Regio- and Stereoselective Allylindation of Alkynes Using InBr<sub>3</sub> and Allylic Silanes: Synthesis, Characterization, and Application of 1,4-Dienylindiums toward Skipped Dienes

Yoshihiro Nishimoto<sup>1,∗</sup>, Junyi Yi<sup>2</sup>, Tatsuaki Takata<sup>2</sup>, Akio Baba<sup>2</sup> and Makoto Yasuda<sup>2,∗</sup>

<sup>1</sup>Frontier Research Base for Global Young Researchers Center for Open Innovation Research and Education (COiRE), Graduate School of Engineering, Osaka University; Osaka 565-0871, Japan
<sup>2</sup>Department of Applied Chemistry, Graduate School of Engineering, Osaka University; Osaka 565-0871, Japan; j_yi@chem.eng.osaka-u.ac.jp (J.Y.);
tatsu_takata@chem.eng.osaka-u.ac.jp (T.T.); baba@chem.eng.osaka-u.ac.jp (A.B.)
* Correspondence: nishimoto@chem.eng.osaka-u.ac.jp (Y.N.); yasuda@chem.eng.osaka-u.ac.jp (M.Y.);
Tel.: +81-6-6879-7386 (Y.N.); +81-6-6879-7384 (M.Y.)

Received: 7 July 2018; Accepted: 27 July 2018; Published: 27 July 2018

Abstract: Regioselective anti-allylindation of alkynes was achieved using InBr<sub>3</sub> and allylic silanes. Various types of alkynes and allylic silanes were applicable to the present allylindation. This sequential process used the generated 1,4-dienylindiums to establish novel synthetic methods for skipped dienes. The 1,4-dienylindiums were characterized by spectral analysis and treated with I<sub>2</sub> to stereoselectively give 1-iodo-1,4-dienes. The Pd-catalyzed cross coupling of 1,4-dienylindium with iodobenzene successfully proceeded in a one-pot manner to afford the corresponding 1-aryl-1,4-diene.

Keywords: indium; allylmetalation; alkyne; allylic silane

1. Introduction

Carbometalation is an important synthetic method in organic synthesis because organometallic compounds are produced with an expansion of the carbon framework [1–7]. In particular, the allylmetalation of alkynes provides metalated skipped dienes (1,4-diene), which are effectively transformed to functionalized skipped dienes via sequential reactions [8–18]. Skipped diene units are present in many biologically important natural products, and are also versatile synthetic building blocks in organic synthesis [19–22]. Therefore, various types of allylmetalation of alkynes have been developed. However, most reported reactions involve a syn-addition to alkynes, and few reports have focused on anti-allylmetalation (Scheme 1). Allylmagnesiations via direct anti-addition of allylic Grignard reagent were also reported (Scheme 1A,B), in which a directing group such as hydroxy and amino groups nearby the alkyne moiety are required [23–29]. Yamamoto reported an allylisilylation of simple alkynes with allylic silanes catalyzed by either HfCl<sub>4</sub> or EtAlCl<sub>2</sub>-Me<sub>3</sub>SiCl (Scheme 1C) [16,30–32]. However, the produced 1,4-dienyltrialkylsilanes cannot be applied to sequential transformations such as Hiyama coupling without activation by a strong base because of their low reactivity. In this context, we achieved regioselective anti-allylindation of simple alkynes using InBr<sub>3</sub> and allylic silanes (Scheme 1D). To the best of our knowledge, anti-allylindation of alkynes has never been established, while several syn-allylindations using allylic indiums have [13,33–39]. The 1,4-dienylindium compounds can be excellent precursors for functionalized skipped dienes due to their moderate reactivity and high compatibility with many functional groups. In fact, the 1,4-dienylindiums synthesized by the present allylindation can be easily transformed to functionalized skipped dienes by iodination or Pd-catalyzed cross coupling without the addition of bases in contrast to 1,4-dienylsilanes produced via allylisilylation.
2. Results

Recently, we reported regioselective anti-carbometalations of alkynes using organosilicon nucleophiles and metal halides such as InBr\(_3\) [40], GaBr\(_3\) [41], BiBr\(_3\) [42], ZnBr\(_2\) [43], and AlBr\(_3\) [44]. In our established carbometalations, a metal halide directly activates an alkyne, and then an organosilicon nucleophile adds to the alkyne from an opposite site of the metal halide. Therefore, we applied a combination of indium trihalides and allylic silanes to establish anti-allylindation of alkynes. First, various indium salts were investigated for the reaction using alkyne 1\(\text{a}\) and methallyl trimethylsilane 2\(\text{a}\) (Table 1). InBr\(_3\), 1\(\text{a}\), and 2\(\text{a}\) were mixed in CH\(_2\)Cl\(_2\), and then the reaction mixture was stirred at room temperature for 24 h. After an I\(_2\) solution in THF was added at −78 °C, alkenyl iodide 4\(\text{aa}\) was obtained as a single isomer in 89% yield (Entry 1). An iodine group was introduced exclusively cis to the allylic group. The production of 4\(\text{aa}\) by quenching with I\(_2\) suggested that anti-allylindation regioselectively proceeded to give the corresponding 1,4-dienylindium 3\(\text{aa}\). The use of InCl\(_3\) instead of InBr\(_3\) afforded 4\(\text{aa}\) in a 42% yield (Entry 2). On the other hand, examinations using InF\(_3\), InI\(_3\), and In(OTf)\(_3\) resulted in no reaction (Entries 3–5). The thermodynamic stability of a generated side product Me\(_3\)SiX might influence the driving force of the reaction. An investigation of the solvent effect was carried out. The reaction performed in non-polar solvents such as toluene resulted in no product because InBr\(_3\) did not dissolve the solvent (Entry 6). Polar solvents such as Et\(_2\)O, CH\(_3\)CN, and THF were not suitable to the present allylindation because of the deactivation of InBr\(_3\) by the solvent coordination (Entries 7–9).
Table 1. Optimization of reaction conditions for carboindation of alkyne 1a with allylic silane 2a.¹

| Entry | InX₃  | Solvent   | Yield/% |
|-------|-------|-----------|---------|
| 1     | InBr₃ | CH₂Cl₂    | 89      |
| 2     | InCl₃ | CH₂Cl₂    | 42      |
| 3     | InF₃  | CH₂Cl₂    | 0       |
| 4     | InI₂  | CH₂Cl₂    | 0       |
| 5     | In(O Tf)₃ | CH₂Cl₂ | 0   |
| 6     | InBr₃ | toluene   | 0       |
| 7     | InBr₃ | Et₂O      | 0       |
| 8     | InBr₃ | CH₃CN     | 0       |
| 9     | InBr₃ | THF       | 0       |

¹ InX₃ (1 mmol), alkyne 1a (1 mmol), allylic silane 2a (2 mmol), solvent (1 mL), room temperature, 24 h. I₂ (1.5 mmol), THF (2 mL). Yields were determined via ¹H-NMR using 1,1,2,2-tetrachloroethane as an internal standard; b Et₂O was used instead of THF.

The scope of the alkenes 1 is shown in Table 2. Sterically hindered aliphatic alkenes 1b and 1c (R = primary alkyl group) that were slightly larger than 1a resulted in lower yields of the corresponding alkenyl iodides 4ba and 4ca, respectively (Entries 1 and 2). Cyclohexylacetylene 1d (R = secondary alkyl group) gave a moderate yield (Entry 3), and the allylindation of tert-butylacetylene 1e did not proceed due to large steric hindrance (Entry 4). These results showed that the steric hindrance on an alkyne disturbs the allylindation. This allylindation system tolerated functionalities such as Ph and alkyl chloride moieties (Entries 5 and 6). Aromatic alkyne 1h was also applicable to the present allylindation. In this case, the addition of Me₂Si(OMe)₂ effectively increased the yield of the desired alkenyl iodide 4ha (Entries 7 and 8), probably because the MeO group of Me₂Si(OMe)₂ coordinated to an indium atom of the produced 1,4-dienylindium 3 to stabilize 3, and to avoid protonation of 3 by alkyne 1h.

Table 2. Scope and limitation of alkyne 1 in allylindation.²

| Entry | Alkyne 1 | Product 4 | Yield/% |
|-------|----------|-----------|---------|
| 1     | 1b       | 4ba       | 64      |
| 2     | 1c       | 4ca       | 41      |

² InBr₃ (1 mmol), alkyne 1 (1 mmol), solvent (1 mL), room temperature, 24 h. I₂ (1.5 mmol), THF (2 mL). Yields were determined via ¹H-NMR using 1,1,2,2-tetrachloroethane as an internal standard; b Et₂O was used instead of THF.
Table 2. Cont.

| Entry | Alkyne 1 | Product 4 | Yield/% |
|-------|----------|-----------|---------|
| 3     | ![Alkyne](image1) | ![Product](image2) | 40      |
| 4     | ![Alkyne](image3) | ![Product](image4) | 0       |
| 5     | ![Alkyne](image5) | ![Product](image6) | 59      |
| 6     | ![Alkyne](image7) | ![Product](image8) | 80      |
| 7     | ![Alkyne](image9) | ![Product](image10) | 65      |
| 8     | ![Alkyne](image11) | ![Product](image12) | 78 b    |

*Alkyne 1 (1 mmol), allylic silane 2a (2 mmol), InBr3 (1 mmol), CH2Cl2 (1 mL). Yields were determined by 1H-NMR using 1,1,2,2-tetrachloroethane as an internal standard; b Me2Si(OMe)2 (1 mmol) was added.

Next, we evaluated the scope of allylic silanes 2 in the allylindation of alkyne 1h in the presence of Me2Si(OMe)2 (Table 3). Allylindation using the simplest allylic silane 2b effectively proceeded to give the desired product 4hb in 48% yield (Entry 1). Allylic silane 2c bearing a Ph group at the 2-position also afforded a high yield (Entry 2). Allylindations using prenylsilane 2d and cinnamylsilane 2e, which have a substituent at the 3-position, effectively occurred to give the corresponding iodinated skipped dienes 4hd and 4he in 72% and 39% yields, respectively (Entries 3 and 4).

Table 3. Scope of allylic silane 2 in allylindation.

| Entry | Allylic Silane 2 | Product 3 | Yield/% |
|-------|-----------------|-----------|---------|
| 1     | ![Allylic Silane](image13) | ![Product](image14) | 48      |
The 1,4-dienylindium 3 synthesized by the present allylindation were isolated and characterized (Figure 1). After the allylindation of alkyne 1h using InBr₃ and methallylsilane 2a, the volatiles were evaporated and the residual oil was washed with hexane to obtain the desired 1,4-dienylindium 3ha as a white solid (Figure 1A). The 1,4-dienylindium 3ha was characterized by NMR spectroscopy. The resonance of a vinylic proton (H₁) at the α-position of the InBr₂ group appeared at δ 5.99 ppm (Figure 1B). The ¹³C-NMR spectrum of 3ha showed a slightly broad signal for C¹ at δ 134.1 ppm. These chemical shift values are similar to those of previously reported alkenylindium generated by the carboidnation of alkyne 1h with InBr₃ and a silyl ketene acetal [41]. A nuclear Overhauser effect between H³ and H⁵ was observed, which showed that anti-allylindation proceeded stereoselectively to give 1,4-dienylindium with a trans-configuration between the InBr₂ and allylic groups.

![Figure 1. Isolation and characterization of 1,4-dienylindium synthesized by allylindation. (A) Isolation of 1,4-dienylindium 3ha. (B) ¹H-NMR spectrum of 3ha.](image)

Table 3. Cont.

| Entry | Allylic Silane 2 | Product 3 | Yield/% |
|-------|------------------|-----------|--------|
| 2     | Ph₂Si(OMe)₂      | 4hc       | 76     |
| 3     | Ph₂Si(OMe)₂      | 4hd       | 72     |
| 4     | Ph₂Si(OMe)₂      | 4he       | 39     |

*Alkyne 1a (1 mmol), allylic silane 2 (2 mmol), InBr₃ (1 mmol), Me₂Si(OMe)₂ (1 mmol), and CH₂Cl₂ (1 mL). Yields were determined by ¹H-NMR using 1,1,2,2-tetrachloroethane as an internal standard.*
A plausible reaction mechanism is illustrated in Scheme 2. A carbon-carbon triple bond of alkyne 1 coordinates to InBr₃, and then the positive charge on the internal carbon atom of alkyne 1 is increased. Allylic silane 2 adds to the internal carbon atom from the opposite side of InBr₃ to give 1,4-dienylindium 3. The iodination of 1,4-dienylindium 3 with I₂ proceeds with retention of the double bond configuration of 3 to yield alkenyl iodide 4 as a single isomer.

![Scheme 2. Plausible reaction mechanism.](image)

Finally, we applied the synthesized 1,4-dienylindium to Pd-catalyzed cross coupling [40,45,46]. After 1,4-dienylindium 3ha was produced via the allylindation of alkyne 1h with allyl silane 2a and InBr₃, iodobenzene, a catalytic amount of Pd(PPh₃)₄, and DMF were added to the reaction mixture in a one-pot manner. Then, the Pd-catalyzed coupling reaction of 3ha with iodobenzene smoothly proceeded at 100 °C to give the desired skipped diene 5 as a single isomer. It should be noted that the coupling product 5 was stereoselectively obtained with retention of the double bond configuration of the alkenylindium (Scheme 3).

![Scheme 3. Pd-catalyzed cross-coupling of alkenylindium with iodobenzene.](image)

3. Materials and Methods

3.1. Analysis

NMR spectra were recorded on a JEOL JNM-400 (400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR) spectrometer (JEOL Ltd., Tokyo, Japan). Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (δ = 0 for ¹H-NMR) with the residual CHCl₃ (δ = 77.0 for ¹³C-NMR) used as an internal reference. ¹H and ¹³C-NMR signals of all new compounds were assigned by using HMQC, HMBC, COSY, and ¹³C off-resonance techniques. Infrared (IR) spectra were recorded on a JASCO FT/IR-6200 Fourier transform infrared spectrophotometer (JASCO Co., Tokyo, Japan). Silica gel column chromatography was performed using an automated flash chromatography system from the Yamazen Co. (W-Prep 2XY) (Yamazen Co., Osaka, Japan). Gel permeation chromatography (GPC) was performed using a NEXT recycling preparative HPLC from the Japan Analytical Industry Co. (Tokyo, Japan) (solvent: CHCl₃; column: JAIGEL-1HH and JAIGEL-2HH). Reactions were carried out in dry solvents under a nitrogen atmosphere, unless otherwise stated. All allylic silanes were prepared by reported methods. Other reagents were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA), the Tokyo Chemical Industry Co., Ltd. (TCI) (Tokyo, Japan) or Wako Pure Chemical
Industries, Ltd. (Osaka, Japan), and used after purification by distillation or used without purification for solid substrates.

3.2. Typical Procedure

Alkyne 1 (1 mmol) was added to a solution of InBr$_3$ (1 mmol) and allylic silane 2 (2 mmol) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h, and then 0.75 M I$_2$ in THF solution (2 mL) was added at $-78 \, ^\circ$C. The resultant mixture was stirred at $-78 \, ^\circ$C for 30 min. The mixture was quenched by saturated Na$_2$S$_2$O$_3$ aq (10 mL), and then extracted with dichloromethane (3 × 10 mL). The collected organic layers were dried over MgSO$_4$, and concentrated under reduced pressure. The yield was determined by $^1$H-NMR using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by flash chromatography (spherical silica gel 60 μm, 30 g, diameter 2.7 cm) and GPC to give the product.

(E)-4-(Iodomethylene)-2,7-dimethyloct-1-ene (4aa)

\[
\begin{align*}
\text{IR: (neat) 1650, 1457 cm}^{-1}; \quad ^1\text{H-NMR: (400 MHz, CDCl}_3\text{) 5.92 (s, 1H, 4-CHI), 4.83 (s, 1H, 1-H), 4.75 (s, 1H, 1-H), 2.87 (s, 2H, 3-H), 2.16 (t, J = 7.8 Hz, 2H, 5-H), 1.65 (s, 3H, 2-Me), 1.43–1.23 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}\text{C-NMR: (100 MHz, CDCl}_3\text{) 149.4 (s, C-4), 142.5 (s, C-2), 113.0 (t, C-1), 76.2 (d, 4-CHI), 45.8 (t, C-3), 36.4 (t, C-5), 31.9 (t), 29.43 (t), 29.38 (t), 29.22 (t), 27.0 (t), 22.7 (t), 21.8 (q, 2-Me), 14.1 (q, C-12); HRMS: (EI, 70 eV) Calculated (C_{14}H_{25}I) 320.1001 (M$^+$), Found: 320.1000.}
\end{align*}
\]

(E)-4-(Iodomethylene)-2,7-dimethyloct-1-ene (4ba)

\[
\begin{align*}
\text{IR: (neat) 1650, 1467, 1455 cm}^{-1}; \quad ^1\text{H-NMR: (400 MHz, CDCl}_3\text{) 5.90 (s, 1H, 4-CHI), 4.83 (s, 1H, 1-H), 4.75 (s, 1H, 1-H), 2.88 (s, 2H, 3-H), 2.18–2.16 (m, 2H, 5-H), 1.65 (s, 3H, 2-Me), 1.62–1.52 (m, 1H, 7-H), 1.30–1.24 (m, 2H, 6-H), 0.93 (d, J = 6.3 Hz, 6H, 8-H and 7-Me); ^{13}\text{C-NMR: (100 MHz, CDCl}_3\text{) 149.5 (s,}
\end{align*}
\]

The alkyne 1-decyne (0.980 mmol, 0.1354 g) was added to a solution of InBr$_3$ (0.996 mmol, 0.3530 g) and methallyl trimethylsilane (2.07 mmol, 0.2654 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to $-78 \, ^\circ$C, and 0.75 M I$_2$ in THF solution (2 mL) was added. The resultant mixture was stirred at $-78 \, ^\circ$C for 30 min. The mixture was quenched by saturated Na$_2$S$_2$O$_3$ aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO$_4$, and evaporated, and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl$_3$) to give the product (0.279 g, 89%).
(E)-4-(Iodomethylene)-2,6-dimethylhept-1-ene

The alkyne 4-methylpent-1-yne (1.06 mmol, 0.0872 g) was added to a solution of InBr3 (1.02 mmol, 0.3606 g) and methallyl trimethylsilane (2.03 mmol, 0.2620 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I2 in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na2S2O3 aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO4. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl3) to give the product (0.0560 g, 20%).

IR: (neat) 1650, 1463 cm−1; 1H-NMR: (400 MHz, CDCl3) 6.01 (s, 1H, 8-H), 4.84 (s, 1H, 1-H), 4.74 (s, 1H, 1-H), 2.87 (s, 2H, 3-H2), 2.09 (d, J = 8.0 Hz, 2H, 5-H2), 1.90 (septet, J = 8.0 Hz, 1H, 6-H), 1.65 (s, 3H, 2-Me), 0.93 (d, J = 0.8 Hz, 6H, 7-H3 and 6-Me); 13C-NMR: (100 MHz, CDCl3) 148.4 (s, C-3), 142.4 (s, C-2), 113.2 (t, C-1), 77.5 (d, 4-CHI), 46.3 (t, C-4), 38.6 (t, C-2), 33.3 (t, C-1), 21.8 (q, C-7 and 6-Me), 21.8 (q, 2-Me); HRMS: (EI, 70 eV) Calculated (C11H19I) 278.0531 (M+), Found: 278.0529.

(E)-4-(Iodomethylene)-2,6-dimethylhept-1-ene (4ca)

Ethynylcyclohexane (1.01 mmol, 0.1094 g) was added to a solution of InBr3 (0.968 mmol, 0.3432 g) and methallyl trimethylsilane (1.98 mmol, 0.2540 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I2 in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na2S2O3 aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO4. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl3) to give the product (0.0607 g, 21%).

IR: (neat) 1650, 1448 cm−1; 1H-NMR: (400 MHz, CDCl3) 5.83 (s, 1H, 11-H), 4.87 (s, 1H, 10-H), 4.77 (s, 1H, 10-H), 2.81 (s, 2H, 8-H2), 2.63–2.56 (m, 1H, 1-H), 1.79–1.55 (m, 8H), 1.4–1.23 (m, 4H), 1.20–1.09 (m, 1H); 13C-NMR: (100 MHz, CDCl3) 151.8 (s, C-7), 142.8 (s, C-9), 113.7 (t, C-10), 76.0 (d, C-11), 47.3 (d, C-1), 42.1 (t, C-8), 29.9 (t), 26.3 (t), 26.0 (t), 22.0 (t, C-12); HRMS: (EI, 70 eV) Calculated (C12H19I) 290.0531 (M+), Found: 290.0530.

(E)-(3-(Iodomethylene)-5-methylhex-5-en-1-yl)benzene (4fa)
Pent-4-yn-1-ylbenzene (1.01 mmol, 0.1314 g) was added to a solution of InBr₃ (0.979 mmol, 0.3471 g) and methallyl trimethylsilane (2.00 mmol, 0.2560 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I₂ in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na₂S₂O₃ aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO₄. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl₃) to give the product (0.1676 g, 59%).

IR: (neat) 1649, 1404, 1494, 1454 cm⁻¹; ¹H-NMR: (400 MHz, CDCl₃) 7.31–7.17 (m, 5H, Ph), 6.00 (s, 1H, 3-CHI), 4.85 (s, 1H, 6-H), 4.76 (s, 1H, 6-H), 2.86 (s, 2H, 4-H₂), 2.72–2.68 (m, 2H, 1-H₂), 2.48–2.44 (m, 2H, 2-H₂), 1.64 (s, 3H, 5-Me); ¹³C-NMR: (100 MHz, CDCl₃) 148.4 (s, C-3), 142.2 (s, C-5), 141.4 (s, C-3), 128.39 (d), 128.35 (d), 126.0 (d, p), 113.3 (t, C-6), 77.2 (d, 3-CHI), 46.3 (t, C-4), 38.6 (t, C-2), 33.3 (t, C-1), 21.8 (q, 5-Me); HRMS: (EI, 70 eV) Calculated (C₁₄H₁₁I) 312.0375 (M⁺), Found: 312.0377.

(E)-7-Chloro-4-(iodomethylene)-2-methylhept-1-ene (4ga)

The alkyne 5-chloropent-1-yne (1.01 mmol, 0.1031 g) was added to a solution of InBr₃ (0.983 mmol, 0.3486 g) and methallyl trimethylsilane (1.99 mmol, 0.2557 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I₂ in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na₂S₂O₃ aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO₄. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) to give the product (0.102 g, 38%).

IR: (neat) 1649, 1443 cm⁻¹; ¹H-NMR: (400 MHz, CDCl₃) 6.01 (s, 1H, 4-CHI), 4.84 (s, 1H, 7-H), 4.76 (s, 1H, 7-H), 3.54 (t, J = 7.3 Hz, 2H, 1-H₂), 2.88 (s, 2H, 5-H₂), 2.31 (t, J = 7.3 Hz, 2H, 3-H₂), 1.88 (quintet, J = 7.3 Hz, 2H, 2-H₂), 1.64 (s, 3H, 6-Me); ¹³C-NMR: (100 MHz, CDCl₃) 147.6 (s, C-4), 141.9 (s, C-6), 113.4 (t, C-7), 77.6 (d, 3-CHI), 46.0 (t, C-5), 44.5 (t, C-1), 33.9 (t, C-3), 30.0 (t, C-2), 21.7 (q, 6-Me); HRMS: (EI, 70 eV) Calculated (C₁₄H₁₁I) 283.9829 (M⁺), Found: 283.9823.

(Z)-(1-Iodo-4-methylpenta-1,4-dien-2-yl)benzene (4ha)

Phenylacetylene (1.08 mmol, 0.110 g) was added to a solution of InBr₃ (1.00 mmol, 0.3541 g), methallyl trimethylsilane (1.99 mmol, 0.2552 g), and Me₂Si(OMe)₂ (1.02 mmol, 0.1230 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I₂ in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na₂S₂O₃ aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO₄. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl₃) to give the product (0.169 g, 55%).

IR: (neat) 1650, 1490, 1442 cm⁻¹; ¹H-NMR: (400 MHz, CDCl₃) 7.38–7.30 (m, 3H, Ar), 7.21 (d, J = 6.8 Hz, 2H, Ar), 6.35 (s, 1H, 1-H), 4.78 (s, 1H, 5-H), 4.66 (s, 1H, 5-H), 3.20 (s, 2H, 3-H), 1.70 (s, 3H, 4-Me);
13C-NMR: (100 MHz, CDCl3) 150.1 (s), 141.9 (s), 141.5 (s), 128.1 (d), 127.9 (d), 127.6 (d), 113.7 (t, C-5), 77.6 (d, C-1), 48.6 (t, C-3); HRMS: (EI, 70 eV) Calculated (C12H13I) 269.9905 (M+), Found: 269.9903.

(Z)-(1-Iodo-3,3-dimethylpenta-1,4-dien-2-yl)benzene (4hb)

Phenylacetylene (1.00 mmol, 0.102 g) was added to a solution of InBr3 (1.11 mmol, 0.3921 g), allyl trimethylsilane (1.96 mmol, 0.2236 g), and Me2Si(OMe)2 (1.00 mmol, 0.1202 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I2 in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na2S2O3 aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO4. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl3) to give the product (0.102 g, 38%).

IR: (neat) 1638 cm−1; 1H-NMR: (400 MHz, CDCl3) 7.42–7.7.31 (m, 3H, Ar), 7.24–7.22 (m, 2H, Ar), 6.35 (t, J = 1.5 Hz, 1H, 1-H), 5.78 (m, 1H, 4-H), 5.11–5.06 (m, 2H, 5-H), 3.25 (dq, J = 6.8, 1.5 Hz, 2H, 3-H2); 13C-NMR: (100 MHz, CDCl3) 150.8 (s, C-2), 142.1 (s), 134.3 (d, C-4), 128.2 (d), 127.8 (d), 127.6 (d), 117.5 (t, C-5), 77.1 (d, C-1), 44.3 (t, C-3); HRMS: (EI, 70 eV) Calculated (C11H11I) 269.9905 (M+), Found: 269.9903.

(Z)-1-Iodo-2,4-diphenylpenta-1,4-diene (4hc)

Phenylacetylene (1.03 mmol, 0.1053 g) was added to a solution of InBr3 (0.98 mmol, 0.3497 g), 2-phenylallyl trimethylsilane (2.00 mmol, 0.3813 g), and Me2Si(OMe)2 (1.00 mmol, 0.1207 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I2 in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na2S2O3 aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO4. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl3) to give the product (0.153 g, 43%).

IR: (neat) 1626, 1492, 1442 cm−1; 1H-NMR: (400 MHz, CDCl3) 7.36–7.23 (m, 8H, Ar), 7.17–7.15 (m, 2H, Ar), 6.33 (s, 1H, 1-H), 5.41 (s, 1H, 5-H), 5.07 (s, 1H, 5-H), 3.65 (s, 2H, 3-H2); 13C-NMR: (100 MHz, CDCl3) 149.9 (s), 143.9 (s), 142.2 (s), 140.1 (s), 128.3 (d), 128.1 (d), 127.8 (d), 127.6 (d), 126.0 (d), 115.8 (t, C-5), 78.6 (d, C-1), 45.6 (t, C-3); HRMS: (EI, 70 eV) Calculated (C17H15I) 346.0218 (M+), Found: 346.0221.

(Z)-(1-Iodo-3,3-dimethylpenta-1,4-dien-2-yl)benzene (4hd)
Phenylacetylene (1.02 mmol, 0.104 g) was added to a solution of InBr3 (1.04 mmol, 0.3701 g), cinnamyl trimethylsilane (2.10 mmol, 0.4007 g), and Me2Si(OMe)2 (1.06 mmol, 0.1280 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I2 in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na2S2O3 aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO4. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl3) to give the product (0.080 g, 23%).

IR: (neat) 1638, 1490, 1462, 1442 cm−1; 1H-NMR: (400 MHz, CDCl3) 7.41–7.7.32 (m, 8H, Ar), 7.04–7.00 (m, 2H, Ar), 6.53 (s, 1H, 1-H), 5.94 (dd, J = 17.4, 10.6 Hz, 1H, 4-H), 5.09 (d, J = 10.6 Hz, 1H, 5-H), 5.03 (d, J = 17.4 Hz, 1H, 5-H), 1.21 (s, 6H, 3-Me2); 13C-NMR: (100 MHz, CDCl3) 159.7 (s, C-2), 145.2 (d, C-4), 142. 4 (s), 128.9 (d), 127.8 (d), 127.1 (d), 112.3 (t, C-5), 80.2 (d, C-1), 45.1 (s, C-3), 26.4 (q, 3-Me2); HRMS: (El, 70 eV) Calculated (C13H15I) 298.0218 (M+), Found: 298.0219.

(Z)-1-Iodo-2,3-diphenylpenta-1,4-diene (4he)

Phenylacetylene (1.02 mmol, 0.1044 g) was added to a solution of InBr3 (1.04 mmol, 0.3701 g), prenyl trimethylsilane (1.96 mmol, 0.2788 g), and Me2Si(OMe)2 (0.962 mmol, 0.1157 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was cooled to −78 °C, and 0.75 M I2 in THF solution (2 mL) was added. The resultant mixture was stirred at −78 °C for 30 min. The mixture was quenched by saturated Na2S2O3 aq (10 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The collected organic layer was dried over MgSO4. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl3) to give the product (0.080 g, 23%).

IR: (neat) 1636 cm−1; 1H-NMR: (400 MHz, CDCl3) 7.29–7.14 (m, 8H, Ar), 6.99 (dd, J = 7.8, 2.0 Hz, 2H, Ar), 6.42 (s, 1H, 1-H), 6.11 (ddd, J = 17.4, 10.1, 7.3 Hz, 1H, 4-H), 5.19 (d, J = 10.1 Hz, 1H, 5-H), 5.00 (d, J = 17.4 Hz, 1H, 5-H), 4.47 (d, J = 7.3 Hz, 1H, 3-H); 13C-NMR: (100 MHz, CDCl3) 159.1 (s), 142.3 (s), 139.8 (s), 138.2 (d, C-4), 128.48 (d), 128.40 (d), 128.2 (d), 127.9 (d), 127.4 (d), 126.8 (d), 117.3 (t, C-5), 80.4 (d, C-1), 58.8 (d, C-3); HRMS: (El, 70 eV) Calculated (C17H13I) 346.0218 (M+), Found: 346.0214.

(Z)-(4-Methyl-2-phenylpenta-1,4-dien-1-yl)indium(III) bromide (3ha)

All manipulations were carried out in a glove box filled with nitrogen gas. Phenylacetylene (0.886 mmol, 0.0905 g) was added to a solution of InBr3 (1.00 mmol, 0.3550 g), methallyl trimethylsilane (1.98 mmol, 0.2541 g), and Me2Si(OMe)2 (1.05 mmol, 0.1267 g) in dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. The volatiles were evaporated and the residual oil was washed with hexane to obtain the desired alkenylindium compound as a white solid (0.106 g, 26%).

1H-NMR: (400 MHz, CDCl3) 7.43–7.22 (m, 5H, Ar), 5.99 (s, 1H, 1-H), 4.83 (s, 1H, 5-H), 4.73 (s, 1H, 5-H), 3.30 (s, 2H, 3-H), 1.72 (s, 3H, 4-Me); 13C-NMR: (100 MHz, CDCl3) 160.6 (s), 145.7 (s), 141.9 (s), 134.1 (d, C-1), 129.5 (d), 128.8 (d), 126.5 (d), 113.9 (t, C-5), 48.1 (t, C-3), 22.1 (q, 4-Me).
(Z)-4-Methy-1,2-diphenylpenta-1,4-diene (5)

Phenylacetylene (0.540 mmol, 0.0551 g) was added to a solution of InBr$_3$ (0.532 mmol, 0.1885 g), methallyl trimethylsilane (1.01 mmol, 0.1290 g), and Me$_2$Si(OMe)$_2$ (0.499 mmol, 0.060 g) in dichloromethane (0.5 mL). The mixture was stirred at room temperature for 3 h. DMF (1 mL) was added to the reaction mixture at -78 °C. Then, the reaction mixture was warmed to room temperature. Phenylacetylene (1.02 mmol, 0.1044 g) was added to a solution of InBr$_3$ (1.04 mmol, 0.3550 g), methallyl trimethylsilane (1.01 mmol, 0.1290 g), and Me$_2$Si(OMe)$_2$ (0.499 mmol, 0.060 g) in dichloromethane (0.5 mL). The mixture was stirred at room temperature for 3 h. DMF (1 mL) was added to the reaction mixture at -78 °C. Then, the reaction mixture was warmed to room temperature. Phenylacetylene (0.540 mmol, 0.0551 g) and Pd(PPh$_3$)$_4$ (0.028 mmol, 0.0325 g) were added to the reaction mixture, and the mixture was heated at 100 °C for 3 h. The mixture was quenched by H$_2$O (10 mL) and Et$_2$O (20 mL) at room temperature. The organic layer was washed by H$_2$O (3 × 10 mL), and was dried over MgSO$_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC (CHCl$_3$) to give the product (0.0686 g, 54%).

IR: (neat) 1650, 1599, 1494, 1444 cm$^{-1}$; $^1$H-NMR: (400 MHz, CDCl$_3$) 7.29–7.20 (m, 3H, Ar), 7.15 (d, $J = 6.8$ Hz, 2H, Ar), 7.12–7.04 (m, 3H, Ar), 6.95 (d, $J = 6.8$ Hz, Ar), 4.79 (s, 1H, 5-H), 4.72 (s, 1H, 5-H), 3.18 (s, 2H, 3-H$_2$), 1.76 (s, 3H, 4-Me); $^{13}$C-NMR: (100 MHz, CDCl$_3$) 142.9 (s, C-4), 141.1 (s), 140.4 (s), 137.3 (s), 129.0 (d), 128.6 (d), 128.3 (d), 128.1 (d), 127.8 (d), 126.9 (d), 126.3 (d), 113.1 (t, C-5), 49.1 (t, C-3), 22.1 (q, 4-Me); HRMS: (EI, 70 eV) Calculated (C$_{18}$H$_{18}$) 234.1409 (M$^+$), Found: 234.1408.

4. Conclusions

We established a regioselective anti-allylindation of alkynes using InBr$_3$ and allylic silanes. Many types of aliphatic and aromatic alkynes were applicable. The present allylindation has a wide scope of aliphatic silanes, and the reactions using allyl, methallyl, prenyl, cinnamyl silanes gave the desired products. A 1,4-dienyl indium compound generated by the present allylindation was successfully isolated and characterized by NMR spectroscopy. The synthesized 1,4-dienyl indiums were applicable to iodonation and Pd-catalyzed cross-coupling with an aryl iodide in a one-pot manner to give the corresponding functionalized skipped dienes.

Supplementary Materials: The following are available online, Supporting Information of NOE Experiments and NMR Spectra.

Author Contributions: Y.N., A.B. and M.Y. conceived and designed the experiments; J.Y. and T.T. performed the experiments; Y.N., J.Y. and T.T. analyzed the data; Yoshihiro Nishimoto, J.Y. and T.T. contributed reagents/materials/analysis tools; Y.N. and M.Y. wrote the paper.

Funding: This research received no external funding.

Acknowledgments: This work was supported by the JSPS KAKENHI Grant Numbers JP15H05848 in Middle Molecular Strategy, JP16K05719, and JP18H01977. Y.N. acknowledges support from the Frontier Research Base for Global Young Researchers, Osaka University, of the MEXT program. N.Y. acknowledges financial support from Mitsui Chemicals Award in Synthetic Organic Chemistry and Shorai Foundation for Science and Technology to Y.N.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Normant, J.F.; Alexakis, A. Carbometallation (C-metallation) of alkynes: Stereospecific synthesis of Alkenyl derivatives. Synthesis 1981, 841–870, 841–870. [CrossRef]
2. Yamamoto, Y.; Asao, N. Selective reactions using allylic metals. Chem. Rev. 1993, 93, 2207–2293. [CrossRef]
3. Asao, N.; Yamamoto, Y. Lewis acid-catalyzed hydrometalation and carbometalation of unactivated alkynes. Bull. Chem. Soc. Jpn. 2000, 73, 1071–1087. [CrossRef]
4. Fallis, A.G.; Forgione, P. Metal mediated carbomethylation of alkynes and alkenes containing adjacent heteroatoms. *Tetrahedron* **2001**, *57*, 5899–5913. [CrossRef]

5. Shirakawa, E.; Hiyama, T. Transition metal-catalyzed carbostannylation of alkynes and dienes. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1435–1450. [CrossRef]

6. Knochel, P. Comprehensive Organometallic Chemistry III; Mingos, D.M.P., Crabtree, R.H., Eds.; Elsevier: Oxford, UK, 2007; Volume 9.

7. Ojima, I. Comprehensive Organometallic Chemistry III; Mingos, D.M.P., Crabtree, R.H., Eds.; Elsevier: Oxford, UK, 2007; Volume 10.

8. Singleton, D.A.; Waller, S.C.; Zang, Z.; Frantz, D.E.; Leung, S.-W. Allylboration of alkenes with allyldihaloboranes. *J. Am. Chem. Soc.* **1995**, *118*, 9986–9987. [CrossRef]

9. Negishi, E.; Miller, J.A. Selective carbon-carbon bond formation via transition metal catalysis. 37. Controlled carbometallation. 16. Novel syntheses of α,β-unsaturated cyclopentenones via allylzincation of alkynes. *J. Am. Chem. Soc.* **1983**, *105*, 6761–6763. [CrossRef]

10. Eishi, J.J.; Bokslawski, M.P. Effects of Lewis acids and bases on the carbotitanation of unsaturated hydrocarbons and ketones with η^2-allyl(di-η^3-cyclopentadienyl)titanium(III). *J. Organomet. Chem.* **1987**, *334*, C1–C4.

11. Yeon, S.H.; Han, J.S.; Hong, E.; Do, Y.; Jung, I.N. Aluminum chloride catalyzed stereo- and regiospecific allylsilylation of alkynes: A convenient route to silyldienes. *J. Organomet. Chem.* **1995**, *499*, 159–165. [CrossRef]

12. Chatani, N.; Amishiro, N.; Morri, T.; Yamashita, T.; Murai, S. Pd-catalyzed coupling reaction of acetylenes, 10. Effects of Lewis acids and bases on the carbotitanation of unsaturated alkynes. *J. Organomet. Chem.* **1995**, *499*, 159–165. [CrossRef]

13. Fujiwara, N.; Yamamoto, Y. Allylation of Unactivated and/or Functionalized Alkynes with Allylindiums. *J. Org. Chem.* **1997**, *62*, 2318–2319. [CrossRef] [PubMed]

14. Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. Mechanistic aspects of palladium-catalyzed allylstannylation of alkynes. *Org. Lett.* **2000**, *2*, 2209–2211. [CrossRef] [PubMed]

15. Matsukawa, Y.; Asao, A.; Kitahara, H.; Yamamoto, Y. Lewis acid catalyzed allylstannylation of unactivated alkynes. *Tetrahedron* **1999**, *55*, 3779–3790. [CrossRef]

16. Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. Lewis acid Catalyzed *trans*-Allylsilylation of Unactivated Alkynes. *J. Am. Chem. Soc.* **1997**, *119*, 6781–6786. [CrossRef]

17. Shin, S.; RajanBabu, T.V. Regio- and Stereochemical Control in Bis-functionalization—Cyclization: Use of Alkene PreCURsors for Carbocyclic and Heterocyclic Synthesis. *J. Am. Chem. Soc.* **2001**, *123*, 8416–8417. [CrossRef] [PubMed]

18. Shinohara, Y.; Kudo, F.; Eguchit, T. A Natural Protecting Group Strategy to Carry an Amino Acid Starter Unit in the Biosynthesis of Macrolactam Polyketide Antibiotics. *J. Am. Chem. Soc.* **2011**, *133*, 18134–18137. [CrossRef] [PubMed]

19. Jie, M.; Pasha, M.K.; Syed-Rahmatullah, M.S.K. Fatty acids, fatty acid analogues and their derivatives. *Nat. Prod. Rep.* **1997**, *14*, 163–189. [CrossRef]

20. Shinohara, Y.; Kudo, F.; Eguchit, T. A Natural Protecting Group Strategy to Carry an Amino Acid Starter Unit in the Biosynthesis of Macrolactam Polyketide Antibiotics. *J. Am. Chem. Soc.* **2011**, *133*, 18134–18137. [CrossRef] [PubMed]

21. Winter, P.; Hiller, W.; Christmann, M. Access to Skipped Polyene Macrolides through Ring-Closing Metathesis: Total Synthesis of the RNA Polymerase Inhibitor Ripostatin B. *Angew. Chem. Int. Ed.* **2012**, *51*, 3396–3400. [CrossRef] [PubMed]

22. Tang, W.; Prusov, E.V. Total Synthesis of RNA-Polymerase Inhibitor Ripostatin B and 15-Deoxyripostatin A. *Angew. Chem. Int. Ed.* **2012**, *51*, 3401–3404. [CrossRef] [PubMed]

23. Eisch, J.J.; Merkley, J.H. Intramolecular coordinative assistance in the addition of Grignard reagents to unconjugated carbon-carbon unsaturation. *J. Organomet. Chem.* **1969**, *20*, P27–P31. [CrossRef]

24. Eisch, J.J.; Merkley, J.H.; Galle, J.E. Rearrangements of organometallic compounds. 16. Novel syntheses of α,β-unsaturated cyclopentenones via allylzincation of alkynes. *J. Am. Chem. Soc.* **1983**, *105*, 6761–6763. [CrossRef]

25. Miller, R.B.; Reichenbach, T. Grignard Addition to Alkynols. *Synth. Commun.* **1976**, *6*, 319–323. [CrossRef]
28. Richey, H.G.; Erickson, W.E.; Heyn, A.S. Promotion by primary and tertiary amine functions of additions of grignard reagents to alkenes and alkynes. Tetrahedron Lett. 1971, 12, 2183–2186. [CrossRef]

29. Mauzé, B.; Nivert, C.; Miginiac, L. Étude de l’addition des organozinciques α-éthyléniques aux amines éthyléniques, acényléniqnes et alléniques. J. Organomet. Chem. 1972, 44, 69–96. [CrossRef]

30. Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. First Exclusive Endo-dig Carbocyclization: HfCl₄-Catalyzed Intramolecular Allylislylation of Alkynes. J. Am. Chem. Soc. 1998, 120, 5339–5340. [CrossRef]

31. Asao, N.; Yoshikawa, E.; Yamamoto, Y. Lewis Acid-Catalyzed trans-Carbosilylation of Simple Alkynes. J. Org. Chem. 1996, 61, 4874–4875. [CrossRef]

32. Jung, I.N.; Yoo, B.R. Lewis Acid-Catalyzed trans-Carbosilylation of Simple Unsaturated Hydrocarbons. Synlett 1999, 519–528, 519–528. [CrossRef]

33. Ranu, B.C.; Majee, A. Indium-mediated regioselective Markovnikov alkylation of unactivated terminal alkynes. Chem. Commun. 1997, 13, 1225–1226. [CrossRef]

34. Araki, S.; Imai, A.; Shimizu, K.; Yamada, M.; Mori, A.; Butsugan, Y. Carboindation of Alkynes. Regio- and Stereoselective Allylation of Carbon-Carbon Triple Bonds of Alkynols by Allylic Indium Reagents. J. Org. Chem. 1995, 60, 1841–1847. [CrossRef]

35. Fujiwara, N.; Yamamoto, Y. Allyl- and Benzylindium Reagents. Carboindation of Carbon–Carbon and Carbon–Nitrogen Triple Bonds. J. Org. Chem. 1999, 64, 4095–4101. [CrossRef]

36. Klaps, E.; Schmid, W. Carboindation of Carbon–Carbon Triple Bonds: Regioselective Indium-Mediated Allylation of Functionalized Alkynes and Transformation into Halogen-Substituted 1,4-Dienes. J. Org. Chem. 1999, 64, 7537–7546. [CrossRef]

37. Goeta, A.; Salterb, M.M.; Shah, H. New indium-mediated cyclisation reactions of tethered haloenynes in aqueous solvent systems. Tetrahedron 2006, 62, 3582–3599. [CrossRef]

38. Salter, M.M.; Sardo-Inffiri, S. Novel Intramolecular Allylindination of Terminal Alkynes in Aqueous Media. Synlett 2002, 2068–2070. [CrossRef]

39. Araki, S.; Imai, A.; Shimizu, K.; Butsugan, Y. Carboindation of alkynols. A facile synthesis of yomogi alcohol. Tetrahedron Lett. 1992, 33, 2581–2582. [CrossRef]

40. Nishimoto, Y.; Moritoh, R.; Yasuda, M.; Baba, A. Regio- and Stereoselective Generation of Alkenylindium Compounds from Indium Tribromide, Alkynes, and Ketene Silyl Acetals. Angew. Chem. Int. Ed. 2009, 48, 4577–4580.

41. Nishimoto, Y.; Ueda, H.; Yasuda, M.; Baba, A. Carbogallation of Alkynes Using Gallium Tribromide and Silyl Ketene Acetals and Synthetic Application to Cross-Coupling with Aryl Iodides. Chem. Eur. J. 2011, 17, 11135–11138. [CrossRef] [PubMed]

42. Nishimoto, Y.; Takeuchi, M.; Yasuda, M.; Baba, A. Regio- and Stereoselective Carbobismuthination of Alkynes. Angew. Chem. Int. Ed. 2012, 51, 1051–1054. [CrossRef] [PubMed]

43. Nishimoto, Y.; Kang, K.; Yasuda, M. Regio- and Stereoselective Anti-Carbozincation of Alkynyl Ethers Using ZnBr₂ toward (Z)-β-Zincated Enol Ether Synthesis. Org. Lett. 2017, 19, 3927–3930. [CrossRef] [PubMed]

44. Nishimoto, Y.; Hirase, R.; Yasuda, M. Anti-Carboalumination of Alkynes Using Aluminum Trihalide and Silyl Ketene Imines: Stereo- and Regioselective Synthesis of Alkenylaluminum Compounds Bearing a Cyano Group. Org. Lett. 2018, 20, 3651–3655. [CrossRef] [PubMed]

45. Hayashi, N.; Hirokawa, H.; Shibata, I.; Yasuda, M.; Baba, A. Hydroindation of allenes and its application to radical cyclization. Org. Biomol. Chem. 2008, 6, 1949–1954. [CrossRef] [PubMed]

46. Lee, J.H.; Kim, S.; Lee, K.; Seomoon, D.; Kim, H.; Lee, S.; Kim, M.; Han, M.; Noh, K.; Livinghouse, T. Cyclization of 1-Bromo-2,7- and 1-Bromo-2,8-Enynes Mediated by Indium. Org. Lett. 2004, 6, 4825–4828. [CrossRef] [PubMed]

Sample Availability: Samples of the compounds are not available from the authors.