, d by $^1J_{CP}$ = 72 Hz), 26.5 (t, PCH_2CH_2, d by $^2J_{CP}$ = 3 Hz), 11.9 (d, PCH_2CH_2CH, d by $^3J_{CP}$ = 17 Hz), 4.6 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 46.7; MS: (EI, 70 eV) *m/z* 270 (M^+, 34), 269 (28), 215(M^+ – $CH_2C_3H_5$, 33), 255 (32), 201 (M^+ – $CH_2CH_2C_3H_5$, 100), 186 (34), 77 (C_6H_5, 23) ; HRMS: (EI, 70 eV) calcd for ($C_{17}H_{19}OP$) 270.1174 (M^+) found *m/z* 270.1169; Analysis: $C_{17}H_{19}OP$ (270.30) Calcd: C, 75.54; H, 7.08; O, 5.92; P, 11.46 Found: C, 75.70; H, 6.89.

***O,O'*-Diethyl (2-cyclopropylethyl)phosphonothioate (3h)**



According to the typical procedure, $InBr_3$ (0.81 mmol, 0.286 g), cyclopropylmethylstannane **1** (84% purity) (1.64 mmol, 0.675 g), and *O,O'*-diethyl iodomethylphosphonothioate **2h** (0.85 mmol, 0.250 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 50/50] gave the product **3h** (0.040 g, 21%). Further purification was performed by distillation under reduced pressure to give the product **3h** as a colorless liquid (0.020, 11 %). bp: 130 °C /0.2 mmHg; IR (neat): 1033 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.18-4.02 (m, 4H, CH_3CH_2 x 2), 2.10-2.02 (m, $^2J_{PH}$ = 7.5 Hz, 2H, PCH_2), 1.57-1.48 (m, 2H, PCH_2CH_2 x 2), 1.29 (td, J = 7.0 Hz, $^4J_{PH}$ = 1.0 Hz, 6H, CH_3 x 2), 0.80-0.70 (m, 1H, PCH_2CH_2CH), 0.47-0.42 (m, 2H), 0.10-0.06 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 62.1 (t, CH_3CH_2OP, d by $^2J_{CP}$ = 7.4 Hz), 34.6 (t, PCH_2, d by $^1J_{CP}$ = 111 Hz), 28.0 (t, PCH_2CH_2, d by $^2J_{CP}$ = 3.3 Hz), 16.1 (q, CH_3, d by $^3J_{CP}$ = 6.6 Hz), 11.4 (d, PCH_2CH_2CH, d by $^3J_{CP}$ = 23 Hz), 4.5 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 113.9; MS: (EI, 70 eV) *m/z* 222 (M^+, 51), 194 (M^+ – CH_3CH_2, 41), 154 ($(CH_3CH_2O)_2PS^+$, 29), 150 (25), 125 (23), 121 (100), 97 (45), 93 (50), 69 (M^+ – $(CH_3CH_2O)_2P(S)$, 21), 65 (33); HRMS: (EI, 70 eV) calcd for ($C_9H_{19}O_2PS$) 222.0843 (M^+) found *m/z* 222.0842; Analysis: $C_9H_{19}O_2PS$ (222.28) Calcd: C, 48.63; H, 8.62; O, 14.40; P, 13.93; S, 14.43 Found: C, 48.40; H, 8.33.

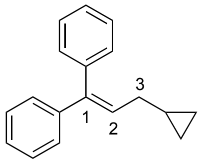
Diethyl (3-cyclopropylpropyl)phosphonate (6)



According to the typical procedure, $InBr_3$ (0.80 mmol, 0.283 g), cyclopropylmethylstannane **1** (86% purity) (1.60 mmol, 0.644 g), diethyl 2-iodoethylphosphonate **5** (0.79 mmol, 0.232 g), and AIBN (0.08 mmol, 0.013 g) gave the crude product. Purification by flash column chromatography [hexane/ethyl acetate = 70/30] gave the product **6** (0.032 g, 18%). Further purification was performed by distillation under reduced pressure. bp: 80 °C /0.26 mmHg; IR (neat): 1246 (P=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.17-4.03 (m, 4H, CH_2OP x 2), 1.82-1.65 (m, 4H, PCH_2 and PCH_2CH_2), 1.42-1.26 (m, 2H, $PCH_2CH_2CH_2$), 1.33 (t, J = 7.0 Hz, 6H, CH_3 x 2), 0.69-0.60 (m, 1H, $PCH_2CH_2CH_2CH$), 0.44-0.40 (m, 2H), 0.07-0.01 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 61.3 (t, CH_2OP, d by $^2J_{CP}$ = 6.6 Hz), 35.4 (t, $PCH_2CH_2CH_2$, d by $^3J_{CP}$ = 17 Hz), 25.4 (t, PCH_2, d by $^1J_{CP}$ = 141 Hz), 22.4 (t, PCH_2CH_2, d by $^2J_{CP}$ = 5 Hz), 16.4 (q, CH_3, d by $^3J_{CP}$ = 6.6 Hz), 10.3 (d, $PCH_2CH_2CH_2CH$), 4.3 (t, two methylene groups in the cyclopropyl ring); ^{31}P NMR: (160 MHz, $CDCl_3$, external standard = 85 wt% D_3PO_4 in D_2O) 47.3; MS: (EI, 70 eV) *m/z* 220 (M^+, 14), 191

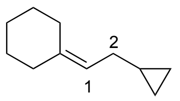
(M^+ – CH_2CH_3, 23), 165 (M^+ – $CH_2C_3H_5$, 53), 152 (M^+ – $CH_2CH_2C_3H_5$, 100), 147 (31), 138 ($(CH_3CH_2O)_2PO^+$, 71), 125 (65), 124 (23), 111 (64), 110 (23), 109 (31), 108 (21), 97 (52), 96 (26), 82 ($CH_2CH_2CH_2C_3H_5^+$, 31), 81 (38), 41 ($C_3H_5^+$, 23); HRMS: (EI, 70 eV) calcd for ($C_{10}H_{21}O_3P$) 220.1228 (M^+) found *m*/*z* 220.1221.

1,1-Diphenyl-3-cyclopropyl-1-propene (10)



According to the typical procedure, *O,O'*-diethyl (2-cyclopropylethyl)phosphonothioate **3h** (0.23 mmol, 0.050 g), *s*-BuLi (1.0 M in hexane, 0.30 mL), and benzophenone (0.24 mmol, 0.043 g) gave the crude product. Purification by flash column chromatography [hexane (200 mL)] gave the product **10** as a colorless liquid (0.030 g, 57%). IR (neat): 1493, 1442, 822, 702 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.38-7.16 (m, 10H, Ar x 2), 6.19 (t, *J* = 7.0 Hz, 1H, 2-H), 2.02 (dd, *J* = 7.0, 7.0 Hz, 2H, 3-H_2), 0.83-0.73 (m, 1H, C=CHCH_2C*H*), 0.46-0.41 (m, 2H), 0.088-0.050 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 142.7 (s, *i*), 141.4 (s, C-1), 140.2 (s, *i*), 129.9 (d), 129.1 (d), 128.1 (d), 128.0 (d), 127.2 (d), 126.8 (d), 126.7 (d), 34.5 (t, C-3), 11.1 (d, C=CHCH_2CH), 4.2 (t, two methylene groups in the cyclopropyl ring); MS: (EI, 70 eV) *m*/*z* 234 (M^+, 46), 205 (100), 193 (M^+ – C_3H_5, 37), 191 (22), 180 (35), 178 (M^+ – $CH_2C_3H_5$, 25), 165 (24), 115 (48), 91 (42) ; HRMS: (EI, 70 eV) calcd for ($C_{18}H_{18}$): 234.1409 (M^+) found *m*/*z* 234.1404; Analysis: $C_{18}H_{18}$ (234.34) Calcd: C, 7.74; H, 92.26 Found: C, 7.66; H, 92.12.

(2-Cyclopropylethylidene)cyclohexane (11)



According to the typical procedure, *O,O'*-diethyl (2-cyclopropylethyl)phosphonothioate **3h** (0.17 mmol, 0.038 g), *s*-BuLi (1.0 M in hexane, 0.20 mL), and cyclohexanone (0.23 mmol, 0.023 g) gave the crude product. Purification by flash column chromatography [hexane (200 mL)] gave the product **11** as a colorless liquid (0.012 g, 51%). IR (neat): 1666 (C=C), 1446, 1014, 849, 818 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 5.16 (t, *J* = 7.0 Hz, 1H, C=C*H*), 2.12-2.07 (m, 4H), 1.92 (dd, *J* = 7.0, 7.0 Hz, 2H, 2-H_2), 1.55-1.43 (m, 6H), 0.74-0.64 (m, 1H, 2-C*H*(CH_2)$_2$), 0.41-0.37 (m, 2H), 0.07-0.03 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 139.8 (s, *C*=CH), 120.1 (d, C=*C*H), 37.2 (t), 31.6 (t, C-2), 28.8, 28.7, 27.9, 27.0, 11.3 (d, *C*H(CH_2)$_2$), 3.95 (t, two methylene groups in the cyclopropyl ring); MS: (EI, 70 eV) *m*/*z* 150 (M^+, 38), 121 (31), 109 (M^+ – C_3H_5, 53), 107 (46), 94 (27), 93 (31) 81 (52), 79 (56), 68 (50), 67 (100), 55 (29), 41 (C_3H_5, 21); HRMS: (EI, 70 eV) calcd for ($C_{11}H_{18}$): 150.1409 (M^+) found *m*/*z* 150.1406.

1-3-5. References

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(19) When the reaction was carried out in the absence of AIBN, the yield of product **6** was decreased to 27%.
(20) The transmetalation (**1**/$InBr_3$ = 2:1) took over 2 hrs for completion, in which no formation of monobutenylindium was observed (See the Experimental Section for details). In additon, the transmetalation of equal molar amount of **1** and $InBr_3$ (**1**/$InBr_3$ = 1:1) in hexane at room temperature also

gave **7** as a single product. These results are different from the transmetalation in toluene, where the mixture of mono- and dibutenylindium species was obtained, see: ref 8.
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(23) The reaction using **1** (0.8 mmol), **2a** (0.8 mmol), and $InBr_3$ (0.4 mmol) resulted in a lower yield (44%).
(24) We have reported that dibutenylindium species is more reactive than monobutenylindium species, see: ref 8.
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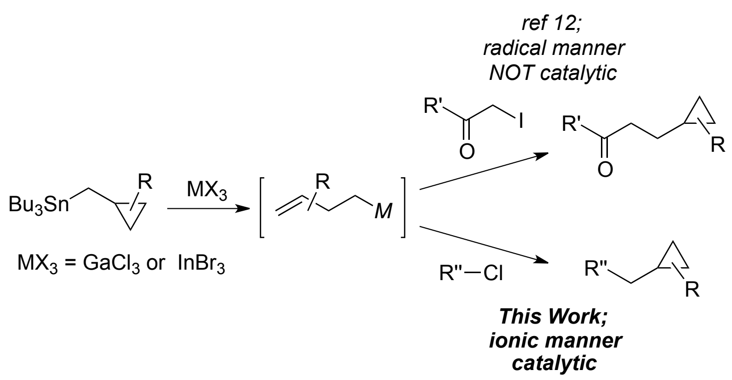
Chapter 2

Cyclopropylmethylation of Benzylic and Allylic Chlorides with Cyclopropylmethylstannane Catalyzed by Gallium or Indium Halide

2-1. Introduction

Cyclopropane functional compounds are versatile synthetic intermediates because of their unique reactivity.[1] Moreover, cyclopropyl rings also exist in many natural compounds that show biological activity.[2] For their preparation, the Simmons-Smith reaction[3] and transition-metal-catalyzed cyclopropanation with diazo compounds[4] have been widely used.[5] Although butenyl metal species are useful reagents for construction of cyclopropyl ring systems, their low nucleophilicity has limited their synthetic applications.[6] Only a few examples have been reported. For example, an equimolar amount of $TiCl_4$ promoted the coupling of butenyltrimethylsilane and acid chlorides.[7] Similar types of reactions have been achieved using butenyltributylstannanes in the presence of Lewis acids.[8] In addition, *in situ* generated butenylgallium, -indium, and -aluminum species from butenyl Grignard reagents have been coupled with α-halocarbonyl compounds[9] in a radical manner.[10] Recently, we confirmed the generation of active indium species bytransmetalation between cyclopropylmethylstannane[11] and indium halide and its radical coupling reaction with α-iodocarbonyl compounds, although a catalytic trial failed.[12] In this communication, we report the $GaCl_3$- or $InBr_3$- catalyzed cyclopropylmethylation of alkyl chlorides, which are readily available but less reactive than iodides or bromides, with cyclopropylmethylstannane (Scheme 1). Contrary to our previous report, this reaction proceeded by an ionic mechanism, which apparently enabled the catalytic coupling. In addition, the generated butenylgallium intermediate was isolated and confirmed by its complexation with a phosphine ligand.

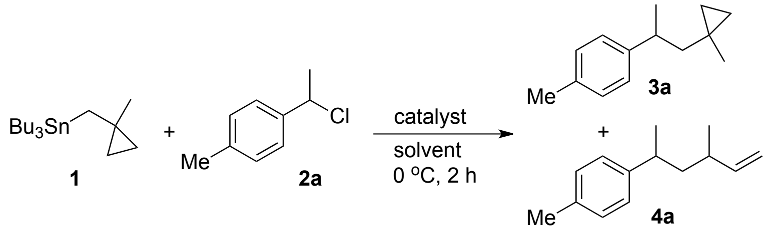
Scheme 1. Reactivity of Butenylgallium or Butenylindium Species



2-2. Results and Discussion

First, we chose the reaction of 1-chloro-1-(4-methylphenyl)ethane (**2a**) with cyclopropylmethylstannane **1** for the investigation of the catalysts (Table 1).[13] No reaction took place without catalyst loading (entry 1). Use of 5 mol % of $InBr_3$ in CH_2Cl_2 effectively promoted the coupling reaction to afford the cyclopropylmethylated product **3a** in 81% yield along with 19% yield of the ring-opening product **4a** (entry 2). Other indium halides, $InCl_3$ or InI_3, gave yields lower than that of $InBr_3$ (entries 3 and 4). Hydrocarbon solvents such as hexane and toluene were also effective (entries 5 and 6), whereas no reaction was observed in MeCN, perhaps because the interaction between the indium catalyst and the substrates was disturbed by its strong coordination ability (entry 7). In addition, it was found that gallium halide was also an efficient catalyst (entries 8 and 9). The reactions were not affected by the addition of a radical inhibitor, such as TEMPO or galvinoxyl, which had completely disturbed the reactions with α-haloesters, as previously reported[12] (entries 10–13). These data strongly indicated that the reaction proceeded in an ionic manner. All previous reactions of organic halides with organoindium species proceed via a radical mechanism. For example, the reduction by indium hydride[14] and the coupling between α-halocarbonyl com- pounds with vinyl-, allyl-, or alkynylindium species[15] are both known to be radical reactions.[16] Organogallium species[9,15,17] also reacted with organic halides in a radical manner. An ionic reaction with organic halides has never been reported for either the organoindium or the organogallium species, as far as we know.

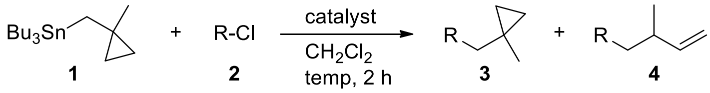
Table 1. Reaction of 1-Chloro-1-(4-methylphenyl)ethane (**2a**) with Cyclopropylmethylstannane **1**[a]

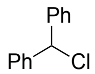
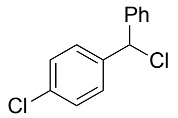
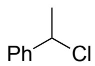
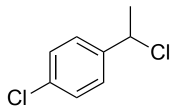
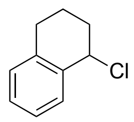
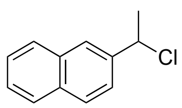
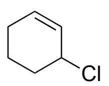
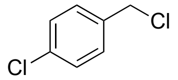
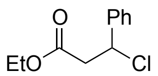


entry	catalyst	solvent	yield/ %[b] 3a	4a
1	none	CH_2Cl_2	0	0
2	$InBr_3$	CH_2Cl_2	81	19
3	$InCl_3$	CH_2Cl_2	69	18
4	InI_3	CH_2Cl_2	58	19
5	$InBr_3$	hexane	59	26
6	$InBr_3$	toluene	52	19
7	$InBr_3$	MeCN	0	0
8	$GaCl_3$	CH_2Cl_2	57	14
9	$GaBr_3$	CH_2Cl_2	55	14
10[c]	$InBr_3$	CH_2Cl_2	55	15
11[d]	$InBr_3$	CH_2Cl_2	73	20
12[c]	$GaCl_3$	CH_2Cl_2	45	13
13[d]	$GaCl_3$	CH_2Cl_2	71	21

[a] All entries were carried out at 0 °C for 2 h using 1.0 mmol of **1**, 1.0 mmol of **2a**, and 0.05 mmol of catalyst. [b] Determined by ^1H NMR. [c] TEMPO (0.05 mmol) was added. [d] Galvinoxyl (0.05 mmol) was added.

Table 2. $GaCl_3$ or $InBr_3$-Catalyzed Cyclopropylmethylation of Various Alkyl Chlorides **2**[a]



entry	2		temp/ °C	product	catalyst	yield/ %[b] 3	4
1		**2b**	0	**3b**	$GaCl_3$	72	16
2					$InBr_3$	79	20
3		**2c**	0	**3c**	$GaCl_3$	82	14
4					$InBr_3$	78	19
5		**2d**	rt	**3d**	$GaCl_3$	59	21
6					$InBr_3$	trace	trace
7		**2e**	80	**3e**	$GaCl_3$	56	22
8					$InBr_3$	trace	trace
9		**2f**	0	**3f**	$GaCl_3$	63	15
10					$InBr_3$	73	17
11		**2g**	0	**3g**	$GaCl_3$	73	20
12					$InBr_3$	80	19
13		**2h**	rt	**3h**	$GaCl_3$	45	12
14					$InBr_3$	15	5
15[c]		**2i**	80	**3i**	$GaCl_3$	36	46
16[c]					$InBr_3$	70	14
17[d]		**2j**	0	**3j**	$GaCl_3$	40	22
18[d]					$InBr_3$	0	0

[a] All entries were carried out with 1.0 mmol of **1**, 1.0 mmol of **2a**, and 0.05 mmol of catalyst. [b] Determined by ^1H NMR. [c] 1.5 mmol of **1** and 0.75 mmol of catalyst were used. [d] 0.5 mmol of catalyst was used.

We next explored the scope of this system using either $InBr_3$ or $GaCl_3$ catalyst (Table 2). Various secondary benzylic chlorides furnished cyclopropylmethylated products in moderate to high yields (entries 1–12).[18] In the case of **2c** and **2e**, which bear two types of chlorine atoms, selective coupling was achieved at benzylic positions. 3-Chlorocyclohexene (**2h**) was also transformed to the corresponding product **3h** (entries 13 and 14). Primary benzylic chloride, *p*-chlorobenzyl chloride (**2i**), gave the product when an equimolar amount of metal halide was used (entries 15 and 16). $GaCl_3$ catalyzed the reaction with β-chloro ester **2j** to afford the ester **3j**, while the starting ester was recoverd in the case of $InBr_3$ (entries 17 and 18).

To confirm the active gallium species, a mixture of an equimolar amount of $GaCl_3$ and **1** was monitored by ^{1}H NMR. Similar signals were observed with two doublets for the vinylic protons (a), two triplets for the allylic protons (c), and two singlets for the methyl protons (b) (Figure 1ii). On the basis of the reported facts,[12] they were assigned the designations of mono- and dibutenylgallium species **5a** and **6a**. The integration ratio of the peaks was ~2.5:1, and the product ratio of **5a/6a** was ~5:1. On the other hand, a 1:2 mixture of $GaCl_3$/**1** preferentially gave **6a** (integration ratio of **5a/6a** ≈ 1:10) with no other highly substituted species (see the Experimental Section). The integration ratio was somewhat different in the case of $InBr_3$ (**5b**/**6b** ≈ 1:1) (Figure 1iii). The addition of benzhydryl chloride (**2b**) to the stirred mixture of **1** and $GaCl_3$ (**1**/$GaCl_3$ = 1:1) for 30 min in dichloromethane-d_2 gave the coupling product in 86% yield ($InBr_3$, 71% yield). These results demonstrated that the active species in the reaction was a mono- and dibutenyl metal species.[12]

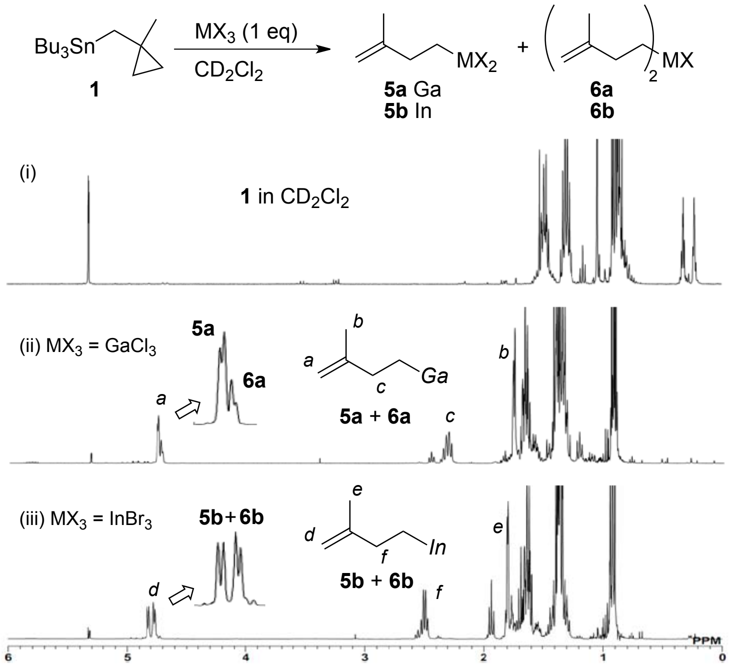
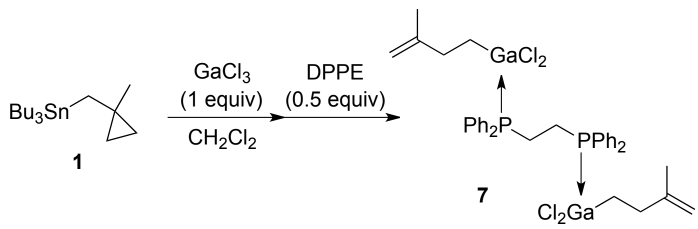


Figure 1. ^{1}H NMR spectra of (i) **1**, (ii) the mixture of $GaCl_3$ and **1**, and (iii) the mixture of $InBr_3$ and **1** in CD_2Cl_2.

Furthermore, we attempted to isolate the butenylgallium species by complexation using external ligands. The addition of DPPE to a 1:1 mixture of $GaCl_3$/**1** in CH_2Cl_2 gave a crystal, which was determined by X-ray crystal structural analysis to be butenylgallium complex **7** (Scheme 2). The structure is shown in Figure 2. The four-coordinated gallium center had a butenyl group, a phosphorus in DPPE, and two chlorines. Each phosphine moiety in DPPE coordinated to the other molecule's gallium centers. The angles for Cl1–Ga–Cl2 (107.02°) and C–Ga–Cl (115.58° and 113.48°) indicated that the gallium center exhibited a distorted tetrahedral structure. This stable structure was different from **12** that of TBP of the indium species.

Scheme 2. Complexation and Isolation of the Butenylgallium Species



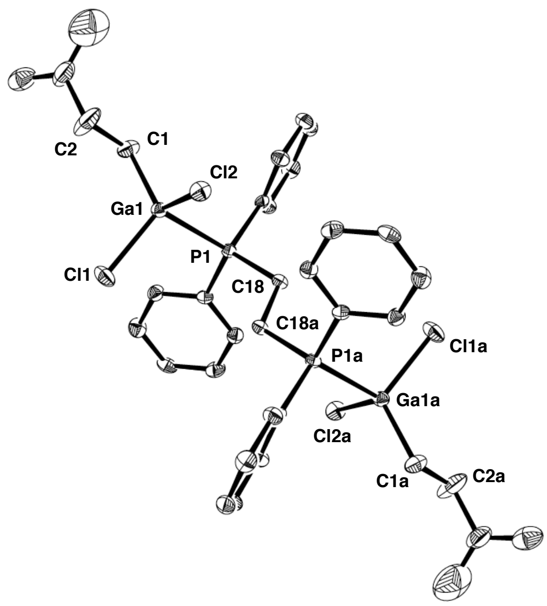
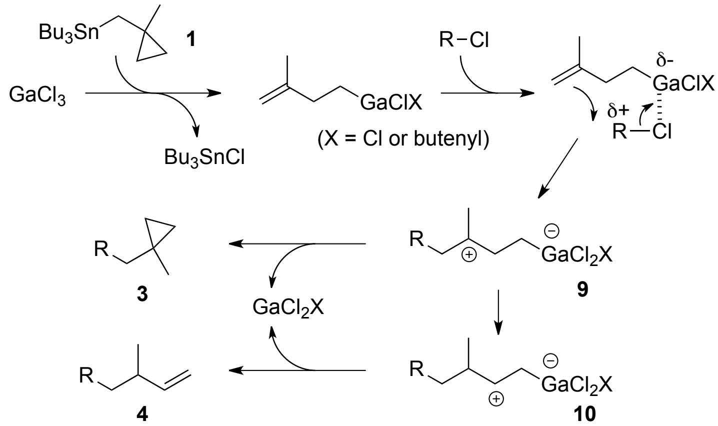


Figure 2. The X-ray structure of **7** (all hydrogens are omitted for clarity).

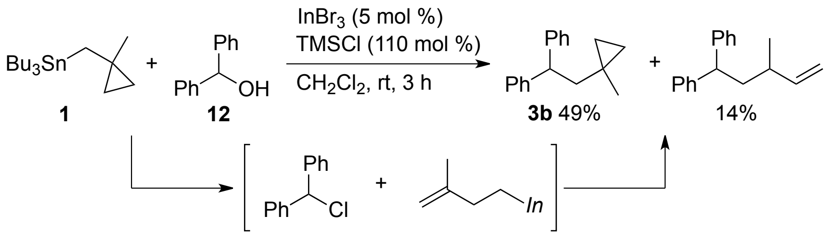
Scheme 3. Plausible Reaction Mechanism



A plausible reaction mechanism is shown in Scheme 3. Transmetalation between **1** and $GaCl_3$ gives butenylgallium species. Then the resulting gallium species activates alkyl chloride by formation of an intermediate **9**, perhaps via the alkyl cation species. Finally, cyclization takes place with the release of gallium chloride to form a cyclopropyl ring. When the isomerization from **9** to **10** via a hydride shift occurs, the ring-opening product is formed.[7a,8b,19] The interaction of the butenylgallium species and alkyl chloride may be a key step in this ionic mechanism to complete the catalytic cycle. The reaction using $InBr_3$ as a catalyst proceeds in a similar manner.

Finally, this reaction system was applied to the direct use of alcohol instead of chloride, as shown in Scheme 4. Using alcohols as substrates would be ideal for synthetic organic chemistry because alcohols are plentiful and readily available. The reaction of **1** with benzhydrol (**12**) in the presence of $InBr_3$ and trimethylsilyl chloride furnished corresponding cyclopropylmethylated product **3b** in 49% yield. It is assumed that a reaction using trimethylsilyl chloride chlorinated alcohol in the presence of $InBr_3$,[20,21] followed by coupling with cyclopropylmethylstannane, would proceed in the manner discussed above.

Scheme 4. Cyclopropylmethylation of Alcohol



2-3. Conclusion

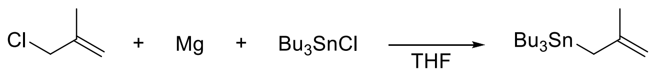
In conclusion, we have developed $GaCl_3$- or $InBr_3$-catalyzed cyclopropylmethylation of benzylic and allylic chlorides with cyclopropylmethylstannane. NMR spectroscopy and X-ray crystal structural analysis revealed the generation of butenylgallium and -indium species.

2-4. Experimental Section

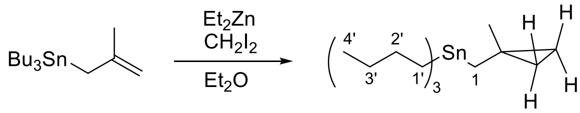
General. New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance techniques, HMQC, HMBC, IR, MS, HRMS, and elemental analysis. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS as internal standard. ^{119}Sn (150 MHz) spectra were obtained with Me_4Sn as external standard. IR spectra were recorded as thin film. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (MERK C60 or Fuji Silysia FL100DX). Recycle GPC was performed with $CHCl_3$ as the eluent. Bulb-toBulb distillation (Kuglrohr) was accomplished at the oven temperature and pressure indicated. Yields were determined by ^{1}H NMR using internal standard.

Materials. Dehydrated dichloromethane, hexane, toluene, and acetonitrile were purchased and used as obtained. 1,2-dichloroethane was distilled from P_2O_5. The catalysts examined in Table 1 were also purchased from commercial sources. Cyclopropylmethylstannane **1** was prepared and the experimental detail is described below (This preparation method was not optimized.). Starting chlorides, **2a**[22], **2e**[22], **2f**[23], **2g**[24], and **2j**[22] were prepared by known methods[20,21] and these compounds were reported. All other starting chlorides and starting alcohol **12** are commercially available. All other reagents were commercially available.

Preparation of (1-methylcyclopropyl)methyltributylstannane (1).

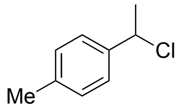


To a flask containing magnesium (180 mmol) in THF (150 mL) was added Bu_3SnCl (150 mmol). The mixture was cooled to 0 °C, and then 3-chloro-2-methylprop-1-en (170 mmol) was added. The mixture was irradiated with ultrasound at 0 °C for 1 h and stirred. After 2 h, the reaction was quenched by water (200 mL), and then organic layer was separated. Hexane (200 mL) was added, and the organic layer was washed using water (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (47.4 g, 92%): bp 82 °C/0.05 mmHg. The analytical data for this compound matched that previously reported.[25]



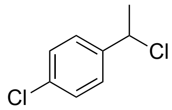
To a solution of 2-methyl allylstannane (30 mmol) in diethyl ether (40 mL), diethylzinc (1.0 M in hexane, 35 mL) was added. To the mixture was added the solution of diiodomethane (70 mmol) in diethylether (30 mL) dropwise within 30 min. The reaction mixture was stirred for 2 h at room temperature, and then quenched by saturated NH_4Cl aq (100 mL). Hexane (200 mL) was added, and the organic layer was washed using saturated NH_4Cl aq (100 mL), saturated NaCl aq (100 mL), and NH_4F aq (10%, 100 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography [solvent; hexane] on silica gel to give the product (83% yield, 93% purity (a small portion was analyzed by ^{1}H NMR using an internal standard)), which was used in the cyclopropylmethylation reaction without further purification. IR: (neat) 3066, 2954, 2850, 1462 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 1.57-1.40 (m, 6H, 2'-H_2 x 3), 1.36-1.25 (m, 6H, 3'-H_2 x 3), 1.04 (s, 3H, Me at cyclopropyl ring), 0.95-0.76 (m, 17H, 4'-H_3 x 3, 1'-H_2 x 3, and 1-H_2), 0.36-0.29 (m, 2H), 0.26-0.20 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 29.3 (t, C-2', d, $^2J_{Sn\text{-}C}$ = 19.6 Hz), 27.5 (t, C-3', d, $^3J_{Sn\text{-}C}$ = 53.2 Hz), 26.7 (q, Me at cyclopropyl ring), 22.2 (t, C-1, d, $^1J_{119Sn\text{-}C}$ = 308.9, $^1J_{117Sn\text{-}C}$ = 294.1 Hz), 16.5 (t, two methylene groups in cyclopropyl ring, d, $^3J_{Sn\text{-}C}$ = 34.4 Hz), 14.8 (s, $SnCH_2C(CH_3)$, d, $^2J_{Sn\text{-}C}$ = 19.7 Hz), 13.7 (q, C-4'), 9.6 (t, C-1', d, $^1J119_{Sn\text{-}C}$ = 308.7, $^1J117_{Sn\text{-}C}$ = 295.7 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) -15.5; MS: (EI, 70 eV) *m/z* 303 (88), 302 (33), 301 (64), 300 (24), 299 (39), 291 (23), 235 (67), 234 (20), 233 (51), 231 (31), 179 (100), 177 (100), 176 (32), 175 (68), 121 (24); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{27}{}^{120}Sn$) 303.1135 (M^+ – Bu) found *m/z* 303.1133.

1-chloro-1-(4-methylphenyl)ethane (2a)[22]



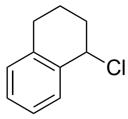
To a stirred solution of $BiCl_3$ (2 mmol) and 1-(4-methylphenyl)ethanol (40 mmol) in dichloromethane (10 mL) was slowly added trimethylsilyl chloride (48 mmol) at room temperature. The mixture was stirred for 2 h, and then quenched by water (50 mL). The mixture was extracted with diethyl ether (50 mL x 3). The collected organic layer was washed with brine (100 mL) and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (5.4 g, 87%): bp 110 ^oC/3 mmHg. The analytical data for this compound matched that previously reported.

1-chloro-1-(4-chlorophenyl)ethane (2e)[22]



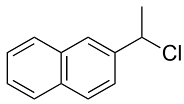
To a stirred solution of $BiCl_3$ (1.5 mmol) and 1-(4-chlorophenyl)ethanol (30 mmol) in dichloromethane (10 mL) was slowly added trimethylsilyl chloride (36 mmol) at room temperature. The mixture was stirred for 2 h, and then quenched by water (50 mL). The mixture was extracted with diethyl ether (50 mL x 3). The collected organic layer was washed with brine (100 mL) and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (4.5 g, 84%): bp 130 ^oC/3 mmHg. The analytical data for this compound matched that previously reported.

1-chloro-1,2,3,4-tetrahydronaphthalene (2f)[23]



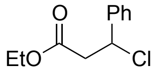
To a stirred solution of $BiCl_3$ (1.5 mmol) and 1,2,3,4-tetrahydronaphthalene-1-ol (30 mmol) in dichloromethane (10 mL) was slowly added trimethylsilyl chloride (36 mmol) at room temperature. The mixture was stirred for 2 h, and then quenched by water (50 mL). The mixture was extracted with diethyl ether (50 mL x 3). The collected organic layer was washed with brine (100 mL) and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product (4.5 g, 91%): bp 95 ^oC/0.2 mmHg. The analytical data for this compound matched that previously reported.

2-(1-chloroethyl)naphthalene (2g)[24]



To a stirred solution of $BiCl_3$ (1.5 mmol) and 2-naphthyl-1-ethanol (30 mmol) in dichloromethane (10 mL) was slowly added trimethylsilyl chloride (36 mmol) at room temperature. The mixture was stirred for 2 h, and then quenched by water (50 mL). The mixture was extracted with diethyl ether (50 mL x 3). The collected organic layer was washed with brine (100 mL) and then dried ($MgSO_4$). The solvent was evaporated to give a solid, which was then washed by hexane to give the product as a white solid (3.3 g, 58%). The analytical data for this compound matched that previously reported.

Ethyl 2-chloro-2-phenylpropanoate (2j)[22]



To a mixture of $InCl_3$ (0.1mmol), benzil (2 mmol) and ethyl 3-hydroxy-3-phenyl-propanoate[26] (2 mmol) in dichloromethane (4 mL) was added chlorodimethylsilane ($HSiMe_2Cl$) (2.2 mmol). The reaction mixture was stirred for 0.1 h a room temperature. The resulting mixture was poured into aqueous $NaHCO_3$ (50 mL) and extracted with EtOAc (50 mL). The organic layer was dried ($MgSO_4$) and the solvent was evaporated and the residue was purified by distillation under reduced pressure to give the product: bp 80 ^{o}C/ 0.11 mmHg. The analytical data for this compound matched that previously reported.

Typical procedure for the reaction of cyclopropylmethylstannane 1 with alkyl chlorides 2 (Table 1, entry 2). To a solution of $InBr_3$ (0.05 mmol) in dichloromethane (1 mL), cyclopropylmethylstannane **1** (1 mmol) was added. The mixture was stirred for 10 min at room temperature. To the reaction mixture was added the solution of alkyl chlorides (1 mmol) in dichloromethane (3 mL) dropwise over 20 min at the temperature described in the text, and then the mixture was stirred for 2 h at same temperature. The reaction mixture was quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR. The detail of further purification was described in Product Data.

Experimental procedure for the reaction of cyclopropylmethylstannane 1 with 4-chlorobenzyl chloride (2i) (Table 2, entries 15 and 16). To a solution of either $GaCl_3$ (0.75 mmol) or $InBr_3$ (0.75 mmol) in 1,2-dichloroethane (2 mL), cyclopropylmethylstannane **1** (1.5 mmol) was added. The mixture was stirred for 10 min at room temperature. To the reaction mixture was added 4-chlorobenzyl chloride **2i** (1 mmol), and then the mixture was stirred for 2 h at 80 ^{o}C. The reaction mixture was quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR. The detail of further purification was described in Product Data.

Experimental procedure for the reaction of cyclopropylmethylstannane 1 with 3-chloro-3-phenylpropanoate (2j) (Table 2, entries 17 and 18). To a mixture of cyclopropylmethylstannane **1** (1 mmol) and ethyl 3-chloro-3-phenylpropanoate **2j** (1 mmol) in dichloromethane (3 mL) was added either $GaCl_3$ (0.5 mmol) or $InBr_3$ (0.5 mmol). The mixture was stirred for 2 h at room temperature, and then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR. The detail of further purification was described in Product Data.

NMR study of transmetalation between 1 and $GaCl_3$ or $InBr_3$ (Figure 1). A mixture of cyclopropylmethylstannane **1** and $GaCl_3$ or $InBr_3$ (the ratio of **1**/$GaCl_3$ = 1:1, **1**/$InBr_3$ = 1:1) was prepared in dichloromethane-d_2. After mixing for 30 min, the mixture was transferred into NMR tube, and the resulting spectrum is shown in Figure 1. The mixture of **1** and $GaCl_3$ (the ratio of **1**/$GaCl_3$ = 2:1) was prepared in dichloromethane-d_2. After mixing for 30 min, the mixture was transferred into NMR tube, and the resulting spectrum is shown below (Figure A).

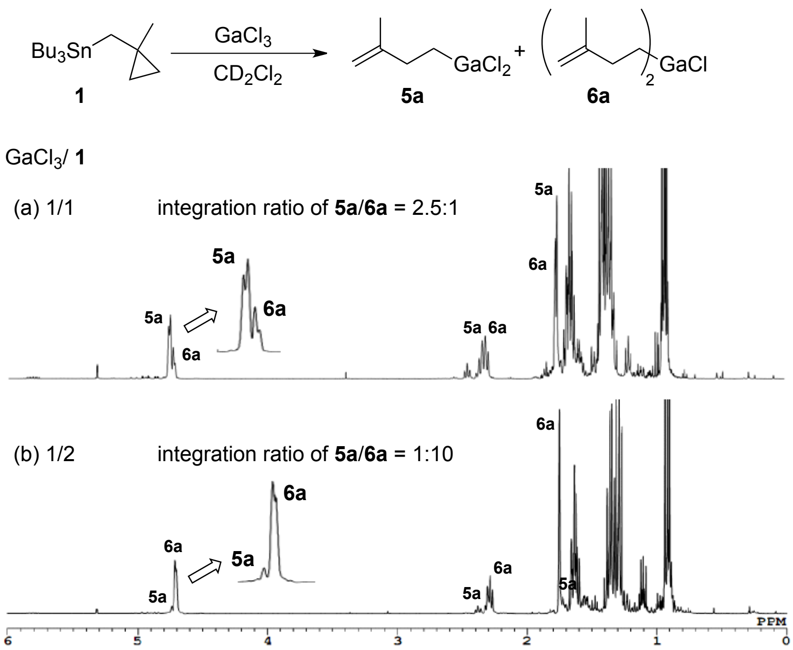
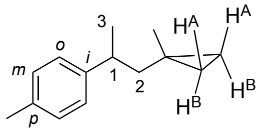


Figure A. [1]H NMR spectra of the reaction mixtures of $GaCl_3$ and **1** with (a) 1/1 and (b) 1/2 ratios in CD_2Cl_2.

Isolation of butenylgallium species (7) (Scheme 2). To a mixture of $GaCl_3$ (0.0885 g, 0.50 mmol) in dichloromethane (1 mL) was added cyclopropylmethylstannane **1** (93% purity) (0.2017 g, 0.52 mmol) at room temperature. The mixture was stirred for 1.5 h, and then 1,2-bis(diphenylphosphino)ethane (0.0957 g, 0.24 mmol) was loaded. The mixture was stirred for 1 h, and then the volatiles were evaporated to give a viscous liquid, which was then washed by hexane to give the product as a white solid (0.246 g) with a small amount of impurity. The product was recrystallized from dichloromethane/hexane for X-ray analysis.

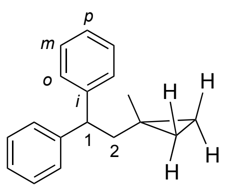
Experimental procedure for the reaction of cyclopropylmethylstannane 1 with benzhydrol (12) (Scheme 4). To a mixture of $InBr_3$ (0.05 mmol), cyclopropylmethylstannane **1** (1 mmol), and benzhydrol **12** (1 mmol) in dichloromethane (3 mL) was added trimethylsilyl chloride (1.1 mmol). The mixture was stirred for 3 h at room temperature, and then quenched by NH_4F aq (10%, 10 mL). The mixture was extracted with diethyl ether (10 mL x 3). The collected organic layers were dried ($MgSO_4$). The evaporation of the ether solution gave the crude product which was analyzed by NMR.

1-(1-methylcyclopropyl)-2-(4-methylphenyl)propane (3a)



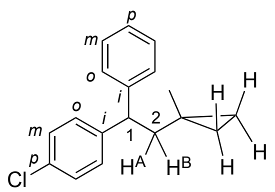
According to the typical procedure, $InBr_3$ (0.0175 g, 0.049 mmol), cyclopropylmethylstannane **1** (91% purity) (0.4012 g, 1.02 mmol), and 1-chloro-1-(4-methylphenyl)ethane **2a** (0.1523 g, 0.98 mmol) gave the crude product (99% **3a**:**4a** = 81:19). Purification by flash column chromatography [solvent; hexane] on silica gel afforded the product (0.137 g, 74% **3a**:**4a** = 81:19). Further purification was performed by gel permeation chromatography [solvent; chloroform]. IR: (neat) 3070, 2962, 2877, 1516, 1454, 1381, 1014, 814 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.09-7.06 (m, 4H, aroma), 2.99 (qdd, *J* = 7.2, 7.2, 7.2 Hz, 1H, 2-H), 2.30 (s, 3H, Me at aromatic ring), 1.67 (dd, *J* = 13.6, 7.2 Hz, 1H, H^A), 1.30 (dd, *J* = 13.6, 8.0 Hz, 1H, H^B), 1.24 (d, *J* = 7.2 Hz, 3H, 3-H_3), 1.00 (s, 3H, Me at cyclopropyl ring), 0.28 (ddd, *J* = 9.6, 4.2, 4.2 Hz, 1H), 0.22 (ddd, *J* = 9.6, 4.2, 4.2 Hz, 1H), 0.05 (ddd, *J* = 9.6, 4.2, 4.2 Hz, 1H), 0.00 (ddd, *J* = 9.6, 4.2, 4.2 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.4 (s, *i*), 135.1 (s, *p*), 128.9 (d, *m)*, 126.8 (d, *o*), 48.2 (t, C-1), 37.7 (d, C-2), 22.8 (q, Me at cyclopropyl ring), 22.2 (q, C-3), 21.0 (q, Me at aromatic ring), 14.0 (s, $CH(CH_3)CH_2\mathit{C}(CH_3))$, 13.5 (t, $CH(CH_3)CH_2C(CH_3)\mathit{C}^AH_2$), 12.8 (t, $CH(CH_3)CH_2C(CH_3)\mathit{C}^BH_2$); MS: (EI, 70 eV) *m*/*z* 188 (M^+, 6), 132 (21), 119 ($M^+ - C_5H_9$, 100), 69 ($C_5H_9^+$, 2); HRMS: (EI, 70 eV) calcd for ($C_{14}H_{20}$) 188.1565 (M^+) found *m*/*z* 188.1565.

2-(1-methylcyclopropyl)-1,1-diphenylethane (3b)



According to the typical procedure, $InBr_3$ (0.0170 g, 0.048 mmol), cyclopropylmethylstannane **1** (92% purity) (0.4085 g, 1.05 mmol), and benzhydryl chloride **2b** (0.1977 g, 0.98 mmol) gave the crude product (99% **3b**:**4b** = 80:20). Purification by flash column chromatography [solvent; hexane] on silica gel afforded the product (0.192 g, 83% **3b**:**4b** = 83:17). Further purification was performed by gel permeation chromatography [solvent; chloroform]. IR: (neat) 3059, 3028, 2924, 1492, 1450, 752, 702 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.29-7.19 (m, 8H, *o*, *m*), 7.17-7.10 (m, 2H, *p*), 4.12 (t, *J* = 7.2 Hz, 1H, 1-H), 2.04 (d, *J* = 7.2 Hz, 2H, 2-H_2), 0.98 (s, 3H, Me at cyclopropyl ring), 0.08-0.00 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.7 (s, *i*), 128.3 (d), 127.9 (d), 125.9 (d, *p*), 49.4 (d, C-1), 45.2 (t, C-2), 23.2 (q, Me at cyclopropyl ring), 14.2 (s, $Ph_2CHCH_2\mathit{C}Me$), 13.2 (t, two methylene groups in cyclopropyl ring); MS: (EI, 70 eV) *m*/*z* 236 (M^+, 4), 180 (32), 168 (22), 167 ($M^+ - C_5H_9$, 100), 165 (24), 69 ($C_5H_9^+$, 5); HRMS: (EI, 70 eV) calcd for ($C_{18}H_{20}$) 236.1565 (M^+) found *m*/*z* 236.1561; Analysis: $C_{18}H_{20}$ (236.35) Calcd: C, 91.47; H, 8.53 Found: C, 91.45; H, 8.64.

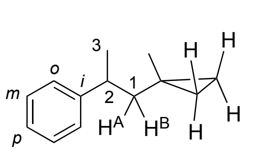
1-(4-chlorophenyl)-1-phenyl-2-(1-methylcyclopropyl)ethane (3c)



Purification was performed by flash column chromatography [solvent; hexane] on silica gel and gel permeation chromatography [solvent; chloroform]. IR: (neat) 3070, 2920, 1493, 1091, 1014, 818 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.28-7.13 (m, 9H, aroma), 4.10 (dd, *J* = 7.2, 7.2 Hz, 1H, 1-H), 2.05 (dd, *J* =

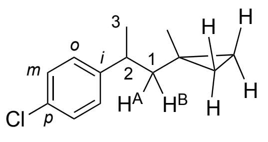
13.6, 7.2 Hz, 1H, 2-H^A), 1.98 (dd, J = 13.6, 7.2 Hz, 1H, 2-H^B), 0.98 (s, 3H, Me at cyclopropyl ring), 0.11-0.01 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.2 (s, *i*), 144.2 (s, *i'*), 131.6 (s, *p'*), 129.3 (d), 128.38 (d), 128.36 (d), 127.8 (d), 126.2 (d, *p*), 48.7 (d, C-1), 45.1 (t, C-2), 23.2 (q, Me at cyclopropyl ring), 14.1 (s, $CH(C_6H_5)CH_2\mathit{C}(CH_3)$), 13.3 (t, $CH(C_6H_5)CH_2C(CH_3)\mathit{C}^AH_2$) 13.1 (t, $CH(C_6H_5)CH_2C(CH_3)\mathit{C}^BH_2$); MS: (EI, 70 eV) *m/z* 272 (M^+ + 2, 2), 270 (M^+, 5), 235 (M^+ - Cl, 5), 216 (9), 214 (27), 203 (M^+ + 2 – C_5H_9, 32), 201 (M^+ – C_5H_9, 100), 166 (M^+ – C_5H_9 – Cl, 35), 165 (51), 69 ($C_5H_9^+$, 23); HRMS: (EI, 70 eV) calcd for ($C_{18}H_{19}Cl$) 270.1175 (M^+) found *m/z* 270.1178; Analysis: $C_{18}H_{19}Cl$ (270.80) Calcd: C, 79.84; H, 7.07; Cl, 13.09 Found: C, 79.60; H, 6.79; Cl, 13.07.

1-(1-methylcyclopropyl)-2-phenylpropane (3d)



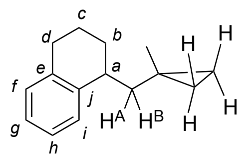
According to the typical procedure, $GaCl_3$ (0.0093 g, 0.053 mmol), cyclopropylmethylstannane **1** (91% purity) (0.3968 g, 1.01 mmol), and 1-chloro-1-phenylethane **2d** (0.1430 g, 1.02 mmol) gave the crude product (80% **3d**:**4d** = 74:26). Purification by flash column chromatography [solvent; hexane] on silica gel afforded the product (0.087 g, 49% **3d**:**4d** = 74:26). Further purification was performed by gel permeation chromatography [solvent; chloroform]. IR: (neat) 3066, 2970, 2908, 1604, 1454, 1381, 1014, 760, 698 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.27-7.23 (m, 2H, *m*), 7.22-7.13 (m, 3H, *o*, *p*), 2.93 (qdd, J = 7.2, 7.2, 7.2 Hz, 1H, 2-H), 1.68 (dd, J = 13.6, 7.2 Hz, 1H, 1-H^A), 1.34 (dd, J = 13.6, 7.2 Hz, 1H, 1-H^B), 1.26 (d, J = 7.2 Hz, 3H, 3-H_3), 1.01 (s, 3H, Me at cyclopropyl ring), 0.30-0.20 (m, 2H), 0.04 (ddd, J = 9.6, 4.8, 4.8 Hz, 1H), -0.03 (ddd, J = 9.6, 4.8, 4.8 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) 148.4 (s, *i*), 128.2 (d, *m*), 127.0 (d, *o*), 125.7 (d, *p*), 48.2 (t, C-1), 38.2 (d, C-2), 22.8 (q, Me at cyclopropyl ring), 22.1 (q, C-3), 14.0 (s, $C_6H_5CH(CH_3)CH_2\mathit{C}(CH_3)$), 13.4 (t, $C_6H_5CH(CH_3)CH_2C(CH_3)\mathit{C}^AH_2$), 12.7 (t, $C_6H_5CH(CH_3)CH_2C(CH_3)\mathit{C}^BH_2$); MS: (EI, 70 eV) *m/z* 174 (M^+, 3), 118 (29), 106 (22), 105 (M^+ – C_5H_9, 100), 69 ($C_5H_9^+$, 5); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{18}$) 174.1409 (M^+) found *m/z* 174.1411; Analysis: $C_{13}H_{18}$ (174.28) Calcd: C, 89.59; H, 10.41 Found: C, 89.32; H, 10.24.

1-(1-methylcyclopropyl)-2-(4-chlorophenyl)propane (3e)



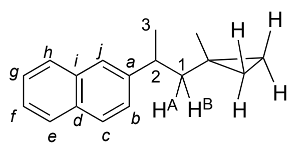
Purification was performed by flash column chromatography [solvent; hexane] on silica gel and gel permeation chromatography [solvent; chloroform]. IR: (neat) 2962, 2916, 1493, 1092, 1014, 825 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.23 (d, J = 8.8 Hz, 2H, *m*), 7.11 (d, J = 8.8 Hz, 2H, *o*), 2.91 (qdd, J = 7.2, 7.2, 7.2 Hz, 1H, 2-H), 1.60 (dd, J = 13.6, 7.2 Hz, 1H, 1-H^A), 1.35 (dd, J = 13.6, 7.2 Hz, 1H, 1-H^B), 1.23 (d, J = 7.2 Hz, 3H, 3-H_3), 0.99 (s, 3H, Me at cyclopropyl ring), 0.28-0.19 (m, 2H), 0.05 (ddd, J = 9.6, 4.8, 4.8 Hz, 1H), -0.05 (ddd, J = 9.6, 4.8, 4.8 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) 146.8 (s, *i*), 131.2 (s, *p*), 128.4 (d), 128.3 (d), 48.1 (t, C-1), 37.6 (d, C-2), 22.8 (q, Me at cyclopropyl ring), 22.2 (q, C-3), 13.9 (s, $CH(CH_3)CH_2\mathit{C}(CH_3)$), 13.3 (t, $CH(CH_3)CH_2C(CH_3)\mathit{C}^AH_2$), 12.9 (t, $CH(CH_3)CH_2C(CH_3)\mathit{C}^BH_2$); MS: (EI, 70 eV) *m/z* 210 (M^+ + 2, 1), 208 (M^+, 3), 173 (M^+ – Cl, 3), 155 (M^+ + 2 – C_4H_7, 2), 154 (18), 153 (M^+ – C_4H_7, 7), 152 (52), 141 (M^+ + 2 – C_5H_9, 32), 139 (M^+ – C_5H_9, 100), 103 (26), 69 ($C_5H_9^+$, 14), 55 ($C_4H_7^+$, 2); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{17}Cl$) 208.1019 (M^+) found *m/z* 208.1028; Analysis: $C_{13}H_{17}Cl$ (208.73) Calcd: C, 74.81; H, 8.21; Cl, 16.99 Found: C, 74.71; H, 8.02; Cl, 16.85.

1-(1-methylcyclopropyl)methyl-1,2,3,4-tetrahydronaphthalene (3f)



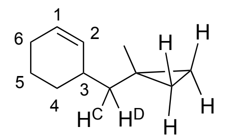
According to the typical procedure, $InBr_3$ (0.0175 g, 0.049 mmol), cyclopropylmethylstannane **1** (91% purity) (0.3990 g, 1.01 mmol), and 1-chloro-1,2,3,4-tetrahydronaphthalene **2f** (0.1622 g, 0.97 mmol) gave the crude product (90% **3f**:**4f** = 81:19). Purification by flash column chromatography [solvent; hexane] on silica gel afforded the product (0.153 g, 78% **3f**:**4f** = 82:18). Further purification was performed by gel permeation chromatography [solvent; chloroform]. IR: (neat) 3070, 2931, 2866, 1450, 1011, 764 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.17-7.00 (m, 4H, aroma), 2.99 (dddd, J = 9.6, 4.8. 4.8, 4.8 Hz, 1H, *a*), 2.76-2.72 (m, 2H, *d*), 2.05-1.98 (m, 1H, H^A), 1.94-1.82 (m, 2H, *b*), 1.82-1.65 (m, 2H, *c*), 1.15-1.09 (m, 1H, H^B), 1.13 (s, 3H, Me at cyclopropyl ring), 0.42-0.32 (m, 2H), 0.23-0.19 (m, 1H), 0.16-0.11 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) 141.9 (s, *j*), 136.9 (s, *e*), 129.0 (d), 128.7 (d), 125.4 (d), 125.3 (d), 46.2 (t, $CHCH_2C(CH_3)$), 35.8 (d, *a*), 29.8 (t, *d*), 26.9 (t, *b*), 22.7 (q, Me at cyclopropyl ring), 19.3 (t, *c*), 14.1 (t, $CHCH_2C(CH_3)C^AH_2$), 13.8 (s, $CHCH_2C(CH_3)$), 12.1 (t, $CHCH_2C(CH_3)C^BH_2$); MS: (EI, 70 eV) *m/z* 200 (M^+, 6), 144 (26), 131 ($M^+ - C_5H_9$, 100), 69 ($C_5H_9^+$, 3); HRMS: (EI, 70 eV) calcd for ($C_{15}H_{20}$) 200.1565 (M^+) found *m/z* 200.1563.

1-(1-methylcyclopropyl)-2-(2-naphthyl)propane (3g)



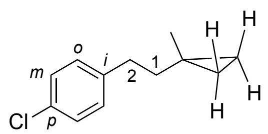
According to the typical procedure, $InBr_3$ (0.0172 g, 0.049 mmol), cyclopropylmethylstannane **1** (91% purity) (0.4025 g, 1.02 mmol), and 2-(1-chloroethyl)naphthalene **2g** (0.1906 g, 1.00 mmol) gave the crude product (99% **3g**:**4g** = 81:19). Purification by flash column chromatography [solvent; hexane] on silica gel afforded the product (0.171 g, 76% **3g**:**4g** = 80:20). ^1H NMR spectrum is shown below. Further purification was performed by gel permeation chromatography [solvent; chloroform]. IR: (neat) 3055, 2958, 2912, 2843, 1601, 1508, 1454, 1381, 1014, 818, 748 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.82-7.70 (m, 3H), 7.60 (s, 1H, *j*), 7.44-7.35 (m, 2H), 7.33 (d, J = 7.2 Hz, 1H), 3.10 (qdd, J = 8.0, 7.2, 7.2 Hz, 1H, 2-H), 1.77 (dd, J = 13.6, 7.2 Hz, 1H, H^A), 1.42 (dd, J = 13.6, 8.0 Hz, 1H, H^B), 1.33 (d, J = 7.2 Hz, 3H, 3-H_3), 1.03 (s, 3H, Me at cyclopropyl ring), 0.29 (ddd, J = 9.6, 4.8, 4.8 Hz, 1H), 0.23, (ddd, J = 9.6, 4.8, 4.8 Hz, 1H), 0.05--0.05 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.8 (s, *a*), 133.6 (s), 132.1 (s), 127.7 (d), 127.6 (d), 127.5 (d), 126.0 (d), 125.7 (d), 125.03 (d), 124.97 (d), 48.0 (t, C-1), 38.3 (d, C-2), 22.9 (q, Me at cyclopropyl ring), 22.2 (q, C-3), 14.1 (s, $CH(CH_3)CH_2C(CH_3)$), 13,5 (t, $CH(CH_3)CH_2C(CH_3)C^AH_2$), 12.9 (t, $CH(CH_3)CH_2C(CH_3)C^BH_2$); MS: (EI, 70 eV) *m/z* 224 (M^+, 29), 156 (35), 155 ($M^+ - C_5H_9$, 100), 69 ($C_5H_9^+$, 2); HRMS: (EI, 70 eV) calcd for ($C_{17}H_{20}$) 224.1565 (M^+) found *m/z* 224.1560; Analysis: $C_{17}H_{20}$ (224.34) Calcd: C, 91.01; H, 8.99 Found: C, 90.90; H, 8.89.

3-[(1-methylcyclopropyl)methyl]cyclohexene (3h)



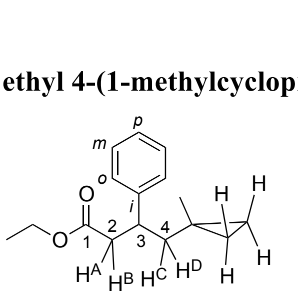
Purification was performed by flash column chromatography [solvent; hexane] on silica gel and gel permeation chromatography [solvent; chloroform]. IR: (neat) 3070, 3016, 2924, 2839, 1651 (C=C), 1450, 1011, 926, 671 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 5.71-5.60 (m, 2H, 1-H and 2-H), 2.36-2.25 (m, 1H, 3-H), 2.02-1.91 (m, 2H, 6-H_2), 1.90-1.81 (m, 1H, 4-H^A), 1.74-1.65 (m, 1H, 5-H^A), 1.59-1.46 (m, 1H, 5-H^B), 1.32 (dd, J = 13.6, 7.2 Hz, 1H, H^C), 1.28-1.19 (m, 1H, 4-H^B), 1.15 (dd, J = 13.6, 8.8 Hz, 1H, H^D), 1.04 (s, 3H, Me at cyclopropyl ring), 0.27-0.21 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) 132.5 (d, C-2), 126.4 (d, C-1), 45.9 (t, $C$$H_2$CMe), 33.6 (d, C-3), 29.6 (t, C-4), 25.4 (t, C-6), 22.6 (q, Me at cyclopropyl ring), 21.5 (t, C-5), 13.4 (s, $CHCH_2C(CH_3)$), 13.3 (t, $CHCH_2C(CH_3)C^AH_2$) 13.1 (t, $CHCH_2C(CH_3)C^BH_2$); MS: (EI, 70 eV) m/z 150 (M^+, 4), 135 (22), 95 ($M^+ - C_4H_7$, 22), 94 (47), 81 ($M^+ - C_5H_9$, 100), 79 (30), 69 ($C_5H_9^+$, 32), 55 ($C_4H_7^+$, 6); HRMS: (EI, 70 eV) calcd for ($C_{11}H_{18}$) 150.1409 (M^+) found m/z 150.1404; Analysis: $C_{11}H_{18}$ (150.26) Calcd: C, 87.93; H, 12.07 Found: C, 87.64; H, 11.97.

2-(1-methylcyclopropyl)-1-(4-chlorophenyl)ethane (3i)



According to the procedure, $InBr_3$ (0.5935 g, 0.744 mmol), cyclopropylmethylstannane **1** (91% purity) (0.5935 g, 1.50 mmol), and 4-chlorobenzyl chloride **2i** (0.1620 g, 1.01 mmol) gave the crude product (84% **3i**:**4i** = 83:17). Purification by flash column chromatography [solvent; hexane] on silica gel afforded the product (0.115 g, 59% **3i**:**4i** = 71:29). Further purification was performed by gel permeation chromatography [solvent; chloroform]. IR: (neat) 3070, 2935, 2862, 1493, 1092, 1014, 806 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.21 (d, J = 8.8 Hz, 2H, m), 7.08 (d, J = 8.8 Hz, 2H, o), 2.66-2.62 (m, 2H, 1-H_2), 1.50-1.46 (m, 2H, 2-H_2), 1.08 (s, 3H, Me at cyclopropyl ring), 0.28-0.21 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) 141.4 (s, i), 131.2 (s, p), 129.7 (d, o), 128.3 (d, m), 41.6 (t, C-2), 32.8 (t, C-1), 22.6 (q, Me at cyclopropyl ring), 15.4 (s, $CH_2CH_2C(CH_3)$), 13.1 (t, two methylene groups in cyclopropyl ring); MS: (EI, 70 eV) m/z 196 (M^+ + 2, 3), 194 (M^+, 9), 159 (M^+ – Cl, 4), 141 ($M^+ + 2 - C_4H_7$, 7), 140 (35), 139 ($M^+ - C_4H_7$, 19), 138 (100), 127 ($M^+ + 2 - C_5H_9$, 30), 125 ($M^+ - C_5H_9$, 78), 69 ($C_5H_9^+$, 21); HRMS: (EI, 70 eV) calcd for ($C_{12}H_{15}Cl$) 194.0862 (M^+) found m/z 194.0868; Analysis: $C_{12}H_{15}Cl$ (194.70) Calcd: C, 74.03; H, 7.77; Cl, 18.21 Found: C, 73.97; H, 7.73; Cl, 18.12

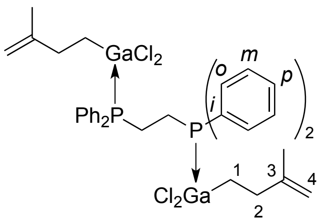
ethyl 4-(1-methylcyclopropyl)-3-phenylbutanoate (3j)



Purification was performed by flash column chromatography [solvent; hexane] on silica gel and gel permeation chromatography [solvent; chloroform]. IR: (neat) 1736 cm^{-1} (C=O); ^{1}H NMR: (400 MHz, $CDCl_3$) 7.29-7.24 (m, 2H, m), 7.22-7.15 (m, 3H, o, p), 4.00 (q, J = 7.2 Hz, 2H, CH_3CH_2O), 3.34 (dddd, J = 8.8, 8.0, 6.4, 6.4 Hz, 1H, 3-H), 2.74 (dd, J = 15.2, 6.4 Hz, 1H, H^A), 2.52 (dd, J = 15.2, 8.8 Hz, 1H, H^B), 1.62 (dd, J = 13.6, 8.0 Hz, 1H, H^C), 1.53 (dd, J = 13.6, 6.4 Hz, 1H, H^D), 1.11 (t, J = 7.2 Hz, 3H, CH_3CH_2O), 1.00 (s, 3H, Me at cyclopropyl ring), 0.26-0.17 (m, 2H), 0.02 (ddd, J = 9.6, 4.8, 4.8 Hz, 1H),

-0.08 (ddd, J = 9.6, 4.8, 4.8 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.4 (s, C-1), 144.6 (s, *i*), 128.2 (d, *m*), 127.5 (d, *o*), 126.3 (d, *p*), 60.1 (t, CH_3CH_2O), 46.1 (t, C-4), 41.4 (t, C-2), 40.5 (d, C-3), 22.7 (q, Me at cyclopropyl ring), 14.1 (q, CH_3CH_2O), 13.7 (s, $CH(C_6H_5)CH_2C(CH_3)$), 13.04 (t, $CH(C_6H_5)CH_2C(CH_3)C^AH_2$), 13.00 (t, $CH(C_6H_5)CH_2C(CH_3)C^BH_2$); MS: (EI, 70 eV) *m/z* 246 (M^+, 6), 217 ($M^+ - C_2H_5$, 26), 177 ($M^+ - C_5H_9$, 29), 176 (21), 159 ($M^+ - C_2H_5OCOCH_2$, 29), 158 (61), 143 (41), 135 (100), 105 (42), 104 (39), 97 (21), 91 (31), 69 ($C_5H_9^+$, 14); HRMS: (EI, 70 eV) calcd for ($C_{16}H_{22}O_2$) 246.1620 (M^+) found *m/z* 246.1624;

butenylic gallium dichloride–dppe complex (7)



Procedure is shown in p. S6. ^{1}H NMR: (400 MHz, CD_2Cl_2) 7.66-7.49 (m, 20H, Ar), 4.69-4.53 (m, 4H, 4-H_2 x 2), 2.93-2.83 (m, 4H, PCH_2CH_2P), 2.10 (t, J = 8.0 Hz, 4H, 2-H_2 x 2), 1.62 (s, 6H, 3-Me x 2), 1.02 (t, J = 8.0 Hz, 4H, 1-H_2 x 2); ^{13}C NMR: (100 MHz, CD_2Cl_2) 147.8 (C-3), 132.7 (*o*, d, $^2J_{P\text{-}C}$ = 11.5 Hz), 132.2 (*p*), 129.4 (*m*, d, $^3J_{P\text{-}C}$ = 10.7 Hz), 123.7 (*i*, d, $^1J_{P\text{-}C}$ = 41.8 Hz), 108.2 (C-4), 32.3 (C-2), 21.5 (3-Me), 18.6 (PCH_2CH_2P, d, $^1J_{P\text{-}C}$ = 24.6 Hz), 15.5 (C-1)

2-5. References

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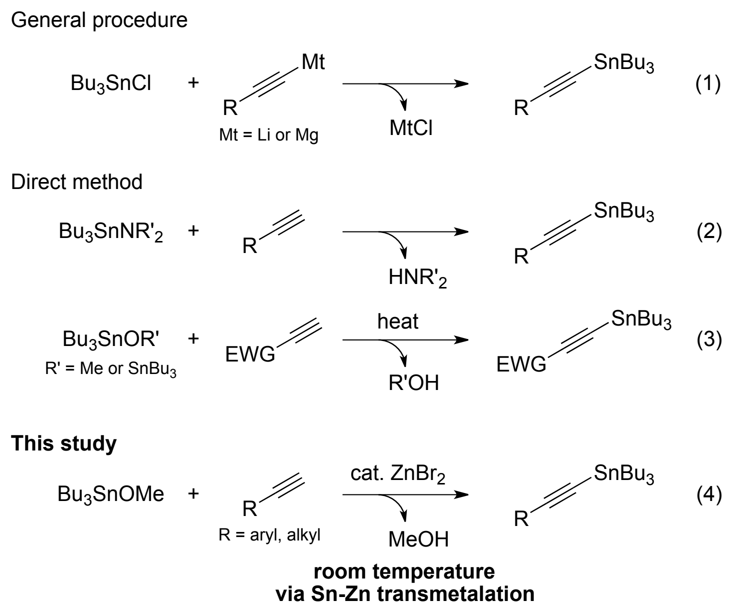
Chapter 3

Direct Synthesis of Alkynylstannanes: $ZnBr_2$ Catalyst for the Reaction of Tributyltin Methoxide and Terminal Alkynes

3-1. Introduction

A carbon–carbon triple bond is a highly valuable and versatile functional group in many natural products, bioactive compounds,[1] and organic materials.[2] Alkynylstannanes, which have high stability, reactivity, and functional group tolerance, are important reagents for introducing an alkynyl moiety into organic molecules.[3] In particular, the Migita–Kosugi–Stille coupling using alkynylstannanes is widely used for the construction of C(sp)–C(sp^2) bonds in the synthesis of aryl alkynes or conjugated enynes.[4] Transmetalation between an organotin halide and an alkynyllithium or alkynylmagnesium compound is the most common route to alkynylstannanes [Eq. (1), Scheme 1].[5] However, the method using those alkynylmetals has some drawbacks such as poor functional group tolerance and the production of an equimolar amount of metal salts. The direct reaction of a tin amide with a terminal alkyne is also employed for the synthesis of alkynylstannanes, but its substrate scope is narrow because of the strong basicity of a tin amide and the production of basic amine by-products [Eq. (2), Scheme 1].[6] In contrast, the direct condensation reaction between a tin alkoxide and a terminal alkyne is regarded as a promising process that is mild because no strong base is required and an alcohol is the only by-product. Only

Scheme 1. Synthetic methods for alkynylstannanes.

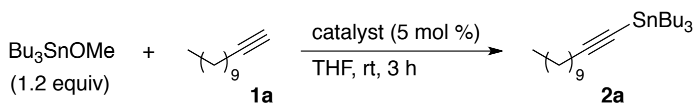


alkynes bearing electron-withdrawing groups (EWGs), however, have been reported to react under reaction conditions requiring heat thus far [Eq. (3), Scheme 1].[7] Activation of alkynes by Lewis acids, instead of EWGs, was expected to achieve this direct coupling under milder reaction conditions as a way to develop a more versatile synthetic method of alkynylstannanes with various types of functional groups. We report herein our serendipitous discovery that a catalytic amount of $ZnBr_2$ effectively promoted a coupling reaction between Bu_3SnOMe and terminal alkynes at room temperature; the $ZnBr_2$ was transmetalated with Bu_3SnOMe rather than acting as a Lewis acid [Eq. (4), Scheme 1]. This reaction system is applicable to various types of aliphatic and aromatic terminal alkynes. In addition, the mild reaction conditions, in which methanol is the only waste, enables the one-pot synthesis of aryl alkynes by the Migita–Kosugi–Stille coupling.

3-2. Results and Discussion

Initially, the addition of weak Lewis acids, which were expected to characteristically interact with alkynes,[8] was examined in the reaction of Bu_3SnOMe with 1-dodecyne (**1a**), as partially summarized in Table 1. Only a trace amount of the product **2a** was formed in the absence of a catalyst even when heated (Table 1, entry 1). In the presence of the transition metal catalysts $PdCl_2$ and CuBr, **2a** was obtained in modest yields (Table 1, entries 2 and 3). While soft Lewis acids like $BiBr_3$ and $InBr_3$ did not improve the yields (Table 1, entries 4 and 5),[9] $Zn(OTf)_2$ produced a high product yield (Table 1, entry 6).[10] In the search for more efficient catalysts, we were delighted to find that inexpensive $ZnBr_2$ was the most practical catalyst employed (Table 1, entries 7 and 8). At ambient temperature, 5 mol % of $ZnBr_2$ afforded the desired alkynylstannane **2a** in 68% yield.

Table 1. Effect of catalysts.[a]

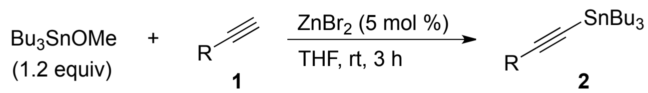


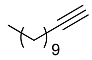
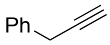
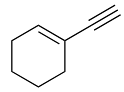
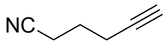
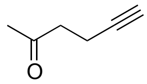
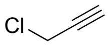
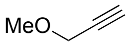
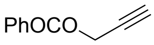
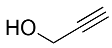
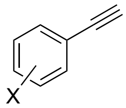
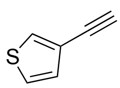
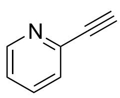
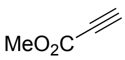
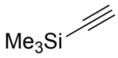
entry	catalyst	yield/ %[b]
1[c]	none	<5
2	$PdCl_2$	14
3	CuBr	40
4	$BiBr_3$	<5
5	$InBr_3$	25
6	$Zn(OTf)_2$	68
7	$ZnCl_2$	42
8	$ZnBr_2$	68

[a] Reaction conditions: Bu_3SnOMe (1.2 mmol), **1a** (1 mmol), catalyst (0.05 mmol), THF (1 mL), RT, 3 h. [b] Determined by ^{1}H NMR. [c] Reaction was performed at 60 ºC.

Under the optimized reaction conditions, reactions with various terminal alkynes were carried out. As summarized in Table 2, a wide range of functional groups were compatible with the reaction

Table 2. Catalytic synthesis of alkynylstannanes **2** from Bu_3SnOMe and terminal alkynes **1**.[a]



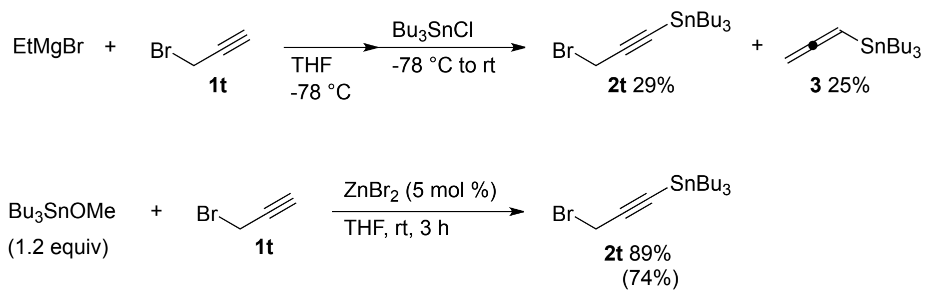
entry	alkyne **1**			product **2**	yield/ %[b]
1			**1a**	**2a**	68 (61)
2			**1b**	**2b**	78 (70, 97[c])
3[d]			**1c**	**2c**	72 (75)
4			**1d**	**2d**	73 (77)
5			**1e**	**2e**	68 (39, 79[c])
6			**1f**	**2f**	75 (62)
7			**1g**	**2g**	56 (46, 92[c])
8			**1h**	**2h**	76 (47)
9			**1i**	**2i**	n.d.
10		X = H	**1j**	**2j**	75 (77)
11		4-MeO	**1k**	**2k**	79 (80)
12[d]		4-*t*Bu	**1l**	**2l**	78 (72)
13		3-Me	**1m**	**2m**	80 (69, 94[c])
14		3-Cl	**1n**	**2n**	84 (61, 84[c])
15		2-F	**1o**	**2o**	88 (74)
16			**1p**	**2p**	72 (74, 92[c])
17			**1q**	**2q**	80 (79)
18[d]			**1r**	**2r**	84 (58, 77[c])
19[d,e]			**1s**	**2s**	65 (49)

[a] Reaction conditions: Bu_3SnOMe (1.2 mmol), **1** (1 mmol), $ZnBr_2$ (0.05 mmol), THF (1 mL), rt, 3 h. [b] Yields of crude products determined by ^{1}H NMR. Values in parentheses are isolated yields. [c] Purity of the products. [d] MeCN was used instead of THF. [e] Bu_3SnOMe (1 mmol) and **1s** (2 mmol) were used.

conditions.[11] Aliphatic terminal alkynes, including base-labile ones bearing a cyano or carbonyl group, afforded the corresponding products **2a**–**2e** in high yields (Table 2, entries 1–5). The products **2f**, **2g**, and **2h** were also obtained effectively from propargyl chloride (**1f**), the propargyl ether **1g**, and propargyl ester **1h**, respectively (Table 2, entries 6–8). Unfortunately, the reaction of propargyl alcohol (**1i**) was suppressed, probably because of the hydroxy proton (Table 2, entry 9). This method was also applicable to aromatic alkynes bearing an electron-donating or electron-withdrawing group (Table 2, entries 10–15). Heteroaromatic compounds **1p** and **1q** gave high yields, as well (Table 2, entries 16 and 17). In addition, alkynes directly connected by ester and silyl moieties are suitable for coupling to produce the corresponding alkynylstannanes **2r** and **2s**, respectively (Table 2, entries 18 and 19).

The synthesis of tributyl(3-bromopropynyl)stannane (**2t**) was examined, because the general reaction using ethyl magnesium bromide, propargyl bromide (**1t**), and Bu_3SnCl resulted in a mixture of **2t** (29%) and **3** (25%) even under controlled reaction conditions (Scheme 2).[12] The generation of 3-bromo-1-propynylmagnesium bromide and propargyl magnesium bromide in the first step led to the formation of the mixture.[13] However, our method provided the desired reaction and produced **2t** in 89% yield with no side reactions. One possible reason might have been that the catalytic amount of $ZnBr_2$ was sufficient and no base stronger than Bu_3SnOMe appeared in the system.

Scheme 2. Synthesis of tributyl(3-bromopropynyl)stannane (**2t**). Yields were determined by ^1H NMR. The value in parenthesis is the isolated yield.



To gain insight into the reaction mechanism, a mixture of Bu_3SnOMe and $ZnBr_2$ was monitored by ^{13}C NMR spectroscopy (Figure 1). When $ZnBr_2$ and 2 equivalents of Bu_3SnOMe were mixed in THF-d_8 at room temperature, the generation of Bu_3SnBr (**5**; $\delta(^{13}C)$ = 30.0, 27.6, 18.3, and 13.8 ppm) and the complete consumption of the starting Bu_3SnOMe were observed (Figure 1b).[14] These results indicate that transmetalation between Bu_3SnOMe and $ZnBr_2$ occurred to give $Zn(OMe)_2$ (**4**; δ = 56.5 ppm ; Figure 1b).[15] The addition of phenylacetylene (**1j**) to the mixture furnished the corresponding alkynylstannane **2j** (Figure 1c). In contrast, when $Zn(OTf)_2$ instead of $ZnBr_2$ was treated with Bu_3SnOMe, no transmetalation was observed (see the Experimental Section). Apparently, an alternative mechanism should be considered.

On the basis of the NMR study, a plausible reaction mechanism is shown in Scheme 3. First, the transmetalation between Bu_3SnOMe and $ZnBr_2$ gives the zinc methoxide **6**, which should be $Zn(OMe)_2$

because Bu_3SnOMe is in large excess of $ZnBr_2$ in the reaction mixture.[16] Next, an abstraction of the terminal proton from alkyne **1** by **6** provides the alkynylzinc species **7**.[17] Finally, the reaction of **7** with Bu_3SnOMe affords the alkynylstannane **2** with the regeneration of **6**. The mechanism using a $Zn(OTf)_2$ catalyst may be the usual one (Table 1, entry 6), whereby the reaction would be started from the activation of the alkyne **1** by coordination to $Zn(OTf)_2$.[18]

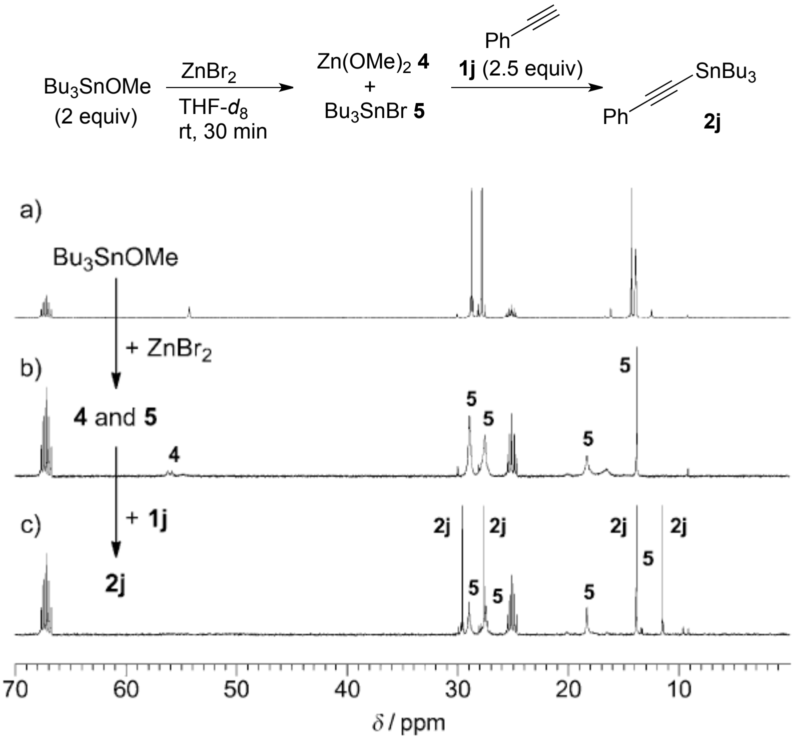
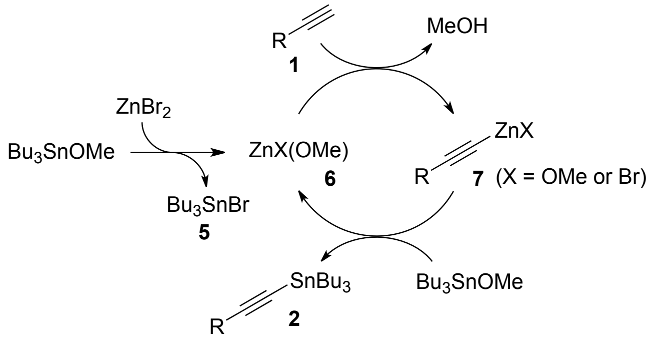


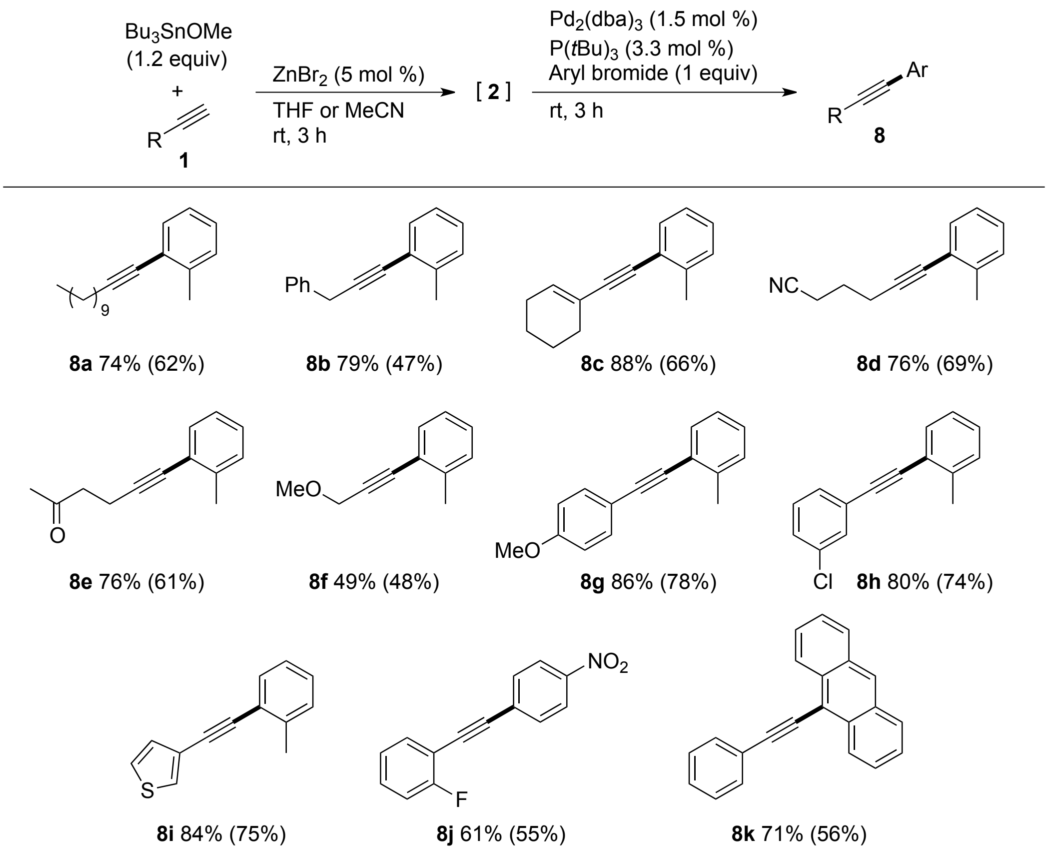
Figure 1. ^{13}C NMR spectra in THF-d_8: a) Bu_3SnOMe. b) The mixture of $ZnBr_2$ and 2 equivalents of Bu_3SnOMe. c) Just after the addition of alkyne **1j** (2.5 equiv) to the mixture (b). See the Experimental Section for the experimental details.

Scheme 3. Plausible reaction mechanism.



This catalytic method allowed the one-pot synthesis of various functionalized aryl alkynes by the Migita–Kosugi– Stille coupling (Scheme 4). The $ZnBr_2$-catalyzed formation of alkynylstannanes **2** was directly followed by palladium-catalyzed coupling with aryl bromides to furnish the corresponding aryl alkynes **8** in good to high yields.[19] In most cases, the yields of coupling products **8** paralleled those of alkynylstannanes **2**, as shown in Table 2. These results indicate that in situ generated alkynylstannanes were fully converted into coupling products without suppression by a zinc catalyst or the by-products MeOH and Bu_3SnBr.

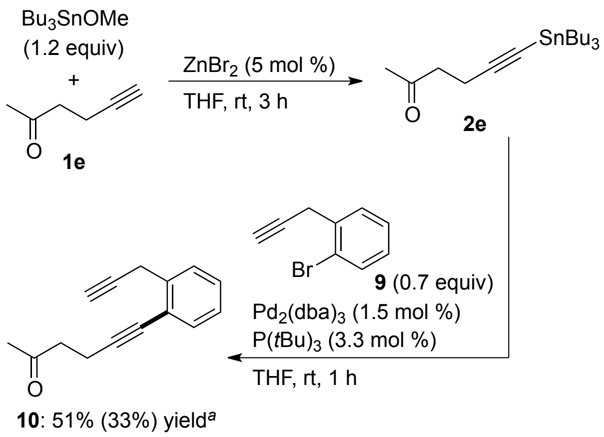
Table 3. One-pot synthesis of aryl alkynes via Migita-Kosugi-Stille coupling.[a]



[a] See the Supporting Information for experimental details. Yields were determined by ^{1}H NMR. Values in parentheses are isolated yields.

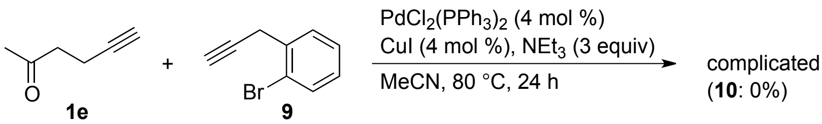
To further expand the utility of this reaction, the synthesis of a diyne compound was investigated.[20] After the $ZnBr_2$-catalyzed reaction of Bu_3SnOMe with **1e**, the resulting **2e** (unpurified) was subjected to the coupling with the aryl bromide **9** bearing a terminal alkyne moiety to give the corresponding product **10** in 51% yield (Scheme 5). On the contrary, when **1e** was treated with **9** under the standard Sonogashira conditions, no product **10** was obtained (Scheme 6).[21,22] The zinc-catalyzed synthesis of alkynylstannanes/Migita–Kosugi–Stille coupling sequence is expected to be a helpful tool in the synthesis of more elaborate molecules.

Scheme 4. Synthesis of diyne compound **10**.



[a] Yield was determined by ^{1}H NMR. The value in parenthesis is the isolated yield.

Scheme 5. Sonogashira reaction of **1e** with **9**.



3-3. Conclusion

In summary, the $ZnBr_2$-catalyzed synthesis of alkynylstannanes with a wide range of functional group compatibility was achieved. As far as can be ascertained, this is the first example of the versatile synthesis of alkynylstannanes from Bu_3SnOMe and terminal alkynes under very mild reaction conditions. The transmetalation between Bu_3SnOMe and $ZnBr_2$ to generate $Zn(OMe)_2$ is proposed as a key process to complete the catalytic cycle. Moreover, aryl alkynes were synthesized using a one-pot protocol that included the Migita–Kosugi–Stille coupling.

3-4. Experimental Section

General. New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance techniques, COSY, HMQC, HMBC, IR, MS, HRMS, and elemental analysis. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS as an internal standard. ^{119}Sn (150 MHz) spectra were obtained with Me_4Sn as an external standard. IR spectra were recorded as thin films or solids in KBr pellets. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (MERK C60 or Fuji Silysia FL100DX). Bulb-to-Bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. Yields were determined by ^{1}H NMR using internal standard.

Materials. Dehydrated acetonitrile, tetrahydrofuran, dichloromethane, and ethanol were purchased and used as obtained. Catalysts examined in Table 1 were also purchased from commercial sources. Tributyltin methoxide was purchased from commercial sources and used after distillation. Alkynes **1a**–**1d** and **1f**–**1t** were purchased from commercial sources. Alkyne **1e** was prepared by known method and this compound was reported.[23] Aryl bromide **9** was prepared by known method and this compound was reported.[24] All other reagents were commercially available.

Typical procedure for the reaction of tributyltin methoxide with alkyne 1a (Table 1) To a solution of catalyst (0.05 mmol) and 1-dodecyne (1 mmol) in THF (1 mL), Bu_3SnOMe (1.2 mmol) was added. The mixture was stirred for 3 h at room temperature, and then quenched by H_2O (10 mL). The mixture was extracted with diethyl ether (3 x 10 mL). The collected organic layers were dried ($MgSO_4$), and evaporation of volatiles gave the crude product which was analyzed by ^1H NMR.

Typical procedure for the reaction of tributyltin methoxide with alkynes 1 (Table 2): To a solution of $ZnBr_2$ in THF (0.05 M, 1 mL) and alkyne **1** (1 mmol) was added Bu_3SnOMe (1.2 mmol). The mixture was stirred for 3 h at room temperature, and then quenched by H_2O (10 mL). The mixture was extracted with diethyl ether (3 x 10 mL). The collected organic layers were dried ($MgSO_4$), and evaporation of volatiles gave the crude product, which was analyzed by ^1H NMR. The crude product was diluted with AcOEt (30 mL) and washed by NH_4F (aq) (10%, 20 mL). The obtained white precipitate was filtered off, and the filtrate was dried ($MgSO_4$). Evaporation of volatiles gave the product.

Experimental procedure for Scheme 2: To a solution of propargyl bromide (0.237 g, 2.00 mmol) in THF (2 mL), EtMgBr in THF (1M, 2 mL) was added dropwised at -78 ºC. After the mixture was stirred for 30 min at -78 ºC, Bu_3SnCl (0.651 g, 2.00 mmol) was added, then the mixture was warmed to room temperature. The mixture was stirred for 3 h and then quenched by H_2O (10 mL). The mixture was extracted with diethyl ether (3 x 10 mL). The collected organic layers were dried ($MgSO_4$), and evaporation of volatiles gave the crude product, which was analyzed by ^1H NMR.

Experimental procedure for NMR study of transmetalation between Bu_3SnOMe and $ZnBr_2$ (Figure 1): The mixture of Bu_3SnOMe (0.095 g, 0.30 mmol) and $ZnBr_2$ (0.032 g, 0.14 mmol) was prepared in THF-d_8 (0.5 mL) in a nitrogen-filled glove box. After mixing at room temperature for 30 min, the mixture was transferred into NMR tube. The resulting ^{13}C NMR spectrum is shown in Figure 1b. ^{119}Sn NMR spectrum is shown below (Figure S2a). Phenylacetylene (0.042 g, 0.41 mmol) was added to the mixture. The resulting ^{13}C NMR spectrum is also shown in Figure 1c.

Experimental procedure for NMR study of transmetalation between Bu_3SnOMe and $Zn(OTf)_2$: When Bu_3SnOMe (0.097 g, 0.30 mmol) was mixed with $Zn(OTf)_2$ (0.052 g, 0.14 mmol) in THF-d_8 (0.5 mL), the signals of Bu_3SnOMe were little changed as shown below (Figure S1a and b). ^{119}Sn NMR spectrum is also shown below (Figure S2b). These results indicate that the transmetalation between Bu_3SnOMe and $Zn(OTf)_2$ did not occur. The addition of phenylacetylene **1j** (0.039 g, 0.38 mmol) to the mixture (b) afforded the corresponding alkynylstannane **2j** (Figure S1c).

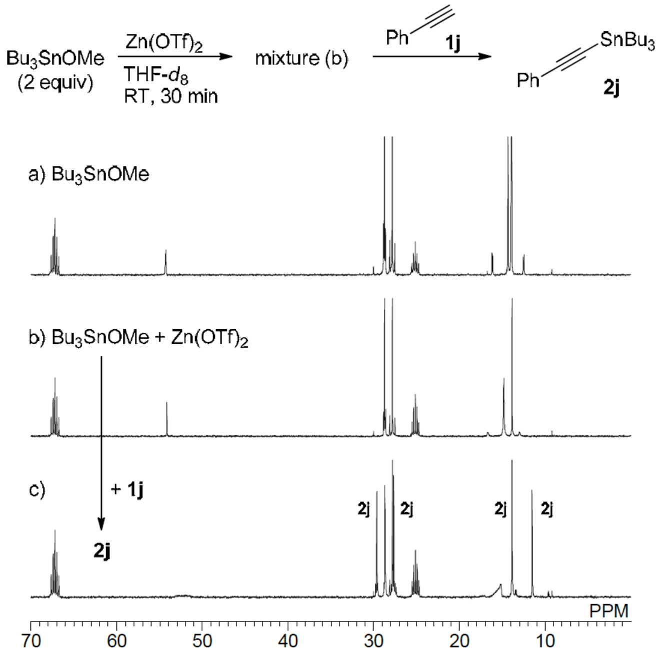


Figure S1. ^{13}C NMR spectra in THF-d_8: a) Bu_3SnOMe. b) The reaction mixture of Bu_3SnOMe (2 equiv) and $Zn(OTf)_2$. c) Just after the addition of alkyne **1j** to the mixture (b).

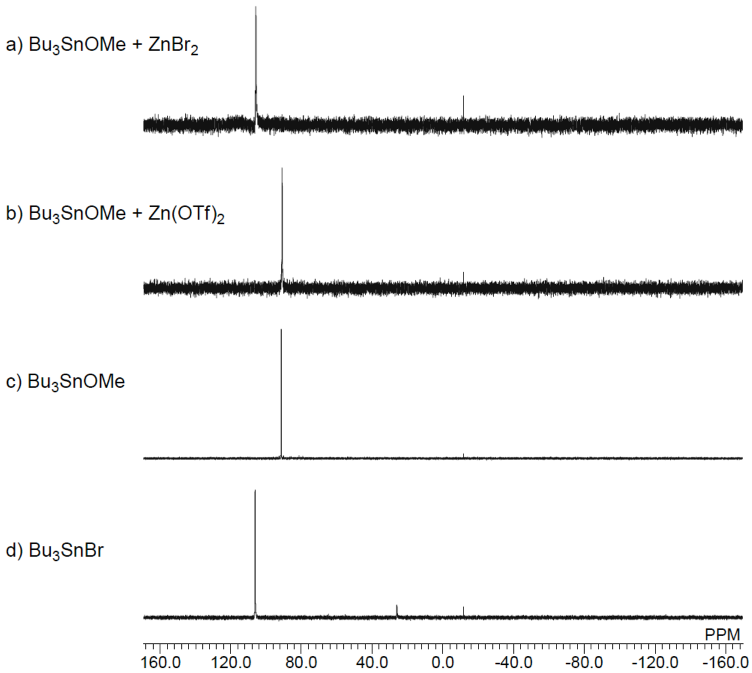


Figure S2. ^{119}Sn NMR spectra in THF-d_8: a) The mixture of $ZnBr_2$ and Bu_3SnOMe (2 equiv). b) The mixture of $Zn(OTf)_2$ and Bu_3SnOMe (2 equiv). c) Bu_3SnOMe. d) Bu_3SnBr.

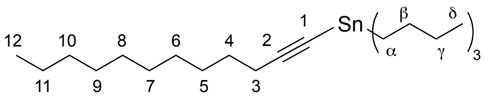
Typical procedure for one-pot synthesis of aryl alkynes (Table 3): To a solution of $ZnBr_2$ in THF (0.05 M, 1 mL) and alkyne (1 mmol) was added Bu_3SnOMe (1.2 mmol). After the mixture was stirred for 3 h at room temperature, *o*-bromotoluene (1 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.015 mmol) was added sequentially. The mixture was stirred for 3 h at room temperature, and then quenched by NH_4F (aq) (10%, 10 mL). The mixture was extracted with diethyl ether (3 x 10 mL). The collected organic layers were dried ($MgSO_4$), and evaporation of volatiles gave a crude product, which was analyzed by ^{1}H NMR. Purification by flash column chromatography gave the product.

Experimental procedure for Scheme 4: To a solution of $ZnBr_2$ in THF (0.05 M, 1 mL) and 5-hexyn-2-one (80% purity) (0.127 g, 1.05 mmol) was added Bu_3SnOMe (0.391 g, 1.22 mmol). The mixture was stirred for 3 h at room temperature, and then quenched by H_2O (10 mL). The mixture was extracted with diethyl ether (3 x 10 mL). The collected organic layers were dried ($MgSO_4$). The solvent was evaporated to give a crude product, which was used in the Migita-Kosugi-Stille coupling without purification. To a solution of the crude 6-(tributyltin)-5-hexyn-2-one in THF (1 mL), was added 1-bromo-2-(prop-2-ynyl)benzene (0.136 g, 0.70 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.3 mL), and $Pd_2(dba)_3$ (0.0139 g, 0.015 mmol) sequentially. The mixture was stirred for 1 h at room temperature, and then quenched by NH_4F (aq) (10 mL). The mixture was extracted with diethyl ether (3 x 10 mL). The collected organic layers were dried ($MgSO_4$). The evaporation of the ether solution gave the crude product, which was analyzed by ^{1}H NMR. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 80/20, column length; 11 cm] gave the product as a pale yellow oil (0.049 g, 33%).

Experimental procedure for Scheme 5: To a solution of 1-bromo-2-(prop-2-ynyl)-benzene (0.101 g, 0.52 mmol), 5-hexyne-2-one (80% purity) (0.064 g, 0.53 mmol), and NEt_3 (0.151 g, 1.49 mmol) in MeCN (3 mL), $PdCl_2(PPh_3)_2$ (0.014 g, 0.02 mmol) and CuI (0.0036 g, 0.019 mmol) was added. The mixture was heated to 80 ºC and stirred for 24 h. The solvent was evaporated, and the residue was analyzed by ^{1}H NMR.

Product data

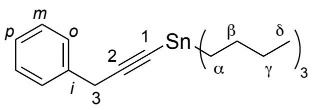
Tributyl(1-dodecynyl)stannane (2a)



According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 1-dodecyne (0.160 g, 0.96 mmol), and Bu_3SnOMe (0.378 g, 1.18 mmol) gave the product as a colorless oil (0.264 g, 61% yield). IR: (neat) 2900, 2148 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 2.24 (t, 2H, J = 14.0 Hz, 3-H_2), 1.66-1.19 (m, 28H), 1.13-0.83 (m, 18H); ^{13}C NMR: (100 MHz, $CDCl_3$) 112.0 (s, C-2, d by $^2J_{Sn\text{-}C}$ = 69.6 Hz), 81.2 (s, C-1, d by $^1J_{119Sn\text{-}C}$ = 372.5 Hz, $^1J_{117Sn\text{-}C}$ = 357.2 Hz), 31.9 (t), 29.6, 29.3, 29.2, 29.1, 28.9, 28.8, 27.0 (t, C-γ, d by $^3J_{Sn\text{-}C}$ = 59.0 Hz), 22.7 (t), 20.1 (t, C-3), 14.1, 13.6 (C-δ), 10.9 (t, C-α, d by $^1J_{119Sn\text{-}C}$ = 384.2 Hz, $^1J_{117Sn\text{-}C}$ = 365.4 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –70.0; MS: (EI, 70 eV) *m/z*

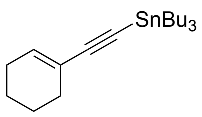
456 (M^+, 0.46), 400 (20), 399 (M^+ – Bu, 100), 398 (39), 397 (73), 396 (30), 395 (40); HRMS: (EI, 70 eV) calcd for ($C_{24}H_{48}Sn$) 456.2778 (M^+) found *m/z* 456.2781

Tributyl(3-phenyl-1-propynyl)stannane (2b)



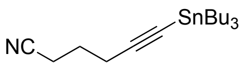
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 3-phenyl-1-propyne (0.119 g, 1.02 mmol), and Bu_3SnOMe (0.394 g, 1.22 mmol) gave the product as a yellow oil (0.301 g, 70% yield, 97% purity (A small portion was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard in order to determine the purity.)). IR: (neat) 2900, 2152 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.37 (d, 2H, J = 8.0 Hz, *o*-H_2), 7.30 (t, 2H, *m*-H_2), 7.25-7.19 (m, 1H, *p*-H), 3.69 (s, 2H, 3-H_2 with d by $^4J_{Sn\text{-}C}$ = 10.4 Hz), 1.67-1.46 (m, 6H, β-H_2 x 3), 1.39-1.29 (m, 6H, γ-H_2 x 3), 1.07-0.97 (m, 6H, α-H_2 x 3), 0.90 (t, 9H, J = 8.0 Hz, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 137.1 (s, C-*i*), 128.2 (d, C-*o*), 127.8 (d, C-*m*), 126.3 (d, C-*p*), 108.3 (s, C-2, d by $^2J_{Sn\text{-}C}$ = 64.7 Hz), 84.5 (s, C-1), 28.9 (t, C-β, d by $^2J_{Sn\text{-}C}$ = 23.7 Hz), 26.9 (t, C-γ, d by $^3J_{Sn\text{-}C}$ = 60.6 Hz), 26.4 (s, C-3), 13.6 (q, C-δ), 11.0 (t, C-α, d by $^1J_{119Sn\text{-}C}$ = 382.5 Hz, $^1J_{117Sn\text{-}C}$ = 366.2 Hz); Sn NMR: (150 MHz, $CDCl_3$) –68.6; MS: (EI, 70 eV) *m/z* 406 (M^+, 0.4), 349 (M^+ – Bu, 100), 348 (37), 347 (75), 346 (29), 345 (42), 235 (30), 233 (22); HRMS: (EI, 70 eV) calcd for ($C_{21}H_{34}Sn$) 406.1682 (M^+) found *m/z* 406.1663

Tributyl(1-cyclohexen-1-ylethynyl)stannane (2c)



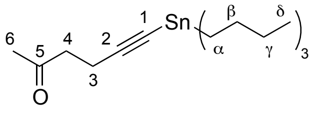
According to the typical procedure, $ZnBr_2$ in MeCN (0.05 M, 1 mL), 2-ethynyl-1-cyclohexene (0.106 g, 1.00 mmol), and Bu_3SnOMe (0.383 g, 1.19 mmol) gave the product as a yellow oil (0.298 g, 75% yield). The analytical data for this compound were in excellent agreement with the reported data.[3b]

Tributyl(5-cyanopent-1-ynyl)stannane (2d)



According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 5-cyano-1-pentyne (0.091 g, 0.98 mmol), and Bu_3SnOMe (0.402 g, 1.25 mmol) gave the product as a colorless oil (0.307 g, 77% yield). The analytical data for this compound were in excellent agreement with the reported data.[3b]

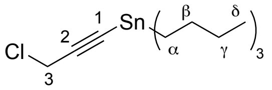
Tributyl(5-oxo-1-hexynyl)stannane (2e)



According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 5-hexyn-2-one (0.092 g, 0.96 mmol), and Bu_3SnOMe (0.389 g, 1.21 mmol) gave the product as a colorless oil (0.145 g, 39% yield, 79% purity (A small portion was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard in order to determine the purity.)). IR: (neat) 2900, 2152 (C≡C), 1720 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 2.67 (t, 2H, J = 8.0 Hz, 4-H_2), 2.50 (t, 2H, J = 8.0 Hz, 3-H_2), 2.17 (s, 3H, 6-H_3), 1.66-1.43 (m, 6H, β-H_2 x 3), 1.39-1.23 (m, 6H, γ-H_2 x 3), 1.04-0.93 (m, 6H, α-H_2 x 3), 0.90 (t, 9H, J = 7.5 Hz, δ-H_3 x 3); ^{13}C

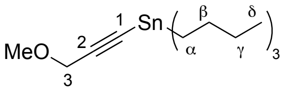
NMR: (100 MHz, $CDCl_3$) 207.0 (s, C-5), 109.2 (s, C-2), 84.5 (s, C-1), 43.1 (t, C-4), 29.9 (q, C-6), 28.8 (t, C-β, d by $^2J_{Sn\text{-}C}$ = 22.9 Hz), 27.0 (t, C-γ, d by $^3J_{Sn\text{-}C}$ = 60.6 Hz), 14.9 (t, C-3), 13.6 (q, C-δ), 10.9 (t, C-α, d by $^1J119_{Sn\text{-}C}$ = 384.2 Hz, $^1J_{117Sn\text{-}C}$ = 367.0 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –69.5; MS: (CI, 200 eV) *m/z* 387 (M + 1, 57), 386 (22), 385 (42), 383 (82), 291 (20), 97 (100); HRMS: (CI, 200 eV) calcd for ($C_{18}H_{35}OSn$) 387.1710 (M^+ + 1) found *m/z* 387.1707

Tributyl(3-chloro-1-propynyl)stannane (2f)



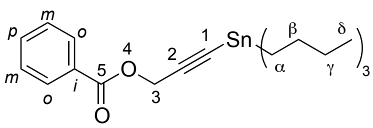
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), propargyl chloride (0.081 g, 1.09 mmol), and Bu_3SnOMe (0.381 g, 1.19 mmol) gave the product as a colorless oil (0.245 g, 62% yield). IR (neat) : 2900, 2156 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.16 (s, 2H, 3-H_2 with d by $^4J_{Sn\text{-}H}$ = 9.6 Hz), 1.67-1.47 (m, 6H, β-H_2 x 3), 1.38-1.29 (m, 6H, γ-H_2 x 3), 1.10-0.97 (m, 6H, α-H_2 x 3), 0.96-0.87 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 104.0 (s, C-2, d by $^2J_{Sn\text{-}C}$ = 53.3 Hz), 91.2 (s, C-1), 31.3 (t, C-3, d by $^3J_{Sn\text{-}C}$ = 7.4 Hz), 28.8 (t, C-β, d by $^2J_{Sn\text{-}C}$ = 23.8 Hz), 26.9 (t, C-γ, d by $^3J_{Sn\text{-}C}$ = 59.8 Hz), 13.6 (q, C-δ), 11.1 (t, C-α, d by $^1J_{119Sn\text{-}C}$ = 382.4 Hz, $^1J_{117Sn\text{-}C}$ = 365.4 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –64.9; MS: (EI, 70 eV) *m/z* 307 (M^+ – Bu, 100), 306 (35), 304 (22), 303 (35), 251 (M^+ – Bu_2 + 1, 19), 249 (M^+ – Bu_2 – 1, 14), 193 (29), 191 (22), 177 (22), 159 (27), 157 (29), 155 (57), 153 (40), 67 (71), 41 (20); HRMS: (EI, 70 eV) calcd for ($C_{11}H_{20}ClSn$) 307.0275 (M^+ – Bu) found *m/z* 307.0273

Tributyl(3-methoxy-1-propynyl)stannane (2g)



According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), methyl-propargyl-ether (0.089 g, 1.27 mmol), and Bu_3SnOMe (0.391 g, 1.22 mmol) gave the product as a colorless oil (0.229 g, 46% yield, 92% purity (A small portion was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard in order to determine the purity.)). IR: (neat) 2900, 2148 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.11 (s, 2H, 3-H_2 with d by $^4J_{Sn\text{-}H}$ =8.8 Hz), 3.39 (s, 3H, OMe), 1.66-1.45 (m, 6H, β-H_2 x 3), 1.39-1.29 (m, 6H, γ-H_2 x 3), 1.03-0.96 (m, 6H, α-H_2 x 3), 0.93-0.87 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 105.6 (s, C-2), 89.8 (s, C-1), 60.6 (t, C-3), 57.2 (q, OMe), 28.8 (t, C-β, d by $^2J_{Sn\text{-}C}$ = 22.9 Hz), 26.9 (t, C-γ, d by $^3J_{Sn\text{-}C}$ = 60.6 Hz), 13.6 (q, C-δ), 11.0 (t, C-α, d by $^1J_{119Sn\text{-}C}$ = 381.8 Hz, $^1J_{117Sn\text{-}C}$ = 365.5 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –67.3; MS: (EI, 70 eV) *m/z* 360 (M^+, 0.7), 303 (M^+ – Bu, 100), 302 (34), 301 (75), 300 (27), 299 (42), 247 (21); HRMS: (EI, 70 eV) calcd for ($C_{16}H_{32}OSn$) 360.1475 (M^+) found *m/z* 360.1480

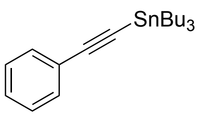
Tributyl(3-benzoyloxy-1-propynyl)stannane (2h)



According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), propargyl benzoate (0.160 g, 1.00 mmol), and Bu_3SnOMe (0.393 g, 1.22 mmol) gave the product as a colorless oil (0.209 g, 47% yield). IR (neat) : 2900, 2160 (C≡C), 1728 (C=O), 1269 (C–O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 8.08 (d, 2H, *J* =

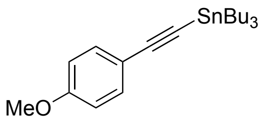
7.2 Hz, *o*-H x 2), 7.57 (t, 1H, J = 7.4 Hz, *p*-H), 7.44 (t, 2H, J = 7.7 Hz, *m*-H x 2), 4.94 (s, 2H with d by ${}^4J_{\text{Sn-H}}$ = 8.2 Hz), 1.66-1.47 (m, 6H, β-H_2 x 3), 1.38-1.29 (m, 6H, γ-H_2 x 3), 1.10-0.95 (m, 6H, α-H_2 x 3), 0.94-0.86 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 165.8 (s, C-5), 133.0 (d, C-*p*), 129.8 (s, C-*i*), 129.7 (t, C-*o*), 128.2 (t, C-*m*), 103.4 (s, C-2, d by ${}^2J_{\text{Sn-C}}$ = 55.6 Hz), 91.1 (s, C-1, d by ${}^1J_{\text{119Sn-C}}$ = 306.4 Hz, ${}^1J_{\text{117Sn-C}}$ = 291.7 Hz), 53.5 (t, C-3), 28.7 (t, C-β, d by ${}^2J_{\text{Sn-C}}$ = 22.1 Hz), 26.9 (t, C-γ, d by ${}^3J_{\text{Sn-C}}$ = 59.8 Hz), 13.6 (q, C-δ), 11.0 (t, C-α, d by ${}^1J_{\text{119Sn-C}}$ = 384.2 Hz, ${}^1J_{\text{117Sn-C}}$ = 364.6 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –65.9; MS: (EI, 70 eV) *m/z* 393 (M^+ – Bu, 100), 392 (38), 391 (74), 390 (29), 389 (42), 241 (63), 239 (47), 237 (27), 105 (75), 77 (20); HRMS: (CI, 200 eV) calcd for ($C_{22}H_{35}O_2Sn$) 451.1659 (M^+ + 1) found *m/z* 451.1656

Tributyl(phenylethynyl)stannane (2j)



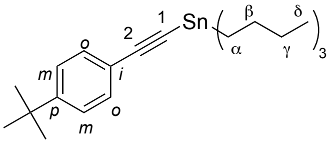
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), phenylacetylene (0.104 g, 1.02 mmol), and Bu_3SnOMe (0.388 g, 1.21 mmol) gave the product as a colorless oil (0.307 g, 77% yield). The analytical data for this compound were in excellent agreement with the reported data.[3b]

Tributyl(4-methoxyphenylethynyl)stannane (2k)



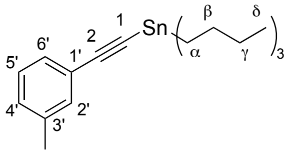
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 4-methoxyphenylacetylene (0.134 g, 1.02 mmol), and Bu_3SnOMe (0.408 g, 1.27 mmol) gave the product as a colorless oil (0.344 g, 80% yield). The analytical data for this compound were in excellent agreement with the reported data.[3b]

Tributyl(4-*tert*-butylphenylethynyl)stannane (2l)



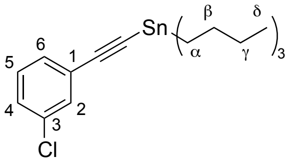
According to the typical procedure, $ZnBr_2$ in CH_3CN (0.05 M, 1 mL), 4-*tert*-butylphenylacetylene (0.150 g, 0.95 mmol), and Bu_3SnOMe (0.390 g, 1.21 mmol) gave the product as a colorless oil (0.307 g, 72% yield). IR (neat) : 2900, 2137 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.38 (d, 2H, J = 8.2 Hz, *o*-H x 2), 7.29 (d, 2H, J = 8.2 Hz, *m*-H x 2), 1.70-1.51 (m, 6H, β-H_2 x 3), 1.42-1.32 (m, 6H, γ-H_2 x 3), 1.23 (s, 9H, *t*Bu), 1.13-0.96 (m, 6H, α-H_2 x 3), 0.95-0.87 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 150.9 (s, C-*p*), 131.6 (d, C-*m*), 125.0 (d, C-*o*), 121.1 (s, C-*i*), 110.2 (s, C-2, d by ${}^2J_{\text{Sn-C}}$ = 63.9 Hz), 92.0 (s, C-1, d by ${}^1J_{\text{119Sn-C}}$ = 339.2 Hz, ${}^1J_{\text{117Sn-C}}$ = 324.4 Hz), 34.6 (s, *C*(CH_3)$_3$), 31.1 (q, C(*C*H_3)$_3$), 28.9 (t, C-β, d by ${}^2J_{\text{Sn-C}}$ = 22.9 Hz), 26.9 (t, C-γ, d by ${}^3J_{\text{Sn-C}}$ = 59.0 Hz), 13.7 (q, C-δ), 11.1 (t, C-α, d by ${}^1J_{\text{119Sn-C}}$ = 384.2 Hz, ${}^1J_{\text{117Sn-C}}$ = 366.2 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –65.9; MS: (EI, 70 eV) *m/z* 448 (M^+, 0.26), 392 (27), 391 (M^+ – Bu, 100), 390 (43), 389 (74), 388 (32), 387 (39), 277 (37), 275 (27); HRMS: (EI, 70 eV) calcd for ($C_{24}H_{40}Sn$) 448.2152 (M^+) found *m/z* 448.2149

Tributyl(3-methylphenylethynyl)stannane (2m)



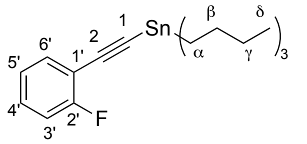
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 3-ethynyltoluene (0.117 g, 1.01 mmol), and Bu_3SnOMe (0.397 g, 1.24 mmol) gave the product as a colorless oil (0.281 g, 69% yield, 94% purity (A small portion was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard in order to determine the purity.)). IR: (neat) 2900, 2129 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.32-7.22 (m, 2H, 2'-H and 6'-H), 7.16 (t, J = 8.0 Hz, 1H, 5'-H), 7.07 (d, J = 8.0 Hz, 1H, 4'-H), 2.31 (s, 3H, Ar*Me*), 1.71-1.50 (m, 6H, β-H_2 x 3), 1.44-1.25 (m, 6H, γ-H_2 x 3), 1.14-0.97 (m, 6H, α-H_2 x 3), 0.96-0.76 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 137.7 (s, C-3'), 132.5 (d, C-2'), 129.0 (d), 128.7 (d), 128.0 (d, C-5'), 123.8 (s, C-1'), 110.2 (s, C-2, d by $^2J_{Sn-C}$ = 59.8 Hz), 92.7 (s, C-1), 28.9 (t, C-β, d by $^2J_{Sn-C}$ = 23.9 Hz), 27.0 (t, C-γ, d by $^3J_{Sn-C}$ = 60.1 Hz), 21.2 (q, Ar*Me*), 13.7 (q, C-δ), 11.2 (t, C-α, d by $^1J_{119Sn-C}$ = 385.2 Hz, $^1J_{117Sn-C}$ = 376.1 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –66.0; MS: (EI, 70 eV) *m/z* 406 (M^+, 0.27), 350 (23), 349 (M^+ – Bu, 100), 348 (41), 347 (75), 346 (32), 345 (41), 293 (M^+ – Bu_2 + 1, 15), 291 (M^+ – Bu_2 – 1, 11), 235 (50), 233 (36); HRMS: (EI, 70 eV) calcd for ($C_{21}H_{34}Sn$) 406.1682 (M^+) found *m/z* 406.1678

Tributyl(3-chlorophenylethynyl)stannane (2n)



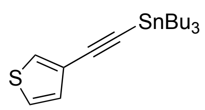
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), *m*-chlorophenylacetylene (0.140 g, 1.02 mmol), and Bu_3SnOMe (0.385 g, 1.20 mmol) gave the product as a colorless oil (0.296 g, 61% yield, 84% purity (A small portion was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard in order to determine the purity.)). In a different batch reaction, further purification was performed by flash column chromatography (hexane) on silica gel to give the product as a colorless oil (0.092 g, 23%). IR: (neat) 2140 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.43 (s, 1H, 2-H), 7.32 (d, J = 7.2 Hz, 1H, 6-H), 7.24 (d, J = 8.0 Hz, 1H, 4-H), 7.19 (dd, J = 8.0, 7.2 Hz, 1H, 5-H), 1.73-1.50 (m, 6H, β-H_2 x 3), 1.47-1.28 (m, 6H, γ-H_2 x 3), 1.16-0.97 (m, 6H, α-H_2 x 3), 0.93 (t, J =7.2 Hz, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 133.8 (s, C-3), 131.7 (d, C-5), 129.9 (d, C-2), 129.3 (d, C-6), 128.0 (d, C-4), 125.6 (s, C-1), 108.3 (s, *C*CSn, d by $^2J_{Sn-C}$ = 58.2 Hz), 95.2 (s, C*C*Sn, d by $^1J_{119Sn-C}$ = 308.0 Hz, $^1J_{117Sn-C}$ = 295.8 Hz), 28.8 (t, C-β, d by $^2J_{Sn-C}$ = 23.1 Hz), 26.9 (t, C-γ, d by $^3J_{Sn-C}$ = 59.2 Hz), 13.6 (q, C-δ), 11.1 (t, C-α, d by $^1J_{119Sn-C}$ = 383.6 Hz, $^1J_{117Sn-C}$ = 375.3 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –64.5; MS: (EI, 70 eV) *m/z* 371 (36), 370 (23), 369 (M^+ – Bu, 100), 368 (38), 367 (24), 366 (24), 365 (34), 313 (27), 257 (39), 255 (63), 254 (20), 253 (42); HRMS: (EI, 70 eV) calcd for ($C_{16}H_{22}ClSn$) 369.0432 (M^+ – Bu) found *m/z* 369.0431; Analysis: $C_{20}H_{31}ClSn$ (425.62) Calcd: C, 56.44; H, 7.34 Found: C, 56.47; H, 7.37

Tributyl(2-fluorophenylethynyl)stannane (2o)



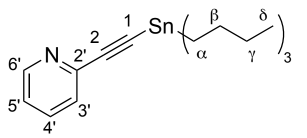
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 2-Fluorophenylacetylene (0.125 g, 1.04 mmol), and Bu_3SnOMe (0.387 g, 1.21 mmol) gave the product as a dilute yellow oil (0.316 g, 74% yield). IR: (neat) 2900, 2140 cm^{-1} (C≡C), 1241 (ArF) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.43 (td, J = 7.6, $^4J_{FH}$ = 2.0 Hz, 1H, 6'-H), 7.26-7.19 (m, 1H, 4'-H), 7.09-6.98 (m, 2H, 3'-H and 5'-H), 1.71-1.53 (m, 6H, β-H_2 x 3), 1.42-1.33 (m, 6H, γ-H_2 x 3), 1.16-0.99 (m, 6H, α-H_2 x 3), 0.95-0.88 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 127.0 (s, C-2', d by $^1J_{CF}$ = 250.7 Hz), 133.9 (d, C-6', d by $^3J_{CF}$ = 1.6 Hz), 129.4 (d, C-4', d by $^3J_{CF}$ = 8.2 Hz), 123.6 (d), 115.3 (d), 112.6 (s, C-1', d by $^2J_{CF}$ = 16.5 Hz), 102.5 (s, C-2, d by $^2J_{Sn\text{-}C}$ = 59.0 Hz), 99.7 (s, C-1, d by $^1J_{119Sn\text{-}C}$ = 310.3 Hz, $^1J_{117Sn\text{-}C}$ = 297.9 Hz, d by $^4J_{F\text{-}C}$ = 3.3 Hz), 28.8 (t, C-β, d by $^2J_{Sn\text{-}C}$ = 22.9 Hz), 26.9 (t, C-γ, d by $^3J_{Sn\text{-}C}$ = 59.8 Hz), 13.6 (q, C-δ), 11.2 (t, C-α, d by $^1J_{119Sn\text{-}C}$ = 381.8 Hz, $^1J_{117Sn\text{-}C}$ = 364.6 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –63.8; ^{19}F NMR: (372 MHz, $CDCl_3$) 112.4; MS: (CI, 200 eV) *m/z* 411 (M^+ + 1, 0.39), 353 (M^+ – Bu + 1, 25), 291 (100), 290 (34), 289 (41), 288 (27), 287 (42); HRMS: (CI, 200 eV) calcd for ($C_{20}H_{32}FSn$) 411.1510 (M^+ + 1) found *m/z* 411.1498

Tributyl(3-thienylethynyl)stannane (2p)



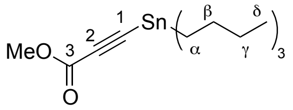
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 3-ethynylthiophene (0.107 g, 0.99 mmol), and Bu_3SnOMe (0.385 g, 1.20 mmol) gave the product as a brown oil (0.314 g, 74% yield, 92% purity (A small portion was analyzed by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard in order to determine the purity.)). The analytical data for this compound were in excellent agreement with the reported data.[3b]

Tributyl(2-pyridylethynyl)stannane (2q)



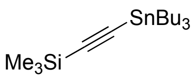
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 2-ethynylpyridine (0.105 g, 1.02 mmol), and Bu_3SnOMe (0.382 g, 1.19 mmol) gave the product as a yellow oil (0.318 g, 79% yield). IR: (neat) 2900 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 8.54 (d, J = 4.8 Hz, 1H, 6'-H), 7.61 (td, J = 8.0, 1.8 Hz, 1H, 4'-H), 7.42 (d, J = 8.0 Hz, 1H, 3'-H), 7.21-7.15 (m, 1H, 5'-H), 1.73-1.50 (m, 6H, β-H_2 x 3), 1.43-1.27 (m, 6H, γ-H_2 x 3), 1.12-0.99 (m, 6H, α-H_2 x 3), 0.96-0.85 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 149.6 (d, C-6'), 143.5 (s, C-2'), 135.8 (d, C-4'), 127.1 (d, C-3'), 122.3 (d, C-5'), 108.6 (s, 2-C, d by $^2J_{Sn\text{-}C}$ = 53.4 Hz), 94.9 (s, 1-C, d by $^1J_{119Sn\text{-}C}$ = 296.6 Hz, $^1J_{117Sn\text{-}C}$ = 281.4 Hz), 28.7 (t, C-β, d by $^2J_{Sn\text{-}C}$ = 22.9 Hz), 26.9 (t, C-γ, d by $^3J_{Sn\text{-}C}$ = 61.4 Hz), 13.5 (q, C-δ), 11.1 (t, C-α, d by $^1J_{119Sn\text{-}C}$ = 381.8 Hz, $^1J_{117Sn\text{-}C}$ = 364.6 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –64.6; MS: (CI, 200 eV) *m/z* 395 (20), 394 (M^+ + 1, 100), 393 (41), 392 (77), 391 (31), 390 (42); HRMS: (CI, 200 eV) calcd for ($C_{19}H_{32}NSn$) 394.1557 (M^+ + 1) Found *m/z* 394.1560

Tributyl(3-methoxy-3-oxo-1-propynyl)stannane (2r)



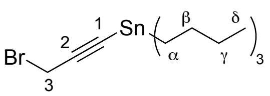
According to the typical procedure, $ZnBr_2$ in MeCN (0.05 M, 1 mL), methyl propionate (0.097 g, 1.15 mmol), and Bu_3SnOMe (0.375 g, 1.17 mmol) gave the product as a colorless oil (0.250 g, 58% yield, 77% purity (A small portion was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard in order to determine the purity.)). IR: (neat) 2900, 2148 (C≡C), 1712 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 3.73 (s, OMe), 1.63-1.48 (m, 6H, β-H_2 x 3), 1.36-1.26 (m, 6H, γ-H_2 x 3), 1.15-0.97 (m, 6H, α-H_2 x 3), 0.92-0.84 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 153.2 (s, C-3 d by $^{3}J_{Sn\text{-}C}$ = 8.2 Hz), 99.1 (s, C-2, d by $^{2}J_{Sn\text{-}C}$ = 32.8 Hz), 96.6 (s, C-1, d by $^{1}J_{119Sn\text{-}C}$ = 208.1 Hz, $^{1}J_{117Sn\text{-}C}$ = 198.3 Hz), 52.3 (q, OMe), 28.7 (t, C-β, d by $^{2}J_{Sn\text{-}C}$ = 23.8 Hz), 26.9 (t, C-γ, d by $^{3}J_{Sn\text{-}C}$ = 61.4 Hz), 13.5 (q, C-δ), 11.3 (t, C-α, d by $^{1}J_{119Sn\text{-}C}$ = 377.7 Hz, $^{1}J_{117Sn\text{-}C}$ = 361.3 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –56.9; MS: (EI, 70 eV) *m/z* 374 (M^+, 0.8), 317 (M^+ – Bu, 100), 316 (34), 315 (75), 314 (28), 313 (43), 261 (M^+ – Bu_2 + 1, 24), 151 (24); HRMS: (EI, 70 eV) calcd for ($C_{16}H_{30}O_2Sn$) 374.1268 (M^+) Found *m/z* 374.1276

Tributylstannyl-trimethylsilyl-acetylene (2s)



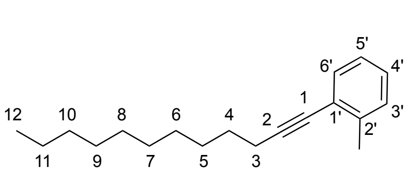
According to the typical procedure, $ZnBr_2$ in MeCN (0.05 M, 1 mL), trimethylsilylacetylene (0.192 g, 1.95 mmol), and Bu_3SnOMe (0.320 g, 1.00 mmol) gave the product as a colorless oil (0.190 g, 49% yield). The analytical data for this compound were in excellent agreement with the reported data.[25]

Tributyl(3-bromo-1-propynyl)stannane (2t)



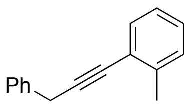
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), propargyl bromide (0.117 g, 0.98 mmol), and Bu_3SnOMe (0.394 g, 1.23 mmol) gave the product as a colorless oil (0.299 g, 74% yield). IR: (neat) 2900, 2152 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 3.95 (s, 2H, 3-H_2 with d by $^{4}J_{Sn\text{-}H}$ =9.2 Hz), 1.67-1.45 (m, 6H, β-H_2 x 3), 1.38-1.29 (m, 6H, γ-H_2 x 3), 1.06-0.96 (m, 6H, α-H_2 x 3), 0.94-0.87 (m, 9H, δ-H_3 x 3); ^{13}C NMR: (100 MHz, $CDCl_3$) 104.3 (s, C-2, d by $^{2}J_{Sn\text{-}C}$ = 55.7 Hz), 92.0 (s, C-1, d by $^{1}J_{119Sn\text{-}C}$ = 299.9 Hz, $^{1}J_{117Sn\text{-}C}$ = 285.9 Hz), 28.7 (t, C-β, d by $^{2}J_{Sn\text{-}C}$ = 24.6 Hz), 26.9 (t, C-γ, d by $^{3}J_{Sn\text{-}C}$ = 60.6 Hz), 15.5 (t, C-3), 13.6 (q, C-δ), 11.0 (t, C-α, d by $^{1}J_{119Sn\text{-}C}$ = 383.4 Hz, $^{1}J_{117Sn\text{-}C}$ = 365.4 Hz); ^{119}Sn NMR: (150 MHz, $CDCl_3$) –64.7; MS: (EI, 70 eV) *m/z* 408 (M^+, 1), 353 (M^+ + 2 – Bu, 62), 351 (M^+ – Bu, 100), 347 (25), 295 (29), 237 (21), 201 (33), 199 (51), 197 (34), 177 (21), 159 (31), 157 (26), 121 (21), 95 (34), 67 (98), 57 (27); HRMS: (EI, 70 eV) calcd for ($C_{15}H_{29}BrSn$) 408.0475 (M^+) found *m/z* 408.0464

1-(2-Methylphenyl)dodec-1-yne (8a)



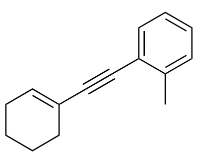
According to the typical procedure, $ZnBr_2$ in CH_3CN (0.05 M, 1 mL), 1-dodecyne (0.167 g, 1.00 mmol), Bu_3SnOMe (0.385 g, 1.20 mmol), *o*-bromotoluene (0.166 g, 0.97 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.013 g, 0.014 mmol) gave a crude product. Purification by flash column chromatography [solvent; hexane, column length; 11 cm] gave the product (0.159 g, 62%). IR: (neat) 2927, 2233 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.36 (d, 1H, J = 8.0 Hz, 6'-H), 7.18-7.06 (m, 3H, 3'-H and 4'-H and 5'-H), 2.44 (t, J = 7.2 Hz, 2H, 3-H_2), 2.41 (s, 3H, ArMe), 1.61 (m, 2H, 4-H_2), 1.51-1.42 (m, 2H, 5-H_2), 1.38-1.19 (m, 12H), 0.88 (t, 3H, 12-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 139.9 (s, C-2'), 131.7 (d, C-6'), 129.2 (d), 127.4 (d), 125.3 (d), 123.8 (s, C-1'), 94.4 (s, C-2), 79.4 (s, C-1), 31.9 (t), 29.6, 29.6, 29.3, 29.2, 28.9, 22.7 (s), 20.7 (q, Ar*Me*), 19.53 (t), 14.1 (q, C-12); MS: (EI, 70 eV) *m/z* 256 (M^+, 60), 171 ($M^+ - C_6H_{13}$, 24), 158 (28), 157 ($M^+ - C_7H_{15}$, 52), 143 ($M^+ - C_8H_{17}$, 30), 131 (100), 129 ($M^+ - C_9H_{19}$, 50), 128 (38), 105 (22); HRMS: (EI, 70 eV) calcd for ($C_{19}H_{28}$) 256.2191 (M^+) found *m/z* 256.2189; Analysis: $C_{19}H_{28}$ (256.43) Calcd: C, 88.99; H, 11.01 Found: C, 88.71; H, 10.95

2-(3-Phenyl-1-propynyl)toluene (8b)



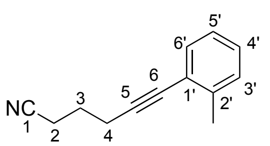
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 3-phenyl-1-propyne (0.111 g, 0.96 mmol), Bu_3SnOMe (0.391 g, 1.22 mmol), *o*-bromotoluene (0.171 g, 1.00 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.013 g, 0.014 mmol) gave the crude product. Purification by flash column chromatography [solvent; hexane, column length; 11 cm] gave the product (0.093 g, 47%). The analytical data for this compound were in excellent agreement with the reported data.[26]

2-(1-Cyclohexenylethynyl)toluene (8c)



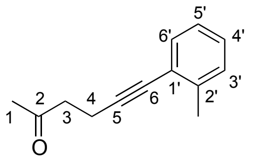
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 2-ethynyl-1-cyclohexene (0.109 g, 1.03 mmol), Bu_3SnOMe (0.385 g, 1.20 mmol), *o*-bromotoluene (0.175 g, 1.02 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.013 g, 0.014 mmol) gave the crude product. Purification by flash column chromatography [solvent; hexane, column length; 11 cm] gave the product (0.133 g, 66%). The analytical data for this compound were in excellent agreement with the reported data.[27]

6-(2-Methylphenyl)hex-5-ynenitrile (8d)



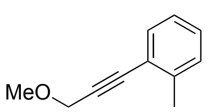
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), hex-5-ynenitrile (0.091 g, 0.98 mmol), Bu_3SnOMe (0.384 g, 1.20 mmol), *o*-bromotoluene (0.172 g, 1.01 mmol), P(*t*-Bu)$_3$ (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.013 g, 0.015 mmol) gave the crude product. Purification by flash column chromatography (hexane/ethyl acetate = 80/20) on silica gel gave the product (0.124 g, 69%). IR: (neat) 2248 (C≡N) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.28 (d, 1H, J = 8.0 Hz, 6'-H), 7.14-7.07 (m, 2H, 3'-H and 4'-H), 7.07-7.00 (m, 1H, 5'-H), 2.55 (t, J = 7.2 Hz, 2H, 4-H_2), 2.47 (t, J = 7.2 Hz, 2H, 2-H_2), 2.32 (s, 3H, Ar*Me*), 1.87 (tt, J = 7.2, 7.2 Hz, 2H, 3-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 139.8 (s, C-2'), 131.7 (d, C-6'), 129.3 (d, C-3'), 127.9 (d, C-4'), 125.4 (d, C-5'), 122.8 (s, C-1'), 119.1 (s, C-1), 90.7 (s, C-5), 81.1 (s, C-6), 24.6 (t, C-3), 20.6 (q, Ar*Me*), 18.5 (t, C-4), 16.0 (t, C-2); MS: (EI, 70 eV) *m/z* 183 (M^+, 100), 182 (97), 141 (24), 129 (72), 128 (69), 127 (23), 115 (ArCC, 23); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{13}N$) 183.1048 (M^+) found *m/z* 183.1046; Analysis: $C_{13}H_{13}N$ (183.25) Calcd: C, 85.21; H, 7.15; N, 7.64 Found: C, 84.93; H, 6.93; N, 7.71

6-(2-Methylphenyl)hex-5-yn-2-one (8e)



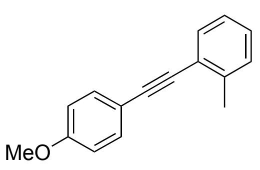
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), hex-5-yn-2-one (80% purity) (0.119 g, 0.98 mmol), Bu_3SnOMe (0.390 g, 1.21 mmol), *o*-bromotoluene (0.175 g, 1.02 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.014 g, 0.015 mmol) gave the crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 80/20, column length; 11 cm] gave the product (0.112 g, 61%). IR: (neat) 2900, 2229 (C≡C), 1720 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.33 (d, 1H, J = 8.0 Hz, 6'-H), 7.19-7.13 (m, 2H, 3'-H and 4'-H), 7.13-7.05 (m, 1H, 5'-H), 2.76 (t, J = 7.2 Hz, 2H, 3-H_2), 2.70 (t, J = 7.2 Hz, 2H, 4-H_2), 2.38 (s, 3H, Ar*Me*), 2.20 (s, 3H, 1-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 206.6 (s, C-2), 139.9 (s, C-2'), 131.7 (d, C-6'), 129.2 (d), 127.6 (d), 125.3 (d, C-5'), 123.2 (s, C-1'), 92.3 (s, C-5), 79.7 (s, C-6), 42.6 (t, C-3), 29.8 (q, C-1), 20.6 (q, Ar*Me*), 14.1 (t, C-4); MS: (EI, 70 eV) *m/z* 186 (M^+, 81), 185 (38), 171 ($M^+ - CH_3$, 83), 143 ($M^+ - CH_3CO$, 36), 129 ($M^+ - CH_3COCH_2$, 31), 128 (100), 127 (23), 115 ($M^+ - CH_3COC_2H_4$, 29), 43 (24); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{14}O$) 186.1045 (M^+) found *m/z* 186.1047

2-(3-Methoxy-1-propynyl)toluene (8f)



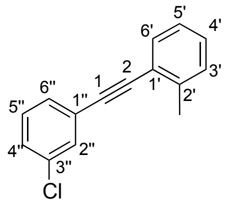
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 3-methoxy-1-propyne (0.072 g, 1.03 mmol), Bu_3SnOMe (0.373 g, 1.16 mmol), *o*-bromotoluene (0.172 g, 1.01 mmol), P(*t*-Bu)$_3$ (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.013 g, 0.015 mmol) gave the crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 97/3, column length; 11 cm] gave the product (0.080 g, 48%). The analytical data for this compound were in excellent agreement with the reported data.[28]

2-(4-Methoxyphenylethynyl)toluene (8g)



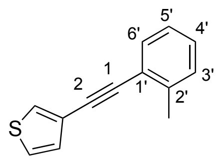
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 4-methoxyphenylacetylene (0.132 g, 1.00 mmol), Bu_3SnOMe (0.386 g, 1.20 mmol), *o*-bromotoluene (0.176 g, 1.03 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.014 g, 0.015 mmol) gave the crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 93/7, column length; 11 cm] gave the product (0.172 g, 78%). The analytical data for this compound were in excellent agreement with the reported data.[29]

2-(3-Chlorophenylethynyl)toluene (8h)



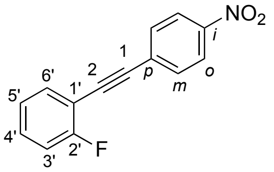
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), *m*-chlorophenylacetylene (0.125 g, 091 mmol), Bu_3SnOMe (0.378 g, 1.18 mmol), *o*-bromotoluene (0.163 g, 0.95 mmol), P(*t*-Bu)$_3$ (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.0132 g, 0.014 mmol) gave a crude product. Purification by flash column chromatography [solvent; hexane, column length; 11 cm] gave the product (0.152 g, 74%). IR: (neat) 2221 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.53-7.46 (m, 2H, 2''-H and 6'-H), 7.40 (d, 1H, J = 7.2 Hz, 6''-H), 7.33-7.20 (m, 4H, 4''-H and 5''-H and 4'-H and 5'-H), 7.17 (t, J = 7.2 Hz, 1H, 5'-H), 2.50 (s, 3H, Me)**;** ^{13}C NMR: (100 MHz, $CDCl_3$) 140.2 (s), 134.1 (s), 131.9 (d), 131.3 (d), 129.6 (d), 129.5 (d), 129.5 (d), 128.6 (d), 128.4 (d), 125.6 (d), 125.2 (s), 122.5 (s), 91.8 (s, C-1), 89.5 (s, C-2), 20.7 (q, Me); MS: (EI, 70 eV) *m/z* 228 (M^+ + 2, 30), 226 (M^+, 100), 191 (M^+ – Cl, 75), 189 (42); HRMS: (EI, 70 eV) calcd for ($C_{15}H_{11}Cl$) 226.0549 (M^+) found *m/z* 226.0546

3-Thienyl-*o*-tolylethyne (8i)



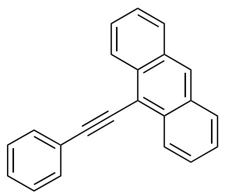
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 3-thienylacetylene (0.103 g, 0.95 mmol), Bu_3SnOMe (0.385 g, 1.20 mmol), *o*-bromotoluene (0.173 g, 1.01 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.014 g, 0.015 mmol) gave a crude product. Purification by flash column chromatography [solvent; hexane/ethyl acetate = 90/10, column length; 11 cm] gave the product (0.141 g, 75%).IR: (neat) 2980, 2202 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.50-7.45 (m, 2H), 7.29-7.25 (m, 1H), 7.23-7.11 (m, 4H), 2.49 (s, 3H, Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 140.0 (s, C-2'), 131.7(d), 129.8 (d), 129.4 (d), 128.2 (d), 128.2 (d), 125.5 (d), 125.3 (d), 122.9 (s), 122.5 (s), 88.3 (s), 87 (s), 20.7 (q, Me); MS: (EI, 70 eV) *m/z* 198 (M^+, 100), 197 (77), 165 (32); HRMS: (EI, 70 eV) calcd for ($C_{13}H_{10}S$) 198.0503 (M^+) found *m/z* 198.0496; Analysis: $C_{13}H_{10}S$ (198.28) Calcd: C, 78.75; H, 5.08; S, 16.17; Found: C, 78.47; H, 5.12; S, 16.02

***p*-(2-Fluorophenylethynyl)nitrobenzene (8j)**



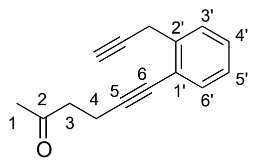
According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), 2-fluorophenylacetylene (0.128 g, 1.06 mmol), Bu_3SnOMe (0.398 g, 1.24 mmol), *p*-bromonitrobenzene (0.205 g, 1.01 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.014 g, 0.015 mmol) gave a crude product, which was washed with hexane to give the product as a blown solid (0.130 g, 55%). IR: (KBr) 2221 cm^{-1} (C≡C), 1516 cm^{-1} (N=O), 1342 cm^{-1} (Ar-NO_2); ^{1}H NMR: (400 MHz, $CDCl_3$) 8.23 (d, 2H, J = 8.0 Hz, *o*-H x 2), 7.70 (d, 2H, J = 8.0 Hz, *m*-H x 2), 7.55 (td, J = 8.0 Hz, $^4J_{FH}$ = 1.6 Hz, 1H, 6'-H), 7.42-7.36 (m, 1H, 4'-H), 7.19-7.12 (m, 2H, 3'-H and 5'-H); ^{13}C NMR: (100 MHz, $CDCl_3$) 162.8 (s, C-2', d by $^1J_{CF}$ = 256.8 Hz), 147.2 (s, C-*i*), 133.5 (d, C-6'), 132.4 (d, C-*m*), 131.1 (d, C-4', d by $^3J_{CF}$ = 8.3 Hz), 129.8 (s, C-*p*), 124.2 (d, C-5', d by $^4J_{CF}$ = 3.3 Hz), 123.6 (d, C-*o*), 115.7 (d, C-3', d by $^2J_{CF}$ = 19.7 Hz), 110.9 (d, C-1', d by $^2J_{CF}$ = 17.3 Hz), 92.3 (s, C-1, d by $^4J_{CF}$ = 3.2 Hz), 87.9 (s, C-2); ^{19}F NMR: (372 MHz, $CDCl_3$) 44.0; MS: (EI, 70 eV) *m/z* 241 (M^+, 100), 211 (M^+ – NO, 20), 195 (M^+ – NO_2, 20), 194 (44); HRMS: (EI, 70 eV) calcd for ($C_{14}H_8FNO_2$) 241.0539 (M^+) found *m/z* 241.0534

9-(2-Phenylethynyl)anthracene (8k)



According to the typical procedure, $ZnBr_2$ in THF (0.05 M, 1 mL), phenylacetylene (0.097 g, 0.95 mmol), Bu_3SnOMe (0.402 g, 1.25 mmol), 9-bromoanthracene (0.258 g, 1.00 mmol), P(*t*Bu)$_3$ in THF (0.1 M, 0.33 mL), and $Pd_2(dba)_3$ (0.013 g, 0.014 mmol) gave the crude product, which was washed with methanol to give the product as a solid (0.1408 g, 56%) including a small amount of starting material 9-bromoanthracen (<9%). Further purification (not optimized) was performed by flash column chromatography [solvent; hexane, column length; 11 cm] gave the product (0.041 g, 16%). The analytical data for this compound were in excellent agreement with the reported data.[30]

6-{2-(Prop-2-ynyl)phenyl}hex-5-yn-2-one (10)



IR: (neat) 1716 (C=O), 2121, 2229 (C≡C), 3294 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.55 (d, 1H, J = 8.0 Hz, 3'-H), 7.36 (d, 1H, J = 8.0 Hz, 6'-H), 7.28 (t, 1H, J = 8.0 Hz , 4'-H), 7.18 (t, J = 8.0 Hz, 1H, 5'-H), 3.72 (d, J = 3.2 Hz, 2H, CH_2CCH), 2.78 (t, 2H, J = 8.0 Hz, 3-H_2), 2.71 (t, 2H, J = 8.0 Hz, 4-H_2), 2.21 (s, 3H, 1-H_3), 2.20 (t, 1H, J = 3.2 Hz, CC*H*); ^{13}C NMR: (100 MHz, $CDCl_3$) 206.5 (s, C-2), 137.7 (s, C-2'), 131.8 (d, C-6'), 128.1 (d, C-4'), 127.7 (d, C-3'), 126.6 (d, C-5'), 122.5 (s, C-1'), 93.8 (s, C-5), 81.5 (dt, *C*CH), 78.7 (s, C-6), 70.7 (d, C*C*H), 42.5 (t, C-3), 29.9 (q, C-1), 23.6 (t, *C*H_2CCH), 14.1 (t, C-4); MS: (EI, 70 eV) *m/z* 210 (M^+, 9), 209 (23), 195 (M^+ – CH_3, 32), 167 (M^+ – CH_3CO, 100), 166 (29), 165 (66), 152 (M^+ – CH_3COCH_2, 87), 43 (24); HRMS: (EI, 15eV) calcd for ($C_{15}H_{14}O$) 210.1045 (M^+) found *m/z* 210.1041

3-5. References

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(11) The products, alkynylstannanes **2**, were decomposed during the isolation by column chromatography.

(12) Even though *n*BuLi or NaH was used instead of EtMgBr, the yields of **2t** were very low (*n*BuLi: 17% and NaH: 13%). The by-products have not been fully identified.

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(14) The generation of Bu_3SnBr was also confirmed by ^{119}Sn NMR spectroscopy (See the Experimental Section).

(15) The transmetalation between a tin alkoxide and zinc halide has been proposed, see: (a) Yasuda, M.; Tsuji, S.; Shibata, I.; Baba, A. *J. Org. Chem.* **1997**, *62*, 8282. (b) Yasuda, M.; Tsuji, S.; Shigeyoshi, Y.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 7440.

(16) We used $Zn(OMe)_2$, which was prepared according to the literature (Mehrotra, R. C.; Arora, M. *Zeitschrift Anorg. Allge. Chemie* **1969**, *370*, 300.), as a catalyst instead of $ZnBr_2$ in the reaction of Bu_3SnOMe with phenylacetylene **1j**. The corresponding product **2j** was obtained in 11% yield. This result supports the catalytic cycle in Scheme 3 including $Zn(OMe)_2$. The solid of zinc species employed was not soluble in the reaction mixture, and it might be a reason for the low yield. In situ generated

$Zn(OMe)_2$ may have high reactivity owing to low aggregation. The detail of the zinc species will be investigated.
(17) The generation of **6** has not been directly observed yet. The detail investigation of the mechanism is now underway.
(18) $Zn(OTf)_2$ is an effective catalyst for the synthesis of alkynylzinc species, and the mechanism via an activation of an alkyne by the coordination to $Zn(OTf)_2$ has been proposed, see: Fassler, R.; Tomooka, C. S.; Frantz, D. E.; Carreira, E. M. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5843.
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(22) Although the reaction of **1e** with **9** was also carried out under copper and amine-free Sonogashira conditions (**1e** (0.5 mmol), **9** (0.5 mmol), $Pd_2(dba)_3$ (2 mol %), Bu_4NOAc (1.5 mmol), DMF (2 mL), rt, 24 h.), product **10** was not obtained. 2-Allenyl bromobenzene (9%) was obtained as a by-product: Urgaonkar, S.; Verkade, J. G. *J. Org. Chem.* **2004**, *69*, 5752.
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Conclusion

This research investigates the transmetalation between less reactive organotin compounds with weak Lewis acid metal halides, and their application to organic synthesis. This work contributes to expanding the utility of organotin compounds for organic synthesis. The results obtained from the present work are summarized as follows.

In chapter 1, the radical couplings of iodocarbonyl compounds or iodo phosphorus compounds with butenylindium species generated by the transmetalation between cyclopropylmethylstannane and indium halide were achieved. Butenylindium was found to be an effective radical reagent, which works not only as an alkylating reagent but also a radical initiator in the presence of a small amount of oxygen. Tin halides generated by the transmetalation had no affect to the reaction system because of their inertness. Employing Sn-In transmetalation was essential for achieving the coupling reactions. The X-ray structural analysis of the mono- and dibutenylindium species succeeded.

In chapter 2, $InBr_3$- or $GaCl_3$-catalyzed coupling reaction of cyclopropylmethylstannane with alkyl chlorides was accomplished. It was found that *in situ* generated butenylindium or butenylgallium species reacted with alkyl chlorides in an ionic mechanism. This is the first finding of the ionic reactivity of organoindium or -gallium compounds.

The results in chapter 1 and 2 show the unique reactivity, radical and ionic reactivity, of the butenylindium and butenylgallium species.

In chapter 3, the catalytic and direct synthesis of alkynylstannanes from tin methoxide and terminal alkynes using a catalytic amount of $ZnBr_2$ was achieved. The transmetalation between $ZnBr_2$ and tin methoxide provides zinc methoxide, which promotes the reaction in mild conditions, and thus a wide range of functionalized terminal alkynes were applicable to this reaction system. Moreover, various functionalized aryl aklyne compounds were synthesized in one-pot protocol that included the zinc catalyzed synthesis of alkynylstannanes and the Migita–Kosugi–Stille coupling.