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Synthesis of arylboronates by boron-induced *ipso*-deantimonation of triarylstibanes with boron trihalides and its application in one-pot two-step transmetallation/cross-coupling reactions

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ABSTRACT

The reaction of triarylstibanes (**1**) with boron trihalides (BCl_3, and BBr_3) afforded arylboron dihalides (**2**) by utilizing all the three aryl groups on the antimony. Boron intermediates (**2**) were transformed to arylboronates (**3**) in good to excellent yields by treatment with methanol and 1,3-propanediol. Further, the Pd-catalyzed reactions of **2** with organic halides such as 1-bromonaphthalene and benzoyl chloride in the presence of H_2O afforded the corresponding cross-coupling products, unsymmetrical biaryls (**4**) and ketones (**5**), in moderate to good yields. The potential energy surfaces for the transmetallations of triarylstibanes (**1**) with BCl_3 affording **2** were determined by molecular orbital calculations. The analyses of substituent effects on theoretically calculated reactivities showed the importance of the resonance effects of the ring substituents on these transmetallations.

Introduction

The synthetic application of organic and inorganic antimony compounds has attracted much interest [1]. With regard to the application of trivalent organoantimony compounds (stibanes), a wide variety of reactions such as self-coupling reaction [2], cross-coupling reaction [3], photoreaction [4], oxidation [5], and asymmetric reaction with optically active organoantimony compounds [6] have been reported during the last two decades. Recently, we reported that trivalent organoantimony compounds such as aryl- and ethynylstibanes are useful transmetallating agents for Pd-catalyzed cross-coupling reactions with organic halides [7,8]. In particular, hypervalent organoantimony compounds, *Sb*-ethynyl- and *Sb*-aryl-1,5-azastibocine having Sb–N intramolecular coordination, found to be powerful transmetallating agents; they could be coupled to acyl chlorides and aryl halides to afford the corresponding ethynylketones, diarylacetylenes, and diarylketones [8]. For example, the reaction of *Sb*-phenyl-1,5-azastibocine with benzoyl chloride in the presence of $PdCl_2(PPh_3)_2$ as a catalyst gave benzophenone in 78% yield. However, non-activated triphenylstibane was ineffective in the same reaction (4% yield, Scheme 1) [8c].

On the other hand, arylborons play an important role in organic synthesis [9], in particular, for the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction using arylboronic acids and boronates for carbon–carbon bond formation [10]. Several approaches for the synthesis of arylboron derivatives have been reported [11]. Among those, Group 14 compounds such as arylsilanes [12] and arylstannanes [13] are known to undergo *ipso*-substitution, allowing smooth transmetallation from silicon and tin to boron by reacting with boron halides (BX_3, X = Cl, Br), affording $ArBX_2$. Furthermore, Snieckus recently reported that this type of boron-induced *ipso*-desilylation of arylsilanes followed by a Pd-catalyzed reaction with aryl halides provides an in situ Suzuki coupling protocol to afford biaryl compounds [12f]. Recently, we also reported that the

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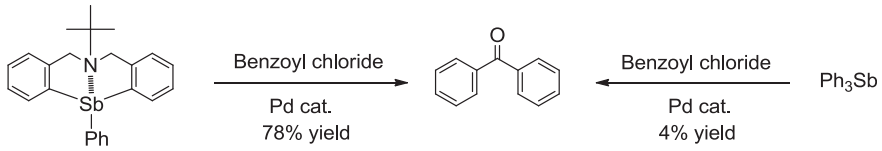


Scheme 1. Cross-coupling reactions of organoantimony(III) compounds with benzoyl chloride.

reaction of triarylstibanes (**1**) with boron trichloride was converted to $ArBCl_2$ (**2**), which was then transformed to arylboronates (**3**) [14]. Herein, we report the complete results of the transmetallation of **1**–**3** and their application in a one-pot two-step transmetallation/cross-coupling reaction for the preparation of unsymmetrical biaryls (**4**) and arylketones (**5**) from non-activated triarylstibanes (Scheme 2). Moreover, the potential energy surfaces for the transmetallations of **1** and boron trihalides forming **2** were determined by molecular orbital calculations.

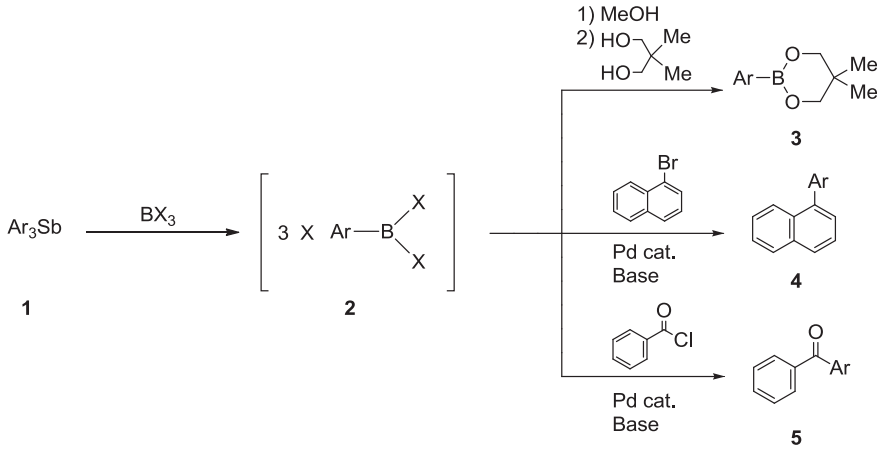
Results and discussion

Synthesis of arylboronates by using boron-induced ipso-deantimonation of triarylstibanes with boron trihalides

Previously, we reported that the reaction of triphenylpnictogen compounds (Ph_3P, Ph_3As, Ph_3Sb, and Ph_3Bi) with BCl_3, followed by quenching with methanol and derivatization with 2,2-dimethyl-1,3-propanediol; triphenylstibane (**1a**) smoothly afforded phenylboronate (**3a**) [14]. To evaluate the generality and applicability of this transmetallation, we examined the reaction between BX_3 (X = Cl, Br, OEt, H) and diverse triarylstibanes. The results and reaction conditions are summarized in Table 1. First, we studied the reactivity of BX_3 as the electrophile. The reaction of **1a** with diverse boron reagents was performed under previous conditions (0 °C, 2 h) (Table 1, entries 1–4). Boron trihalides (BCl_3, and BBr_3) afforded the expected product, arylboronate (**3a**), in an excellent yield, and other boron regents were ineffective. Next, the substrate scope of this transmetallation was evaluated by investigating the reaction of boron trihalides with diverse triarylstibanes (**3b**–**o**) (Table 1, entries 5–18). The reaction of **1b**–**l** with BCl_3 at 0 °C for 2 h, followed by treatment with methanol and 2,2-dimethyl-1,3-propanediol gave arylboronate (**3b**–**l**) in moderate to good yields by utilizing the three aryl groups on the antimony (Table 1, entries 5–15). In the case of **1m**–**o** containing more electron-withdrawing groups on the phenyl rings, the same reaction using BBr_3 instead of BCl_3 at room temperature afforded the corresponding **3m**–**o** in 40–73% yields, even though a prolonged reaction time was required (Table 1, entries 16–18). This result shows that present reaction is affected by the substituents on the phenyl rings in the starting antimony compounds and on boron reagents. A detailed substituent effect is discussed in the molecular orbital calculation section. Arylsilanes have a tendency to undergo *ipso*-substitution allowing the smooth transmetallation from Si to B by treatment with boron halides, affording $ArBX_2$ [12]. In the case of tris(4-trimethylsilylphenyl)stibane (**1e**), the reaction afforded only **3e** in high yields, and the carbon–silicon bond was not affected (Table 1, entry 8). A double transmetallation from Sb and Si to B was not detected even when BBr_3 was used as the electrophile. This result indicates that the reactivity of the *ipso*-position on the antimony part is higher than that of the silicon part. The reaction of arylstibane bearing two *ortho*-substituents afforded arylboronates (**3d**) in a good yield (Table 1, entry 7). Notably, the reaction proceeded smoothly with sterically hindered arylstibane. In addition, the reaction of **1j** also gave the corresponding heterocyclic boronate (**3j**) (Table 1, entry 13). Unfortunately, the reaction of tris(4-cyanophenyl)-, tris(4-ethoxycarbonyl)-, and tris(pentafluorophenyl)stibane resulted in a complex mixture and did not afford the desired transmetallating products.

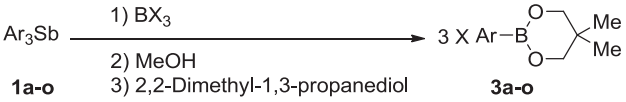
In-situ boron-induced ipso-deantimonation of triarylstibanes and Pd-catalyzed cross-coupling reaction

The Pd-catalyzed cross-coupling reaction of aryl halides by the in-situ formation of arylboron derivatives has recently attracted much attention [12f,15]. Therefore, we investigated whether the transmetallation of **1**–**2** could be extended to the synthesis of unsymmetrically substituted biaryls and ketones by a one-pot, two-step transmetallation/cross-coupling reaction. In this manner, the non-activated trivalent antimony compounds could be utilized in carbon–carbon bond formation. This method was performed by adding aryl halide after the completion of the borylation step in the same reaction flask. After **1** was converted to **2** using the standard protocol (Table 1), 1-bromonaphthalene was added to the reaction



Scheme 2. Boro-induced *ipso*-deantimonation and its application.

Table 1
Transmetallation of triarylstibanes into arylboronates.[a]



1a-o **3a-o**

Entry	Substrate	Ar	BX_3	Temp. (°C)	Time (h)		Yield(%)[b]
1	**1a**	Phenyl	BCl_3	0	2	**3a**	88
2	**1a**	Phenyl	BBr_3	0	2	**3a**	84
3	**1a**	Phenyl	$B(OEt)_3$	0	2	**3a**	0 (92)[c]
4	**1a**	Phenyl	BH_3·THF	0	2	**3a**	0 (98)[c]
5	**1b**	4-Methoxyphenyl	BCl_3	0	2	**3b**	57
6	**1c**	4-*tert*-Butylphenyl	BCl_3	0	2	**3c**	79
7	**1d**	2,4,6-Trimethylphenyl	BCl_3	0	2	**3d**	60
8	**1e**	4-Trimethylsilylphenyl	BCl_3	0	2	**3e**	81
9	**1f**	4-Methylphenyl	BCl_3	0	2	**3f**	85
10	**1g**	3-Methylphenyl	BCl_3	0	2	**3g**	83
11	**1h**	2-Methylphenyl	BCl_3	0	2	**3h**	68
12	**1i**	1-Naphthyl	BCl_3	0	2	**3i**	80
13	**1j**	2-Benzo[*b*]thienyl	BCl_3	0	2	**3j**	78
14	**1k**	4-Fluorophenyl	BCl_3	0	2	**3k**	83
15	**1l**	4-Chlorophenyl	BCl_3	0	2	**3l**	92
16	**1m**	4-Trifluoromethylphenyl	BBr_3	rt	4	**3m**	73 (17)[d]
17	**1n**	3,5-Dichlorophenyl	BBr_3	rt	24	**3n**	68 (23)[d]
18	**1o**	3,5-Bis(trifluoromethyl)phenyl	BBr_3	rt	24	**3o**	40 (ND)[d]

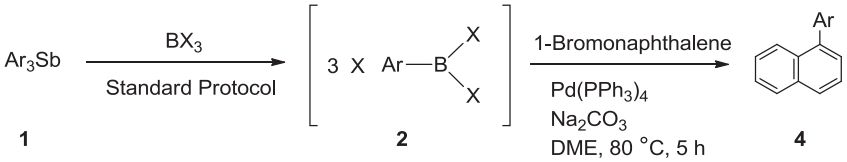
[a] All reaction were carried out using Ar3Sb (1 mmol), BX3 (3.6 mmol), MeOH (3 mL) and propanediol (10 mmol).
[b] Isolated yield.
[c] Recovery of **1a**.
[d] Using BCl_3 at room temperature for 24 h in parenthesis.

mixture as the electrophile of the coupling reaction, followed by 1,2-dimethoxyethane, 5 mol% $Pd(PPh_3)_4$, and 2 M Na_2CO_3 aqueous solution. Then, the reaction mixture was heated at 80 °C for 5 h to afford the biaryl products (**4**). The results are summarized in Table 2; in general, moderate yields were obtained without homo-coupling products. Furthermore, arylketones (**5**) were also obtained in moderate yields when benzoyl chloride was treated with **2** using 5 mol% $PdCl_2(PPh_3)_2$ and $K_3PO_4 \cdot nH_2O$ in toluene at 100 °C for 3 h along with a small amount of homo-coupling products biaryl (4–6%) (Table 3). When the reaction was performed in the absence of water or water of crystallization present in a base, the yields of the coupling products **4a** (5%) and **5a** (6%) were unsatisfactory because of the incomplete conversion from **2** to arylboronic acids. These results are the first examples of cross-coupling reaction between non-activated triarylstibanes and electrophiles such as aryl bromide and benzoyl chloride even though it is a two-step reaction via the transmetallation of triarylstibanes to arylboron dihalides.

Theoretical investigation of the mechanisms of boron-induced ipso-deantimonations

We elucidated the mechanisms of these transmetallations using the molecular orbital theory to provide useful information on the molecular design of various arylboronates [16]. The potential energy surface for the transmetallation of **1a** and BCl_3 affording phenylboron dichloride (**2a**) is shown as a plotted line of **a** in Fig. 1. First the reaction affords coordination compound **14a** as the kinetic product through transition state **13a**. Next, the electrophilic attack of BCl_3 on the *ipso*-position of **1a** forms transition state **7a** with a similar structure as the Wheland complex. This is the rate-

Table 2
Preparation of biaryls by using one-pot two-step transmetallation/cross-coupling reactions.[a]

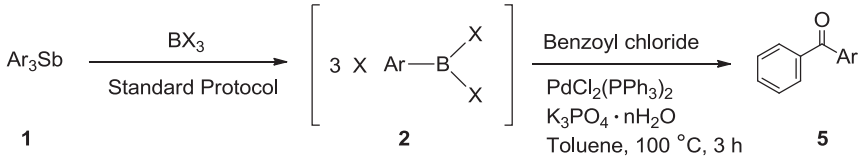


1 **2** **4**

Entry	Substrate	Ar	Yield (%)[b]
1	**1a**	Phenyl	**4a**: 76
2	**1b**	4-Methoxyphenyl	**4b**: 87
3	**1f**	4-Methylphenyl	**4f**: 58
4	**1i**	1-Naphthyl	**4i**: 98
5	**1j**	2-Benzo[*b*]thienyl	**4j**: 52
6	**1l**	4-Chlorophenyl	**4l**: 77
7	**1m**	4-Trifluoromethylphenyl	**4m**: 57

[a] **1** (0.5 mmol), boron trihalide (1.8 mmol), 1-bromonaphthalene (1.0 mmol), $Pd(PPh_3)_4$ (5 mol%), 2 M Na_2CO_3 aq (9.6 mmol).
[b] Isolated yield.

Table 3
Preparation of ketones by using one-pot two-step transmetallation/cross-coupling reactions.[a]



Entry	Substrate	Ar	Yield (%)[b]
1	**1a**	Phenyl	**5a**: 66
2	**1b**	4-Methoxyphenyl	**5b**: 70
3	**1f**	4-Methylphenyl	**5f**: 76
4	**1i**	1-Naphthyl	**5i**: 73
5	**1j**	2-Benzo[*b*]thienyl	**5j**: 78
6	**1l**	4-Chlorophenyl	**5l**: 84
7	**1m**	4-Trifluoromethylphenyl	**5m**: 49

[a] **1** (0.5 mmol), boron trihalide (1.8 mmol), benzoyl chloride (1.5 mmol), $Pd(PPh_3)_4$ (5 mol%), $K_3PO_4 \cdot nH_2O$ (6 mmol).
[b] Isolated yield.

determining step of this transmetallation; the activation energy is 18.1 kcal mol^{-1}. Then, the Ph_2Sb moiety rearranges on the *ortho*-position to afford intermediate **9a**. In the next step, a bond formation between one of the Cl atoms and Sb smoothly afforded the thermodynamic product **11a** which is a complex of **2a** and Ph_2SbCl. The structure of the transition state **10a** is close to that of **9a**.

As mentioned above, the transition-state structure of the rate-determining step is **7a** which is the key to explain the reactivities of the transmetallation of **1a** and various BX_3 reagents. Because of the negative charge on the boron atom in **7a**, the electron-withdrawing nature of Cl and Br in BX_3 makes **7a** stable. On the other hand, the electron-donating nature of the MeO group and H in BX_3 makes **7a** unstable. Therefore, boron trihalides (BCl_3 and BBr_3) afforded **3a** in an excellent yield, while other boron reagents (BH_3 and $B(OMe)_3$) showed no activity. We also determined the potential energy surfaces for the transmetallations of **1** with various ring substituents such as *p*-NH_2 (**p**), *p*-MeO (**b**), *p*-Me (**f**), *p*-MeO-*m*-Cl (**q**), *p*-Cl (**l**), *m*-Cl (**r**), *p*-CN (**s**), and *p*-CF_3 (**m**), as shown in Fig. 1. All these reaction coordinates are similar to those of the unsubstituted derivative (**a**). First, the reactions afforded coordination compounds **14** as the kinetic product through the transition state (**13**). The larger the electron-donating ability of the ring substituents to stabilize the cationic center of Sb in **13**, the smaller is the activation energy of the reactions. Next, the electrophilic attack of BCl_3 on the *ipso*-position of **1** forms the rate-determining transition state **7** in which positive charges are generated at the *ortho* and *para* positions. The larger electron-donating ability of the ring substituents to stabilize **7**, the smaller is the activation energy of the reactions. This explained the remarkably decreased yields in the reactions of **m**, **n**, and **o** containing strong electron-withdrawing groups on the phenyl rings. Then, the reactions afforded intermediate **8** or **9**, followed by the rapid rearrangement of chloride ions to afford the thermodynamic product (**11**). The activation energies obtained were analyzed in terms of the Yukawa–Tsuno equation (1) to understand the detailed natures of the transition states.

$$\Delta\Delta E_X = \rho\left(\sigma^0 + r\Delta\overline{\sigma}_R^+\right) \quad (1)$$

Thus, the reaction affording kinetic product **14** has a ρ value of −5.9 and an *r* value of 0.10 with an excellent correlation coefficient of 0.998. The ρ value on the gas phase stabilities of cumyl cations is −26.4 at the same theoretical level. The small ρ value of this reaction shows that a small positive charge is generated at the cationic Sb atom. By definition, the *r* value, which is a measure of the degree of resonance, becomes unity ($r = 1.00$) for the gas-phase stabilities of cumyl cations. The small *r* value of this reaction shows little resonance interaction between the cationic Sb and ring substituents. The reaction affording thermodynamic product **11** has a ρ value of −12.3 and an *r* value of 0.91 with an excellent correlation coefficient of 0.993. The unremarkable ρ value shows that the charge separation in transition state **7** is insignificant. However, a significant *r* value was observed, indicating that the resonance ability of the ring substituents play an important role in promoting this transmetallation. These analyses of substituent effects were applied to the activation energies calculated in the gas phase, while actual reactions occurred in the solution phase. However, it has been shown that the *r* values of the reactions through cationic transition states in the solution phase are the same as those obtained for the corresponding stabilities in the gas phase [17]. This indicates that the order of reactivities for the respective ring-substituted derivatives obtained in these calculations is the same as that in the actual reactions in the solutions. Therefore, these analyses of substituent effects quantitatively predict the reactivities of the corresponding ring-substituted derivatives. Calculated energies were refined by thermal corrections and single-point DFT calculations. These methods brought little change in both the shape of potential energy surfaces and the *r* values, showing contributions of the entropy term and the electron correlation are negligible.

Conclusion

The reaction of triarylstibanes with boron trihalides (BCl_3 and BBr_3) followed by the derivatization with methanol and 1,3-propanediol afforded arylboronates in good to excellent yields by utilizing all the three aryl groups on the antimony. Further, a one-pot two-step method for the synthesis of unsymmetrical biaryls (**4**) and ketones (**5**) was developed by employing the Pd-catalyzed cross-coupling reaction of 1-bromonaphthalene and benzoyl chloride via the boron-induced *ipso*-deantimonation of triarylstibanes with boron trihalides. These reactions resulted from the cross-coupling reaction of non-active triarylstibanes having electron-donating and −withdrawing substituents by one-pot two-step reactions. The potential energy surfaces for the transmetallations of triarylstibanes (**1**) containing various ring substituents on the phenyl rings and BCl_3 affording arylboron dichloride (**2**) were determined by molecular orbital calculations. Apparently, all these transmetallations are initiated by the electrophilic attack at the *ipso*-position of **1** by BCl_3 to afford the Wheland-type rate-determining transition states. The resulting

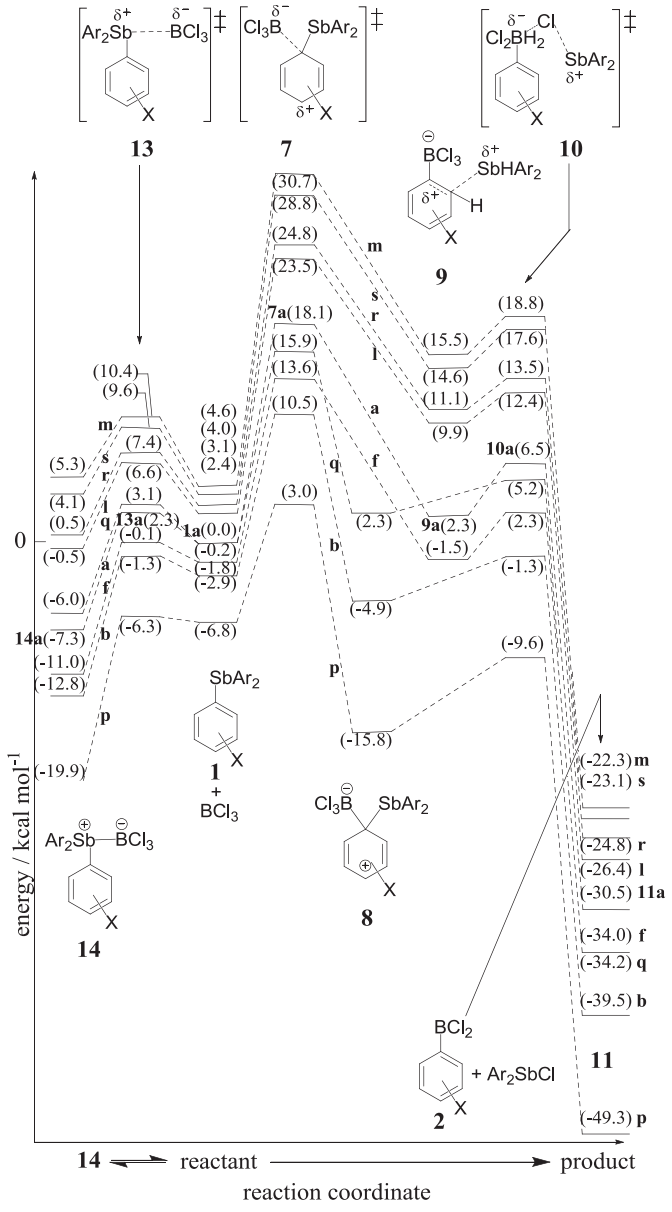


Fig. 1. Calculated reaction coordinates relevant to the transmetallation of **1** and BCl_3 forming **2**. Numbers of parentheses are relative energies against unsubstituted reactant (**1a** + BCl_3).

activation energies were applied for the analyses of substituent effects using the Yukawa–Tsuno equation. A significant *r* value of 0.91 indicates that the resonance contributions from the ring substituents play an important role in promoting these transmetallations. Further functional group exchange reactions of triarylstibanes with other electrophiles and cross-coupling reactions via the boron-induced *ipso*-deantimonation of triarylstibanes with boron trihalides are currently in progress and will be reported in the future.

Experimental

General

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus (MP–S3) and are not corrected. ^{1}H NMR (TMS: δ: 0.00 as an internal standard) and ^{13}C NMR ($CDCl_3$: δ: 77.00 as an internal standard) spectra were recorded on a JEOL JNM-ECA400 (400 MHz and 100 MHz) spectrometers in $CDCl_3$ unless otherwise stated. Mass spectra (MS) were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA). All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey–Nagel Pre-coated TLC plates Sil G25 UV_{254}. Triphenylstibane (**1a**) was purchased from Sigma–Aldrich, Inc., USA, and **1b** [18], **1d** [19], **1f** [19], **1g** [20], **1h** [19], **1i** [21], **1k** [5], **1l** [5,18], and **1m** [5,18] were prepared according to the reported procedures.

*Preparation of triarylstibanes (**1c**, **1e**, **1j**, **1n** and **1o**)*

*Synthesis of tris(4-tert-butylphenyl)stibane (**1c**)*

A solution of antimony (III) chloride (6.16 g, 27.0 mmol) in ether (60 mL) was added to (4-tert-butylphenyl)magnesium bromide (2.0 M in ether, 48 mL, 96.0 mmol) at 0 °C for 30 min. The resulting mixture was gradually raised to room temperature and stirred for 16 h. The reaction mixture was diluted with chloroform (150 mL) at 0 °C, added with water (1 mL) and vigorous stirred for a while. Then anhydrous magnesium sulfate was added and the mixture was refluxed in a water bath for 10 min, and filtration. This work-up was repeated until all the content dissolved in the chloroform (150 mL × 4). The combined extracts were dried over anhydrous magnesium sulfate. The organic layer was concentrated under reduced pressure. The residue was purified by recrystallization to give **1c** (10.8 g, 77% yield). Colorless prisms (mp 267–270 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (27H, s), 7.34 (6H, d, J = 7.8 Hz), 7.39 (6H, d, J = 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.26 (q), 34.61 (s), 125.80 (d), 134.78 (s), 135.99 (d), 151.36 (s). LRMS (EI) *m/z*: 520 (32), 387 (5), 254 (100). Anal. Calc. for $C_{30}H_{39}Sb$: C, 69.11; H, 7.54. Found: C, 69.30; H, 7.45.

*Synthesis of tris(4-trimethylsilylphenyl)stibane (**1e**)*

To a solution of (4-Bromophenyl)trimethylsilane (2.29 g, 10.0 mmol) in ether (15 mL), BuLi (1.63 M in hexane, 6.3 mL, 10.3 mmol) was added using syringe through septum cap at 0 °C for 30 min, and the mixture was stirred for 1 h at 0 °C. After the mixture was raised gradually to room temperature, the stirring was continued for 1.5 h. To the reaction mixture a solution of antimony (III) chloride (684 mg, 3.0 mmol) in ether (8 mL) was added dropwise at 0 °C, and the resulting mixture was gradually raised to room temperature and stirred overnight. The reaction mixture was diluted with dichloromethane (20 mL), and quenched with water. The mixture was extracted with dichloromethane (20 mL). The combined extracts were washed with brine and dried over anhydrous magnesium sulfate. The dried organic layer was concentrated under reduced pressure. The residue was purified by recrystallization to give **1e** (1.0 g, 59% yield). Colorless prisms (mp 209–211 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.29 (27H, s), 7.48 (6H, d, J = 7.3 Hz), 7.51 (6H, d, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.20 (q), 133.63 (d), 135.53 (d), 138.98 (s), 140.76 (s). LRMS (EI) *m/z*: 568 (14), 533 (7), 480 (6), 417 (6), 346 (21), 283 (100), 270 (23), 207 (18). Anal. Calc. for $C_{27}H_{39}SbSi$: C, 56.93; H, 6.90. Found: C, 56.53; H, 6.63.

*Synthesis of tris-2-benzo[b]thiophenylstibane (**1j**)*

To a solution of Benzo[*b*]thiophene (7.96 g, 59.4 mmol) was dissolved in THF (110 mL), BuLi (1.58 M in hexane, 41.4 mL, 65.3 mmol) was added using syringe through septum cap at −78 °C for 30 min, and the mixture was stirred for 2 h from −78 °C to −10 °C. To the reaction mixture a solution of antimony (III)

bromide (5.97 g, 16.5 mmol) in THF (50 mL) was added dropwise at −10 °C, and the resulting mixture was gradually raised to room temperature and stirred overnight. The reaction mixture was diluted with ether (200 mL) quenched with water and insoluble substances were filtered off. The mixture was extracted with ether (200 mL). The combined extracts were washed with brine and dried over anhydrous magnesium sulfate. The dried organic layer was concentrated under reduced pressure. The residue was purified on silica gel column chromatography (hexane:CH_2Cl_2 = 4:1) to give **1j** (4.6 g, 54% yield). Colorless needles (mp 205–207 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.36 (6H, m), 7.63 (3H, s), 7.79 (3H, d, J = 7.8 Hz), 7.83 (3H, d, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 122.04 (d), 123.51 (d), 124.22 (d), 124.57 (d), 134.31 (s), 134.71 (d), 140.56 (s), 144.85 (s). LRMS (EI) m/z: 520 (25), 266 (100), 254 (52), 134 (3). Anal. Calc. for $C_{24}H_{15}S_3Sb$: C, 55.29; H, 2.90. Found: C, 55.11; H, 3.06.

*Synthesis of tris(3,5-dichlorophenyl)stibane (**1n**) and tris[3,5-bis(trifluoromethyl)phenyl]stibane (**1o**): general procedure*

3,5-Dichloro-1-bromobenzene (7.46 g, 33.0 mmol) or 3,5-bis(trifluoromethyl)-1-bromobenzene (9.67 g, 33.0 mmol) was dissolved in ether (70 mL). To this solution, BuLi (1.58 M in hexane, 20.9 mL, 33.0 mmol) was added using syringe through septum cap at −78 °C for 20 min, and the mixture was stirred for 2 h at −78 °C. To the reaction mixture a solution of antimony (III) boromide (3.61 g, 10.0 mmol) in ether (50 mL) was added dropwise at −78 °C, and the resulting mixture was gradually raised to room temperature and stirred overnight. The reaction mixture was diluted with ether (150 mL) quenched with water. The mixture was extracted with ether (150 mL). The combined extracts were washed with brine and dried over anhydrous magnesium sulfate. The dried organic layer was concentrated under reduced pressure. The residue was purified on silica gel column chromatography to give **1n** (hexane, 4.5 g, 80% yield) and **1o** (hexane:CH_2Cl_2 = 4:1, 6.9 g, 91% yield).

*Tris(3,5-dichlorophenyl)stibane (**1n**)*: Colorless prisms (mp 136–137 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (6H, s), 7.40 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.95 (d), 133.56 (d), 136.25 (s), 139.96 (s). LRMS (EI) m/z: 560 (19), 413 (19), 268 (100). Anal. Calc. for $C_{18}H_9Cl_6Sb$: C, 38.62; H, 1.62. Found: C, 38.66; H, 1.85.

*Tris[3,5-bis(trifluoromethyl)phenyl]stibane (**1o**)*: Pale yellow prisms (mp 113–115 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (6H, s), 7.95 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 122.89 (d), 124.01 (d), 132.66 (q), 135.62 (d), 139.24 (s). LRMS (EI) m/z: 760 (8), 741 (11), 547 (12), 407 (100). Anal. Calc. for $C_{24}H_9F_{18}Sb$: C, 37.88; H, 1.19. Found: C, 37.95; H, 1.49.

Reaction of triarylstibanes with boron trihalides: general procedure

All reactions were carried out under argon using standard Schlenk techniques. Boron trichloride (1.0 M solution in dichloromethane, 1.8 mL, for **1a**–**l**) or boron tribromide (1.0 M solution in dichloromethane, 1.8 mL, for **1m**–**o**) was added to a stirred solution of triarylstibane **1a**–**o** (0.5 mmol) in dichloromethane (0.5 mL) at 0 °C. The mixture was stirred for 2 h at 0 °C (for **1a**–**l**) or 4 h at room temperature (for **1m**) or 24 h at room temperature (for **1n** and **1o**). The solvent was removed under reduced pressure at room temperature and the residual oil was dissolved in methanol (1.5 mL). After the mixture was stirred for 30 min, 2,2-dimethyl-1,3-propanediol (5.0 mmol) was added and the stirring was continued for 1 h. The solvent was removed under reduced pressure. The residue was purified on silica gel column chromatography (hexane: CH_2Cl_2) to give arylboronate **3**. The products were confirmed by comparison of NMR data and MS spectra with that in the literature.

*5,5-Dimethyl-phenyl-1,3,2-dioxaborinane (**3a**)* [14]: Colorless plates (mp 62–64.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (6H, s), 3.78 (4H, s), 7.27–7.44 (3H, m), 7.81 (2H, d, J = 6.9 Hz).

*5,5-Dimethyl-2-(4-methoxyphenyl)-1,3,2-dioxaborinane (**3b**)* [14]: Colorless prisms (mp 54–56 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.01 (6H, s), 3.75 (4H, s), 3.82 (3H, s), 6.88 (2H, d, J = 8.7 Hz), 7.74 (2H, d, J = 8.7 Hz).

*5,5-Dimethyl-2-(4-t-butylphenyl)-1,3,2-dioxaborinane (**3c**)* [22]: Colorless prisms (mp 78–78.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.01 (6H, s), 1.32 (9H, s), 3.76 (4H, s), 7.39 (2H, d, J = 8.2 Hz), 7.74 (2H, d, J = 8.2 Hz).

*5,5-Dimethyl-2-(2,4,6-trimethylphenyl)-1,3,2-dioxaborinane (**3d**)* [23]: Colorless prisms (mp 45–46.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.09 (6H, s), 2.23 (3H, s), 2.35 (6H, s), 3.77 (4H, s), 6.77 (2H, s).

*5,5-Dimethyl-2-(4-trimethylsilylphenyl)-1,3,2-dioxaborinane (**3e**)* [24]: Colorless prisms (mp 73.5–75 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.30 (9H, s), 1.05 (6H, s), 3.80 (4H, s), 7.55 (2H, d, J = 7.8 Hz), 7.81 (2H, d, J = 7.8 Hz).

*5,5-Dimethyl-2-(4-methylphenyl)-1,3,2-dioxaborinane (**3f**)* [14]: Colorless plates (mp 92–95 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.01 (6H, s), 2.36 (3H, s), 3.75 (4H, s), 7.17 (2H, d, J = 7.8 Hz), 7.69 (2H, d, J = 7.8 Hz).

*5,5-Dimethyl-2-(3-methylphenyl)-1,3,2-dioxaborinane (**3g**)* [25]: Colorless prisms (mp 94–95 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (6H, s), 2.35 (3H, s), 3.77 (4H, s), 7.24–7.62 (4H, m).

*5,5-Dimethyl-2-(2-methylphenyl)-1,3,2-dioxaborinane (**3h**)* [14]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03 (6H, s), 2.51 (3H, s), 3.77 (4H, s), 7.13–7.29 (3H, m), 7.72 (1H, d, J = 7.3 Hz).

*5,5-Dimethyl-2-(1-naphthyl)-1,3,2-dioxaborinane (**3i**)* [14]: Colorless prisms (mp 68–70 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10 (6H, s), 3.89 (4H, s), 7.44–7.51 (3H, m), 7.82 (1H, d, J = 8.7 Hz), 7.89 (1H, d, J = 8.3 Hz), 8.03 (1H, d, J = 6.9 Hz), 8.73 (1H, d, J = 8.2 Hz).

*5,5-Dimethyl-2-(2-benzo[b]thienyl)-1,3,2-dioxaborinane (**3j**)* [26]: Colorless prisms (mp 138–139.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (6H, s), 3.79 (4H, s), 7.31–7.36 (2H, m), 7.81 (1H, s), 7.83–7.90 (2H, m).

*5,5-Dimethyl-2-(4-fluorophenyl)-1,3,2-dioxaborinane (**3k**)* [14]: Colorless needles (mp 65–67 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (6H, s), 3.76 (4H, s), 7.00–7.05 (2H, m), 7.76–7.80 (2H, m).

*5,5-Dimethyl-2-(4-chlorophenyl)-1,3,2-dioxaborinane (**3l**)* [14]: Colorless plates (mp 97–99 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03 (6H, s), 3.77 (4H, s), 7.33 (2H, d, J = 8.2 Hz), 7.73 (2H, d, J = 8.2 Hz).

*5,5-Dimethyl-2-(4-trifluoromethylphenyl)-1,3,2-dioxaborinane (**3m**)* [22]: Colorless needles (mp 106–108 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03 (6H, s), 3.79 (4H, s), 7.59 (2H, d, J = 7.8 Hz), 7.90 (2H, d, J = 7.8 Hz).

*5,5-Dimethyl-2-(3,5-dichlorophenyl)-1,3,2-dioxaborinane (**3n**)*: Colorless prisms (mp 64–66 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.01(6H, s), 3.76 (4H, s), 7.39 (1H, t, J = 1.8 Hz), 7.63 (2H, d, J = 1.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.80 (q), 31.88 (s), 72.39 (t), 130.45 (d), 131.91 (d), 134.50 (s). LRMS (EI) m/z: 258 (100), 187 (8). Anal. Calc. for $C_{11}H_{13}BCl_2O_2$: C, 51.02; H, 5.06. Found: C, 51.13; H, 4.98.

*5,5-Dimethyl-2-[3,5-bis(trifluoromethyl)phenyl]-1,3,2-dioxaborinane (**3o**)*: Colorless prisms (mp 89–93 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (6H, s), 3.81 (4H, s), 7.91 (1H, s), 8.24 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.80 (q), 31.96 (s), 72.46 (t), 123.64 (d), 124.14 (d), 130.61 (q), 133.83 (d). LRMS (EI) m/z: 326 (100), 307 (60), 283 (65), 255 (20). Anal. Calc. for $C_{13}H_{13}BF_6O_2$: C, 47.89; H, 4.02. Found: C, 47.40; H, 4.03.

One-pot two-step transmetallation/cross-coupling reactions

Synthesis of unsymmetrical biaryls: general procedure

All reactions were carried out under argon using standard Schlenk techniques. Boron trichloride (1.0 M solution in

dichloromethane, 1.8 mL, for **1a**, **1b**, **1f**, **1i**, **1j**, and **1l**) or boron tribromide (1.0 M solution in dichloromethane, 1.8 mL, for **1m**) was added to a stirred solution of triarylstibane (0.5 mmol) in dichloromethane (0.5 mL) at 0 °C. The mixture was stirred for 2 h at 0 °C (for **1a**, **1b**, **1f**, **1i**, **1j**, and **1l**) or 4 h at room temperature (for **1m**). The solvent was removed under reduced pressure at room temperature and the residual oil was dissolved in 1,2-dimethoxyethane (20 mL). Then 1-bromonaphthalene (1.0 mmol) and 2.0 M Na_2CO_3 solution (4.8 mL) was added, the mixture was stirred for 10 min at room temperature. After the addition of $Pd(PPh_3)_4$ (0.05 mmol), the reaction mixture was stirred at 80 °C for 5 h. The reaction mixture was diluted with ether (50 mL) quenched with water. The mixture was extracted with ether (50 mL). The combined extracts were washed with water and brine. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified on silica gel column chromatography to give **4a**, **4f**, **4i**, **4l**, **4m** (hexane) and **4b**, **4j** (hexane: dichloromethane). The products were confirmed by comparison of NMR data and MS spectra with that in the literature.

*1-Phenylnaphthalene (**4a**)* [27]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.54 (9H, m), 7.86 (1H, d, J = 8.2 Hz), 7.90 (2H, d, J = 8.7 Hz).

*1-(4-Methoxyphenyl)-naphthalene (**4b**)* [28]: Colorless needles (mp 116–117 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.89 (3H, s), 7.02–7.04 (2H, m), 7.39–7.53 (6H, m), 7.83–7.93 (3H, m).

*1-(4-Methylphenyl)-naphthalene (**4f**)* [27]: Colorless prisms (mp 53–54 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (3H, s), 7.30 (2H, d, J = 7.8 Hz), 7.38–7.53 (6H, m), 7.84 (1H, d, J = 8.2 Hz), 7.91 (2H, t, J = 9.2 Hz).

*1,1′-Binaphthyl (**4i**)* [29]: Colorless prisms (mp 163–165 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24–7.60 (10H, m), 7.93–7.96 (4H, m).

2-(1-Naphthalenyl)-benzo[b]thiophene (4j) [30]: Colorless plates (mp 106–108 °C). 1H NMR (400 MHz, CDCl3) δ: 7.35–7.43 (2H, m), 7.46 (1H, s), 7.51–7.55 (3H, m), 7.66 (1H, d, J = 7.3 Hz), 7.84–7.92 (4H, m), 8.29 (1H, d, J = 8.7 Hz).

*1-(4-Chlorophenyl)-naphthalene (**4l**)* [31]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.53 (8H, m), 7.83–7.91 (3H, m).

*1-(4-Trifluoromethylphenyl)-naphthalene (**4m**)* [32]: Colorless plates (mp 44–45 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.56 (4H, m), 7.62 (2H, d, J = 7.8 Hz), 7.76 (2H, d, J = 8.2 Hz), 7.81 (1H, d, J = 8.2 Hz), 7.92 (2H, t, J = 8.5 Hz).

Synthesis of unsymmetrical ketones: general procedure

All reactions were carried out under argon using standard Schlenk techniques. Boron trichloride (1.0 M solution in dichloromethane, 1.8 mL, for **1a**, **1b**, **1f**, **1i**, **1j**, and **1l**) or boron tribromide (1.0 M solution in dichloromethane, 1.8 mL, for **1m**) was added to a stirred solution of triarylstibane (0.5 mmol) in dichloromethane (0.5 mL) at 0 °C. The mixture was stirred for 2 h at 0 °C (for **1a**, **1b**, **1f**, **1i**, **1j**, and **1l**) or 4 h at room temperature (for **1m**). The solvent was removed under reduced pressure at room temperature and the residual oil was dissolved in toluene (5 mL). Then $K_3PO_4 \cdot nH_2O$ (6.0 mmol) was added, the mixture was stirred for 10 min at room temperature. After the addition of benzoyl chloride (1.5 mmol) and $PdCl_2(PPh_3)_2$ (0.075 mmol), The reaction mixture was stirred at 100 °C for 3 h. The reaction mixture was diluted with ether (50 mL) quenched with water. The mixture was extracted with ether (50 mL). The combined extracts were washed with water and brine. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified on silica gel column chromatography to give **5** (hexane: dichloromethane). The products were confirmed by comparison of NMR data and MS spectra with that in the literature.

*Benzophenone (**5a**)* [32]: Colorless prisms (mp 48–50 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (4H, t, J = 7.8 Hz), 7.59 (2H, t, J = 7.3 Hz), 7.81 (4H, d, J = 7.3 Hz).

*4-Methoxybenzophenone (**5b**)* [33]: Colorless plates (mp 61–62 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.87 (3H, s), 6.95 (2H, d, J = 8.7 Hz), 7.45 (2H, t, J = 7.8 Hz), 7.55 (1H, t, J = 7.8 Hz), 7.74 (2H, d, J = 7.8 Hz), 7.81 (2H, d, J = 8.7 Hz).

*4-Methylbenzophenone (**5f**)* [33]: Colorless prisms (mp 54–56 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.44 (3H, s), 7.28 (2H, d, J = 8.2 Hz), 7.47 (2H, t, J = 7.3 Hz), 7.57 (1H, t, J = 7.3 Hz), 7.72 (2H, d, J = 8.2 Hz), 7.78 (2H, d, J = 7.3 Hz).

*1-Naphthyl phenyl ketone (**5i**)* [34]: Colorless prisms (mp 74–75 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.62 (7H, m), 7.87 (2H, d, J = 7.3 Hz), 7.92 (1H, d, J = 7.3 Hz), 8.01 (1H, d, J = 8.2 Hz), 8.09 (1H, d, J = 7.8 Hz).

*Benzo[b]thien-2-yl phenyl ketone (**5j**)* [35]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.63 (5H, m), 7.86–7.93 (5H, m).

*4-Chlorobenzophenone (**5l**)* [33]: Colorless plates (mp 73–75 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43–7.49 (4H, m), 7.58 (1H, t, J = 7.3 Hz), 7.73–7.76 (4H, m).

*4-Trifluoromethylbenzophenone (**5m**)* [36]: Colorless needles (mp 116–117 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (2H, t, J = 7.8 Hz), 7.63 (1H, t, J = 7.8 Hz), 7.76 (2H, d, J = 8.7 Hz), 7.80 (2H, d, J = 7.8 Hz), 7.90 (2H, d, J = 8.7 Hz).

Theoretical calculation

All molecular orbital calculations were performed at the RHF/LanL2DZ level of theory using Gaussian 03 program [37]. Transition state structures relevant to the transmetallation of triphenylstibane and BCl_3 forming phenylboron dichloride were optimized with Synchronous Transit-Guided Quasi-Newton (STQN) method [38,39], which were confirmed by frequency calculation giving one imaginary frequency. The reaction paths were followed from the transition states in both directions by IRC calculations [40,41]. Following optimizations yielded structures and energies of reactants, an intermediate, and products. The same manner was applied to triarylstibanes in which electronically various ring substituents such as *p*-NH_2 (**p**), *p*-MeO (**b**), *p*-Me (**f**), *p*-MeO-*m*-Cl (**q**), *p*-Cl (**l**), *m*-Cl (**r**), *p*-CN (**s**), and *p*-CF_3 (**m**) were introduced, in order to find out potential energy surfaces of all these derivatives. Activation energies of these reactions were determined as differences between energies of transition states and sums of energies of triarylstibanes and BCl_3. Substituent effects on the activation energies were analyzed in terms of the Yukawa–Tsuno equation [42] with substituent constants (σ values) which are determined in the same manner with that described in a literature [43].

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.04.017.

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