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Hypervalent organoantimony compounds 12-ethynyl-tetrahydrodibenz[c,f][1,5]azastibocines: Highly efficient new transmetallating agent for organic halides

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Abstract

Extremely efficient and high-speed ethynylation of acyl chlorides, aryl iodides and bromides was demonstrated by palladium-catalyzed cross-coupling reaction of *N*-*t*-butyl-*Sb*-ethynyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine under mild conditions. Optimization and generalization of the hypervalent antimony-mediated coupling reaction are presented in detail. Single-crystal X-ray analysis of the *N*-methyl-1,5-azastibocine revealed that the remarkable reactivity enhancement of the azastibocine was derived from elongation of the antimony–ethynyl carbon bond originated from Sb–N intramolecular non-bonding interaction.

Keywords: Antimony; Cross-coupling; 1,5-Azastibocine; Aryl halide; Reactivity enhancement; Palladium catalysis

1. Introduction

There is surging demand for high-speed reactions. One reason is the recent remarkable development in the screening method of biologically active compounds with high throughput screening technique in medicinal chemistry [1]. This technique demands chemical reactions to be completed in short time under mild conditions and to provide a large number of compounds urgently as a library of lead compounds for medicinal and other biologically important compounds.

Acceleration of metal-catalyzed cross-coupling reactions has attracted much attention and several approaches have been reported. Some examples involve microwave irradiation [2,3], employment of bulky and electron-rich ligands [4,5], and use of ionic liquid [6,7]. Activation of a transmetallating agent with neighboring group participation is another promising strategy not only for speeding up the cross-coupling, but also for enhancement of the reactivity of the coupling reagent [8].

It has been well documented that typical heavier elements (Si, Ge, Sn, P, Sb, Bi, S, Se, Te, etc.) easily result in coordination between heteroatoms such as nitrogen and oxygen to form hypervalent bond which bring about high reactivity of ligands on the elements [9]. Incorporation of the hypervalent elements in a transmetallating agent may be a convincing clue to activate the coupling reaction; viz. it will be possible to carry out the coupling reaction with unstable and less reactive compounds in shorter time under milder reaction conditions [10].

As a part of our continuing research on making use of organoantimony(III) compounds (stibanes) as a practical organic reagent, we have previously reported that a series of ethynylstibanes (**1**) can serve as a new ethynylating agent of various organic halides in palladium(Pd)-catalyzed

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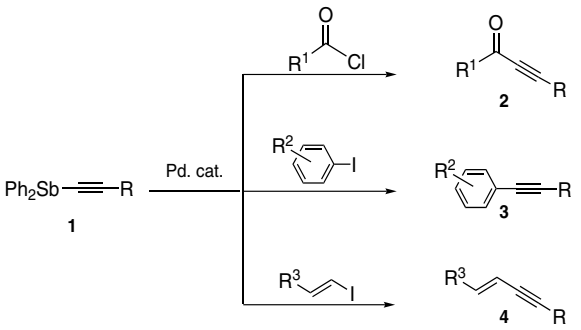


Scheme 1. Pd-catalyzed cross-coupling reaction of ethynyldiphenylstibane **1** with organic halides.

cross-coupling reactions [11]. Ethynyldiphenylstibanes can be coupled with acyl, vinyl, and aryl halides in the presence of Pd catalyst to afford ethynyl ketones (**2**), diarylacetylenes (**3**) and 1,3-enynes (**4**) in good to moderate yields, respectively. However, the reaction required prolonged heating at 80 °C and must be conducted in basic amine or hazardous HMPA as solvent in the case of less reactive organic halides (Scheme 1).

In order to overcome these drawbacks, we considered utilization of ethynyl-1,5-azastibocine derivatives as substrate for this coupling reaction in anticipation of reactivity enhancement of the ethynyl moiety by Sb–N intramolecular coordination. Thus, the reaction of a variety of *N*-alkyl-*Sb*-ethynyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocines with acyl and aryl halides was performed in the presence of Pd catalyst. As we expected, the reactivity of ethynylstibanes was remarkably enhanced and the reactions proceeded in a few minutes at room temperature. We describe here the details of the high-speed cross-coupling reactions by use of ethynyl-1,5-azastibocines as an ethynylating agent under quite mild reaction conditions [12].

2. Results and discussion

2.1. Preparation of ethynyl-1,5-heterostibocines

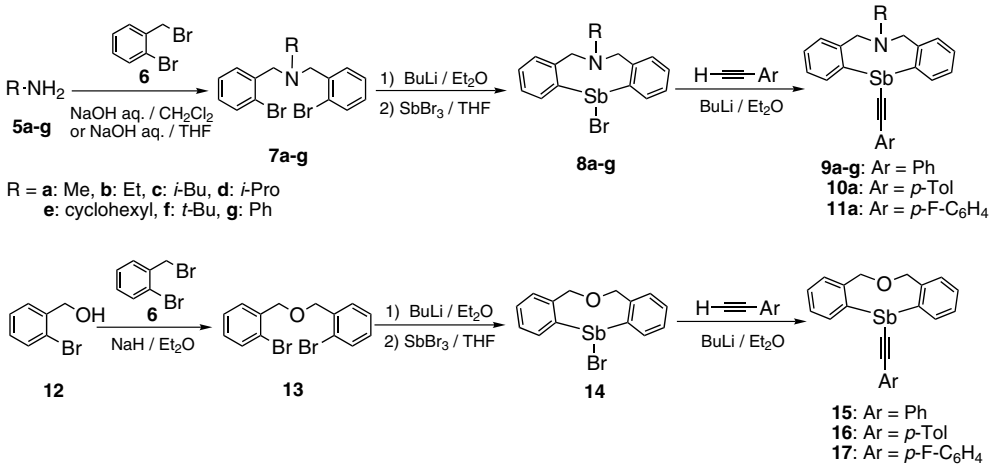
As Akiba and his co-workers have already mentioned that the coordination between the heteroatom and antimony in the 1,5-position of 1,5-heterostibocines forms rather rigid boat conformation, in that the distance between the heteroatom and the antimony is shorter than the sum of van der Waals radii of both elements [13,14]. The relationship in the 1,5-position of electron-donating and -accepting orbital of each element led to the construction of an appropriate [3,3,0]bicyclic system for strong activation of the substituent on the antimony by Sb–heteroatom intramolecular non-bonding interaction. Thus, introduction of an ethynyl group on the antimony in this system is considered to be attractive to draw a highly reactive ethynylating agent in the cross-coupling reaction. Besides these stereochemical features of 1,5-heterostibocines, the electronic character of heteroatom can affect the intensity of the interaction between antimony and heteroatom. In order to investigate this electronic effect, heteroatoms (N and O) having different electron-donating ability were incorporated in 1,5-heterostibocines and their reactivity was compared. Thus, aza- and oxa-stibocines were prepared. In the case of 1,5-azastibocines, substituents on the nitrogen were also varied from the less electron-donating primary to a more donating and bulky tertiary carbon substituent.

Ethynyl-1,5-azastibocines were prepared according to the general route based on modified Akiba's method [13]. Primary amines (**5a**–**g**) were reacted with *o*-bromobenzyl bromide (**6**) to afford tertiary amines (**7a**–**g**). Metal exchange reaction of the bromo function on **7a**–**g** with *n*BuLi, followed by addition of antimony(III) bromide, gave *Sb*-bromo-1,5-azastibocines (**8a**–**g**). Treatment of these compounds with appropriate lithium acetylides furnished ethynyl-1,5-azastibocines (**9**–**11**).

This simple and efficient procedure can be adopted for the preparation of a variety of 1,5-azastibocines with different carbon substituents on the nitrogen, such as methyl (**9a**), ethyl (**9b**), isobutyl (**9c**), isopropyl (**9d**), cyclohexyl (**9e**), *t*-butyl (**9f**) and phenyl groups (**9g**). An almost similar method was applied for the preparation of ethynyl-1,5-oxastibocines (**15**–**17**). *o*-Bromobenzy alcohol (**12**) was condensed with **6** in the presence of sodium hydride to give bis(*o*-bromobenzyl) ether (**13**). The dibromo compound (**13**) was lithiated with *n*BuLi and the resulting dilithio compound was immediately reacted with antimony(III) bromide. The bromo-1,5-oxastibocine (**14**) thus obtained was ethynylated with lithium salt of appropriate acetylenes (Scheme 2). All of the 1,5-heterostibocines obtained here were air-stable crystals and can be stored at room temperature for extended periods.

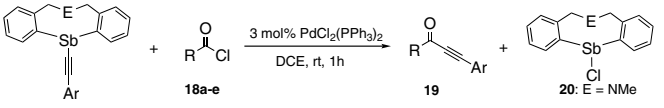
2.2. Reaction of ethynyl-N-methyl-1,5-azastibocines with acyl chlorides

Acceleration of the antimony-based coupling reaction was first demonstrated by Pd-catalyzed ethynylation of benzoyl chloride (**18a**) with *N*-methyl-1,5-azastibocines (**9a**, **10a**, **11a**). The cross-coupling reaction of **18a** with ethynyldiphenylstibane (**1**) which has no neighboring group participation required heating at 80 °C for 2 h in 1,2-dichloroethane (DCE) for completion of the reaction, although the yield of the cross-coupling product ethynylketone (**19**) was satisfactory (87%). On the contrary, similar reaction proceeded in 1 h at room temperature by use of **9a** bearing highly activated antimony atom by intramolecular nitrogen. In the reaction of **18a** with the 1,5-azastibocine (**9a**), Sb–Cl compound (**20**) was isolated in 40–50% yield after chromatographic separation of the reaction mixture. This reaction is quite selective toward the cross-coupling reaction, and no homo-coupling product 1,4-diphenyl-1,3-butadiyne (**21**) was formed at all. Various arylethynyl groups on *N*-methyl-1,5-azastibocine were also coupled with benzoyl chloride in good yields in short time without heating (entries 1–3 in Table 1).



Scheme 2. Preparation of ethynyl-aza- and oxastibocines.

Table 1
Pd-catalyzed cross-coupling reaction of 1,5-aza- **9a–11a** and oxa-stibocines **15** with acyl chlorides **18a–e**



Entry	Sb-reagent	Acyl chloride	Yield of **19**[a]
1	**9a**	**18a**	80 (87)
2	**10a**	**18a**	81 (80)
3	**11a**	**18a**	84 (76)
4	**9a**	**18b**	78 (37)
5	**9a**	**18c**	79 (47)
6	**9a**	**18d**	63 (26)
7	**9a**	**18e**	72 (33)
8[b]	**15**	**18a**	19

[a] Isolated yields. The values in parentheses show the yields obtained from the reaction of **1** with **18** reported previously [11a].

[b] The reaction was performed at 80 °C for 19 h, because no reaction proceeded at room temperature for 24 h. The homo-coupling product (**21**) was also formed in 64% yield.

The intramolecular activation of the ethynyl moiety on antimony also brought about increased yield of the product (**19**) as well as speeding up the reaction even when aliphatic acid chloride was used instead of aromatic acid chlorides. Generally, Pd-catalyzed coupling reaction of non-activated ethynylstibanes with aliphatic acyl chlorides gave rather inferior results [11a], presumably due to the instability of the chlorides at high reaction temperature for a long time. However, the ethynylation with 1,5-azastibocines (**9a**) proceeds quickly under much milder conditions. Thus, propionyl chloride (**18b**), heptanoyl chloride (**18c**), pivaloyl chloride (**18d**), phenylacetyl chloride (**18e**) were reacted with **9a** at room temperature to afford the corresponding ethynylketones in good yields (entries 4–7 in Table 1).

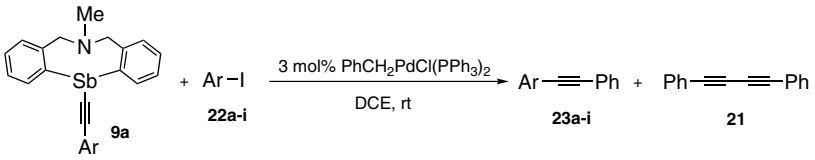
The potential for effective ethynylation was also investigated with Sb–O coordinated ethynyl-1,5-oxastibocines (**15**). In the presence of 3 mol% of $PdCl_2(PPh_3)_2$, **15** was treated with **18a** at room temperature, but no reaction proceeded at all even after 24 h. The reaction was completed only when the mixture was heated at over 80 °C for a long time (19 h). In this reaction, the yield of the cross-coupling product (**19**: 19%) was unsatisfactory and a large amount of a homo-coupling product (**21**: 64%) was formed. No promotion of the cross-coupling reaction was observed with intramolecular activation of antimony by oxygen in the ethynyl-1,5-oxastibocine (**15**) (entry 8 in Table 1).

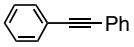
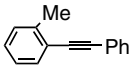
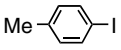
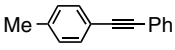
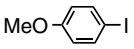
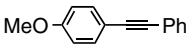
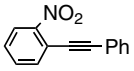
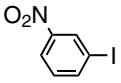
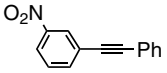
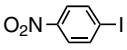
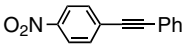
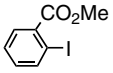
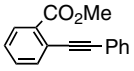
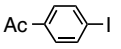
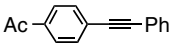
2.3. Pd-catalyzed ethynylation of aryl iodides with 1,5-azastibocines

Recently, Pd-catalyzed ethynylation of aryl halides and sulfonates has been greatly developed since the substituted acetylenes are useful building blocks for various valuable organic materials, natural products, and biologically active compounds. Especially, studies on Sonogashira-type reactions are markedly expanding due to their advantages of atom economy and green chemistry, and many improved methods which proceed under mild conditions have been investigated [15]. Also, the coupling reactions of the activated heteroatom-acetylides still continue to be explored, due to their unexpected high reactivity in transmetallation [16–22]. However, application of hypervalent organoantimony compounds to this type of coupling reaction is relatively underdeveloped. In order to reveal the transmetallating ability of ethynyl-1,5-azastibocines, we next examined Pd-catalyzed coupling reaction with aryl iodides (**22**).

Reaction of *N*-methyl-1,5-azastibocine (**9a**) and *m*-iodonitrobenzene (**22f**) was selected as a model for the survey of optimal reaction conditions. The coupling was attempted at room temperature by use of 3 mol% $PdCl_2(PPh_3)_2$ in various solvents, such as DCE, tetrahy-

Table 2
Pd-catalyzed cross-coupling reaction of ethynyl-1,5-azastibocine **9a** with aryl iodides **22a–i**

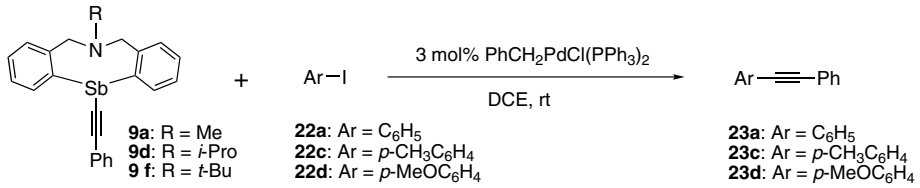


	Aryl iodides (**22**)	Product (**23**)	Time (min)	Yield (%)[a]	
				23	**21**
a			5	58	7
b			5	54	11
c			5	57	12
d			20	66	10
e			5	81	5
f			5	96	4
g			5	95	3
h			5	88	3
i			5	98	–

[a] GC yield.

drofuran (THF), diethylamine (DEA), and hexamethylphosphoramide (HMPA). In all these solvents, the reactions were finished in 5–20 min and the yields of the cross-coupling product (**23f**) were good to excellent (93% in DCE, 95% in THF, 75% in DEA, 82% in HMPA). In the reaction of non-activated ethynylstibane (**1**) with vinyl halides and **22**, heating the mixture at 55–80 °C for over 20 h in coordinative solvents (DEA, HMPA) was indispensable; these solvents can coordinate to antimony in intermolecular fashion and activate the ethynyl moiety on **1** [11b]. However, such intermolecular activation by these basic or hazardous solvents was unnecessary in the reaction with **9a**, because the ethynyl group on **9a** was already activated by intramolecular coordination between antimony and nitrogen. Next, several palladium catalysts were screened using DCE as solvent. The results showed that both phosphine-ligated and ligandless Pd catalysts afforded the coupling product (**23f**) in excellent yields at room temperature in a few minutes [93% with $PdCl_2(PhCN)_2$, 88% with $Pd(OAc)_2$, 93% with $PdCl_2$, 93% with $Pd(PPh_3)_4$]. It is noteworthy that the use of Pd catalysts having a phosphine ligand was preferable in the reaction of non-activated ethynylstibane (**1**) with iodocyclopentene under heating conditions [11b]. Other than these palladium catalysts, inexpensive nickel catalysts [$NiCl_2(PPh_3)_2$/Zn] can be used for this reaction and the product (**23f**) was obtained in acceptable yield (60%). Although the reaction conditions have not been fully

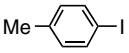
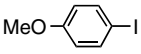
Table 3
Pd-catalyzed cross-coupling reaction of 1,5-azastibocine **9a**,**d**,**f** with aryl iodides **22a**,**c**,**d**



9a: R = Me
9d: R = *i*-Pro
9 f: R = *t*-Bu

22a: Ar = C_6H_5
22c: Ar = *p*-$CH_3C_6H_4$
22d: Ar = *p*-$MeOC_6H_4$

23a: Ar = C_6H_5
23c: Ar = *p*-$CH_3C_6H_4$
23d: Ar = *p*-$MeOC_6H_4$

	Aryl iodide (**22**)	Time (min)	Yield (%)[a]		
			R = Me	R = *i*-Pr	R = *t*-Bu
a		5	58	80	85
c		5	57	73	83
d		20	66	68	72

[a] GC yield.

optimized at present, the best result was obtained when the reaction was carried out at room temperature with 3 mol% $PhCH_2PdCl(PPh_3)_2$ in DCE for 5 min.

Under these conditions, **9a** was reacted with various aryl iodides (**22a**–**i**) and the results are summarized in Table 2. The yields of the coupling products (**23**) are sensitive to the electronic nature of substituents on aryl iodides, and the iodides with an electron-withdrawing group (**22e**–**i**) were ethynylated smoothly in high yields, whereas those without an electron-attracting group (**22a**–**d**) gave **23a**–**d** in moderate yields.

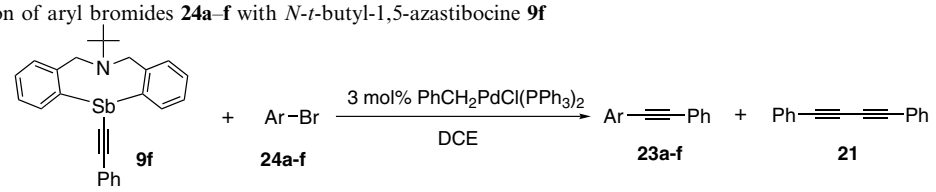
To reinforce the transmetallating ability of the ethynyl-1,5-azastibocines, substituents on nitrogen of the 1,5-azastibocine were transformed from the methyl group to more electron-donating and bulky *i*-propyl (**9d**) and *t*-butyl groups (**9f**). The electronic nature and bulkiness of these substituents might be transmitted to the antimony atom through non-bonding interaction to activate the ethynyl group on the antimony. In the ethynylation of less reactive *p*-iodotoluene (**22c**), use of *N*-methyl-1,5-azastibocine (**9a**) gave the product (**23c**) in 57% yield at room temperature in 5 min as noted above. On the other hand, *N*-*i*-propyl group (**9d**) promoted the coupling reaction to some extent (73%) and a more electron-donating and bulky *t*-butyl group (**9f**) improved the yield to satisfactory level (83%), as expected. As can be seen in Table 3, similar tendencies were observed in the ethynylation of the iodobenzene (**22a**) and *p*-iodoanisole (**22d**), and 1,5-azastibocine (**9f**) with a *t*-butyl group on nitrogen gave better results than that with a methyl and *i*-propyl group. Superiority of the *t*-butyl group on ethynyl-1,5-azastibocine was also shown by comparison with the reaction of **22a** using a series of 1,5-azastibocines having other primary, secondary and aromatic carbon substituents such as ethyl (**9b**: 55%), *i*-butyl (**9c**: 60%), cyclohexyl (**9e**: 81%) and phenyl (**9g**: 42%) groups and the reactivity is almost parallel with the electron-donating ability of these substituents.

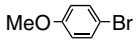
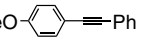
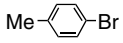
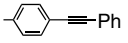
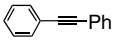
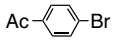
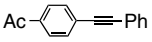
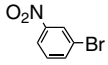
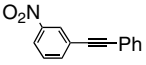
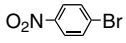
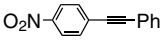
2.4. Pd-catalyzed ethynylation of aryl bromides with ethynyl-1,5-azastibocines

As noted above (Section 2.3), 1,5-azastibocines (**9**) can couple with aryl iodides (**22**) to afford the corresponding cross-coupling products in good yields under mild conditions in short time, and also the alkyl substituent on the nitrogen remarkably influences the reactivity of the ethynyl group. On the contrary, the cross-coupling reaction of **9** with aryl bromides was attained only when the bromide furnishes an electron-attracting substituent, because bromides are less reactive than the corresponding iodides. For instance, the reaction of *N*-methyl-1,5-azastibocine (**9a**) with *p*-bromoacetophenone (**24d**) led to the formation of cross-coupling products (**23d**) in 43% yield (8 h at 80 °C in DCE), whereas that with bromobenzene (**24c**) gave no cross-coupling product under the same reaction conditions. It is well known that aryl bromides and chlorides are less reactive in a variety of transition metal-catalyzed coupling reaction [4a,23].

Taking these results and our new finding that the ethynyl group on *N*-*t*-butyl-1,5-azastibocine (**9f**) shows higher reactivity into consideration, we performed the reaction of **9f** with various aryl bromides bearing electron-withdrawing and -donating groups on the benzene ring, and the results are shown in Table 4. The reaction of **9f** with aryl bromides having electron-withdrawing groups (**24d**–**f**) resulted in smooth cross-coupling reaction to afford the corresponding products (**22f**,**g**,**i**) in short time (5–20 min) at room temperature. Whereas, when the aryl bromides having electron-donating groups (**24a** and **b**) or bromobenzene (**24c**) were

Table 4
Pd-catalyzed ethynylation of aryl bromides **24a–f** with *N*-*t*-butyl-1,5-azastibocine **9f**



	Aryl bromides (**24**)	Product (**23**)	Temperature (°C)	Time	Yield (%)[a]	
					23	**21**
a		**23d** : 	80	7.0 h	41	31
b		**23c** : 	80	5.0 h	60	30
c		**23a** : 	80	4.5 h	57	37
d		**23i** : 	rt	20 min	65	11
e		**23f** : 	rt	5 min	75	12
f		**23g** : 	rt	5 min	77	7

[a] GC yield.

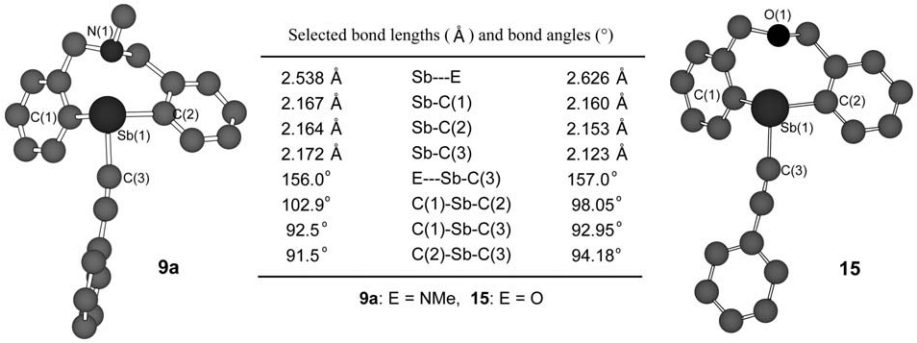


Fig. 1. X-ray crystal structure of ethynyl-1,5-aza- **9a** and oxastibocine **15**. All hydrogen atoms are omitted for clarity.

employed as a coupling partner, heating of the reaction mixture at 80 °C for 4.5–7 h was required to complete the reaction. In the latter reactions carried out under heating condition, prominent formation of homo-coupling products (**21**) was observed.

2.5. X-ray crystal structure of 1,5-aza- and 1,5-oxastibocines

Existence of hypervalent coordination between antimony and nitrogen on 1,5-azastibocine has already been established by Akiba and his co-workers through NMR technique [9b]. Our interest was directed toward how intramolecular coordination between the antimony and nitrogen atoms was reflected in the reactivity enhancement of 1,5-azastibocines. In order to investigate the structural difference between the reactive 1,5-azastibocine (**9a**) and the less activated 1,5-oxastibocine (**15**), their structures in solid state were explored by single-crystal X-ray analysis (Fig. 1).

The bond angles and bond lengths indicated that the central antimony atoms of **9a** and **15** exhibit a pseudo-trigonal bipyramidal (TBP) structure, in that both the C(1) and C(2) atoms for **9a** and **15** exist in an equatorial position of TBP along with a lone pair of antimony and the N(1) for **9a** or O(1) for **15** and C(3) are adopted in apical position.

The distance between N(1) and Sb(1) of **9a** is 2.538 Å which corresponds to 68% of the sum of the van der Waals radii of the nitrogen and antimony atoms (3.74 Å) and accord with 117% of covalent bond length (2.17 Å),

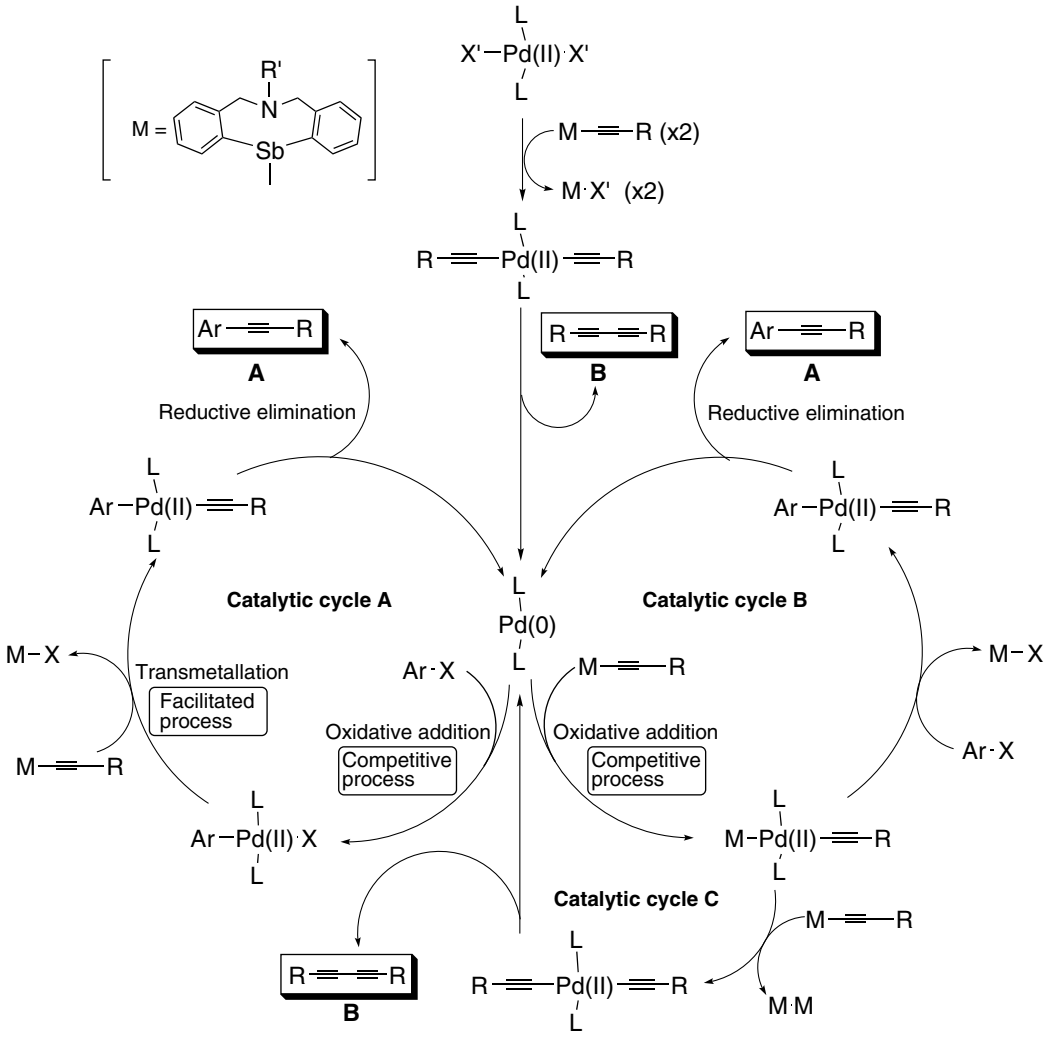


Fig. 2. Catalytic cycles for the reaction of ethynyl-1,5-azastibocine with aryl halides.

suggesting the existence of strong non-bonding interaction between the nitrogen and antimony atoms. The ethynyl carbon C(3) is located to trans position of N(1) with the C(3)–Sb(1)–N(1) angle of 156.1°. The C(1)–Sb(1)–C(3) and the C(2)–Sb(1)–C(3) angles are 92.5° and 91.5°, respectively, which show the ethynyl carbon C(3) is nearly perpendicular to the C(1)–Sb(1)–C(2) plane. Although the angles are narrow for the theoretical value of the TBP structure (120°), the C(1)–Sb(1)–C(2) angle of the 1,5-azastibocine (**9a**) was expanded to 102.9° which is wider than that of 1,5-oxastibocine (**15**) (98.1°). The Sb(1)–C(1) bond (2.167 Å) and the Sb(1)–C(2) bond (2.164 Å) were shorter than the Sb(1)–C(3) bond (2.172 Å). In the crystal structure of (phenylethynyl)di(1-napthyl)stibane, the bond length between antimony and the ethynyl carbon bond [Sb–C(sp): 2.085 Å] is remarkably shorter than that of the two antimony and aryl carbon bonds [Sb–$C_{(sp^2)}$: 2.151 and 2.155 Å] [24]. These facts imply that the Sb–N coordination in **9a** brought about marked elongation of the Sb(1)–$C(1)_{(sp)}$ bond. It is also well known that an equatorial bond is shorter than an apical bond in the antimony of the TBP structure [25].

In the case of 1,5-oxastibocine (**15**), distance between O(1) and Sb(1) is 2.626 Å, corresponding to 73% of the sum of the van der Waals radii of the oxygen and antimony atoms (3.60 Å), and to 131% of the covalent bond length (2.00 Å). These values also suggested that the coordination between the oxygen and antimony atoms, although it was less tight than that of 1,5-azastibocine (**9a**). Three bond angles around the antimony atom were almost equal: 98.1° for C(1)–Sb(1)–C(2), 93.0° for C(1)–Sb(1)–C(3), and 94.2° for C(2)–Sb(1)–C(3), implying that C(1), C(2), C(3) and lone pair of antimony constituted a quasi-tetrahedral (TH) structure rather than a pseudo-TBP structure.

Distinctive structural difference that can explain the different reactivity between 1,5-azastibocine (**9a**) and 1,5-oxastibocine (**15**) is the Sb(1)–C(3) bond length. For the reactive **9a**, the bond between Sb(1) and C(3) was elongated to 2.172 Å, whereas that of **15** was 2.123 Å. The elongation was caused by donation of the pair of electrons on the N(1) or O(1) into the anti-bonding $\sigma^*_{Sb(1)-C(3)}$ orbital, extending at the back side of the Sb(1)–C(3) bond. We considered that high electron-donating ability of the nitrogen resulted in tight coordination to bring about the

Sb(1)–C(3) bond elongation with activation for the facile transmetallation; however, interaction between Sb(1) and O(1) was not tight enough for effective elongation, due to high electron negativity of the oxygen.

2.6. Possible reaction mechanism

These Pd-catalyzed cross-coupling reactions of ethynyl-1,5-azastibocine with acyl chlorides and aryl halides are considered to proceed through a Stille-type catalytic cycle [26]. Possible reaction mechanisms of the reaction between 1,5-azastibocine and aryl halide resulting in the formation of aryl acetylene (**A**) and 1,3-diyne derivatives (**B**) are depicted in Fig. 2. The Pd(0) species [$Pd(0)L_2$] were generated by reductive elimination of a diethynylpalladium complex [R–≡–Pd(II)–≡–R] formed from the Pd(II) catalyst and two equivalents of 1,5-azastibocine. Oxidative addition of aryl halides (Ar–X) to the Pd(0) species afforded an Ar–Pd(II)–X complex. Transmetallation of the ethynyl group from the hypervalent antimony to the Pd(II) complex might be accelerated quickly, because of the elongation of the Sb-ethynyl carbon bond in ethynyl-1,5-azastibocine. This transmetallation might be the rate-determining step giving rise to the cross-coupling product (**A**) in catalytic cycle **A**. Following reductive elimination of Pd(0) from the aryl ethynyl Pd(II) complex [Ar–Pd(II)–≡–R] gave the coupling product (**A**). When the azastibocines bearing bulky isopropyl (**9d**) and *t*-butyl (**9f**) groups on the nitrogen were employed in the present reaction, electronic effect of the substituents, which bring about elongation of the antimony–ethynyl carbon bond with stronger Sb–N coordination and/or steric interaction between these bulky substituents and the ethynyl moiety, would promote easy transmetallation. However, when less reactive aryl bromides having electron-donating substituents such as 4-methoxy- (**24a**) and 4-methyl (**24b**) groups, or non-activated bromobenzene (**24c**) are used as coupling partners, an alternative pathway to the formation of the cross-coupling product (**A**) and homo-coupling product (**B**) with catalytic cycles B and C may be possible, due to the low reactivity of **24a–c** toward oxidative addition to the Pd(0) species. The oxidative addition of the non-activated aryl bromides to the Pd(0) species in the catalytic cycle A and of the ethynyl moiety on the 1,5-azastibocine in the catalytic cycle B will be competitive. Thus, 1,4-diphenyl-1,3-diyne (**21**) was formed in moderate yield along with **24a–c** in the latter reaction with catalytic cycles C. The same process for forming **21** would be also occurred when less reactive aryl iodides such as **22a–d** were employed in the reaction with **9a**. Supportive observation on this interpretation was reported in the Stille coupling, in that direct interaction between Sn-reagent and Pd is the initial process of the reaction [27,28]. A similar mechanism can be applied to the Sb-mediated coupling reaction with less reactive aryl halides, although the details are not clear at present.

3. Conclusion

In conclusion, a mild and quick ethynylation by use of 1,5-azastibocine was proved to be applicable to a wide range of acyl chloride and aryl halides. Single-crystal X-ray analyses of ethynyl-1,5-azastibocine and oxastibocine revealed the elongation of Sb-ethynyl carbon which led to efficient transmetallation in the ethynylation of aryl halides. Less reactive aryl bromides could be also ethynylated with a commercially available Pd catalyst using electron abundant 1,5-azastibocine with a bulky *t*-butyl substituent on the nitrogen, *N*-*t*-butyl-*Sb*-ethynyl-1,5-azastibocine (**9f**). The difference observed in the reactivity of *N*-methyl- (**9a**) and *N*-*t*-butyl-1,5-azastibocines (**9f**) may be ascribed to the different ability toward oxidative addition to the Pd(0) catalyst. Further applications of these 1,5-azastibocines and similar hypervalent organoantimony compounds to other types of cross-coupling reaction are also under way.

4. Experimental

4.1. General

All reactions were carried out in pre-dried glassware under an argon atmosphere. Ether was distilled from its $LiAlH_4$ suspension and dried over sodium wire. Elementary combustion analyses were determined by a Yanako CHN CORDER MT-5 and melting points were taken on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and were not corrected. ^1H NMR (TMS: δ 0.00 ppm as an internal standard) and ^{13}C NMR ($CDCl_3$: δ 77.00 ppm as an internal standard) spectra were recorded on a JEOL JNM-ECP-500 (500 and 125 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Mass spectra (EI-MS) and high-resolution mass spectra (EI-HRMS) were obtained on a JEOL JMS-SX 102A instrument and IR spectra were recorded on a HORIBA FT-720 instrument. GLC analyses of the products were made using Shimazu GC-14B. All chromatographic separations were accomplished with either Kieselgel 60 (Merck) or Silica Gel 60 N (Kanto Chemical Co. Inc.). Thin-layer chromatography (TLC) was performed with Macherey–Nagel Precoated TLC plates Sil G25 UV_{254}. *o*-Bromobenzyl bromide (**6**) was prepared according to the reported procedure [14b], and butyllithium (BuLi: 1.51–1.58 M in hexane solution) was purchased from Kanto Chemical Co. Inc., Japan.

4.2. Preparations of N,N-bis(2-bromobenzyl)-N-alkyl-(7*a*–*f*) and N-phenyl-amine (7*g*)

4.2.1. N,N-bis(2-bromobenzyl)-N-methylamine (7*a*)

o-Bromobenzyl bromide (**6**: 100 g, 0.40 mol) was dissolved in dichloromethane (CH_2Cl_2: 400 ml) and 40% aqueous solution of methylamine (**5a**: 62.0 g, 0.80 mol) was added dropwise under ice cooling. The reaction mixture was stirred for 4 h at 0 °C and was diluted with

hexane. The organic layer was separated, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the resulting residue was purified on silica gel column chromatography (hexane:benzene = 4:1) to give **7a** (63.5 g, 86% yield). Colorless oil. EI-MS *m*/*z*: 369 (M^+, 78%), 288 (7%), 212 (100%), 169 (7%), 91 (23%). HRMS *m*/*z*: Calcd. for $C_{15}H_{15}Br_2N$: 366.9971. Found: 367.0112. ^{1}H NMR δ ppm: 2.25 (3H, s), 3.70 (4H, s), 7.08 (2H, dd, $J_{3,4} = J_{4,5} = 7.79$ Hz), 7.27 (2H, dd, $J_{4,5} = J_{5,6} = 7.79$ Hz), 7.52 (2H, d, $J_{5,6} = 7.79$ Hz), 7.55 (2H, d, $J_{3,4} = 7.79$ Hz). ^{13}C NMR δ ppm: 42.2 (q), 61.3 (t), 124.5 (s), 127.2 (d), 128.3 (d), 130.6 (d), 132.7 (d), 138.4 (s).

4.2.2. *N,N-bis(2-bromobenzyl)-N-ethylamine (**7b**)*

To an ice cooling solution of the bromide (**6**: 27.5 g, 0.11 mol) in dichloromethane (CH_2Cl_2: 100 ml), an aqueous solution of sodium hydroxide (NaOH: 10.0 g in 50 ml of water, 0.25 mmol) and ethylamine (**5b**: 3.20 g, 0.05 mol) were added. After stirring for 4 h at 0 °C, the reaction mixture was diluted with CH_2Cl_2 and water. The organic layer was separated, washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified on silica gel column chromatography (hexane:benzene = 3:1) to give **7b** (14.64 g, 76% yield). Colorless oil. EI-MS *m*/*z*: 383 (M^+, 21%), 368 (100%), 226 (12%), 169 (72%). ^{1}H NMR δ ppm: 1.11 (3H, t, $J = 7.10$ Hz), 2.59 (2H, q, $J = 7.10$ Hz), 3.72 (4H, s), 7.06 (2H, dd, $J_{3,4} = J_{4,5} = 7.33$ Hz), 7.26 (2H, dd, $J_{4,5} = J_{5,6} = 7.33$ Hz), 7.49 (2H, d, $J = 7.33$ Hz), 7.60 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 11.9 (q), 48.1 (t), 57.5 (t), 124.2 (d), 128.1 (d), 130.4 (d), 132.6 (d), 139.0 (s).

4.2.3. *N,N-bis(2-bromobenzyl)-N-(2-methylpropyl)amine (**7c**)*

The amine (**7c**) was prepared according to the procedure described for **7b** in Section 4.2.2. The crude product obtained from **6** (1.84 g in 30 ml of CH_2Cl_2, 4.0 mmol), NaOH (1.2 g in 30 ml of water, 30 mmol), and *iso*-butylamine (**5c**: 438 mg, 6.0 mmol) was purified on silica gel column chromatography (hexane) to give **7c** (2.49 g, quant.). Colorless needles (m.p. 62–63 °C, from ethanol (EtOH)). Elemental analysis: Calcd. for $C_{18}H_{21}Br_2N$: C, 52.58; H, 5.15; N, 3.41. Found: C, 52.63; H, 5.21; N, 3.39. EI-MS *m*/*z*: 411 (M^+, 7%), 368 (100%), 288 (8%), 169 (55%). ^{1}H NMR δ ppm: 0.88 (6H, d, $J = 6.42$ Hz), 1.88 (1H, m), 2.27 (2H, d, $J = 6.42$ Hz), 3.69 (4H, s), 7.06 (2H, dd, $J_{3,4} = J_{4,5} = 7.33$ Hz), 7.26 (2H, dd, $J_{4,5} = J_{5,6} = 7.33$ Hz), 7.49 (2H, d, $J = 7.33$ Hz), 7.64 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 21.0 (q), 26.4 (d), 58.6 (t), 63.1 (t), 124.2 (s), 127.2 (d), 128.1 (d), 130.5 (d), 132.5 (d), 138.8 (s).

4.2.4. *N,N-bis(2-bromobenzyl)-N-isopropylamine (**7d**)*

The amine (**7d**) was prepared according to the procedure described for **7b** in Section 4.2.2. The crude product obtained from **6** (30.0 g in 100 ml of CH_2Cl_2, 0.12 mol), NaOH (9.6 g in 100 ml of water, 0.24 mol), and isopropylamine (**5d**: 2.83 g, 0.048 mmol) was purified on silica gel column chromatography (hexane:benzene = 2:1) to give **7d** (17.26 g, 91% yield). Colorless needles (m.p. 43–44 °C, from EtOH). Elemental analysis: Calcd. for $C_{17}H_{19}Br_2N$: C, 51.41; H, 4.82; N, 3.53. Found: C, 52.52; H, 4.93; N, 3.59. EI-MS *m*/*z*: 397 (M^+, 14%), 382 (100%), 339 (8%), 171 (57%). ^{1}H NMR δ ppm: 1.13 (6H, d, $J = 6.42$ Hz), 2.96 (1H, septet, $J = 6.42$ Hz), 3.72 (4H, s), 7.03 (2H, dd, $J_{3,4} = J_{4,5} = 7.33$ Hz), 7.23 (2H, dd, $J_{4,5} = J_{5,6} = 7.33$ Hz), 7.46 (2H, d, $J = 7.33$ Hz), 7.60 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 18.1 (q), 50.1 (d), 53.3 (t), 124.1 (s), 127.2 (d), 127.9 (d), 130.2 (d), 132.5 (d), 139.5 (s).

4.2.5. *N,N-bis(2-bromobenzyl)-N-cyclohexylamine (**7e**)*

The amine (**7e**) was prepared according to the procedure described for **7b** in Section 4.2.2. The crude product obtained from **6** (1.2 g in 50 ml of CH_2Cl_2, 15.0 mmol), NaOH (1.2 g in 30 ml of water, 0.24 mol), and cyclohexylamine (**5e**: 594 mg, 6.0 mmol) was purified on silica gel column chromatography (hexane:benzene = 2:1) to give **7e** (2.15 g, 82% yield). Colorless prisms (m.p. 83–84 °C, from EtOH). Elemental analysis: Calcd. for $C_{20}H_{23}Br_2N$: C, 54.94; H, 5.30; N, 3.20. Found: C, 55.01; H, 5.39; N, 3.15. EI-MS *m*/*z*: 437 (M^+, 43%), 394 (100%), 356 (76%), 300 (7%), 266 (16%), 169 (60%). ^{1}H NMR δ ppm: 1.06–1.24 (3H, m), 1.32–1.42 (2H, m), 1.61 (1H, d, $J = 12.15$ Hz), 1.79 (2H, d, $J = 12.15$ Hz), 1.97 (2H, d, $J = 12.15$ Hz), 2.46–2.53 (1H, m), 3.78 (4H, s), 7.03 (2H, dd, $J_{3,4} = J_{4,5} = 7.33$ Hz), 7.22 (2H, dd, $J_{4,5} = J_{5,6} = 7.33$ Hz), 7.46 (d, $J = 7.33$ Hz), 7.58 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 26.2 (t), 26.4 (t), 28.9 (t), 54.0 (t), 59.6 (t), 124.0 (s), 127.2 (d), 127.9 (d), 130.2 (d), 132.4 (d), 139.7 (s).

4.2.6. *N,N-bis(2-bromobenzyl)-N-t-butylamine (**7f**)*

The bromide (**6**: 100.0 g, 0.40 mol) and *t*-butylamine (**5f**: 13.3 g, 0.182 mol) was dissolved in tetrahydrofuran (THF: 300 ml). An aqueous solution (200 ml) of potassium hydroxide (25.4 g, 0.455 mmol) was added and the reaction mixture was stirred for 72 h at 80 °C. After cooling, the mixture was diluted with ether and the product was extracted with 10% HCl. The HCl layer was neutralized with 10% NaOH solution and the liberated amine was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried over anhydrous magnesium sulfate and the solvent was removed in vacuo. The residue was purified on silica gel column chromatography (hexane:benzene = 4:1) to give **7f** (60.1 g, 80% yield). Colorless needles (m.p. 95–97 °C, from EtOH). Elemental analysis: Calcd. for $C_{18}H_{21}Br_2N$: C, 52.58; H, 5.15; N, 3.41. Found: C, 55.38; H, 5.21; N, 3.55. EI-MS *m*/*z*: 411 (M^+, 6%), 396 (100%), 339 (7%), 226 (8%), 169 (45%). ^{1}H NMR δ ppm: 2.61 (9H, s), 5.24 (4H, s), 8.29 (2H, dd, $J_{3,4} = J_{4,5} = 7.33$ Hz), 8.49 (2H, dd, $J_{4,5} = J_{5,6} = 7.33$ Hz), 8.71 (2H, d, $J = 7.33$ Hz), 8.96 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 27.1 (q), 53.9 (t), 56.2 (s), 123.4 (d), 126.6 (d), 127.6 (d), 131.1 (d), 132.1 (d), 140.5 (s).

4.2.7. N,N-bis(2-bromobenzyl)-N-phenylamine (7g)

The bromide (**6**: 1.25 g, 5.00 mmol) and aniline (**5g**: 232 mg, 2.50 mmol) was dissolved in THF (50 ml). An aqueous solution (40 ml) of sodium hydroxide (2.00 g, 0.050 mmol) was added and the reaction mixture was stirred for 48 h at 80 °C. After cooling, the mixture was diluted with ether and water. The organic layer was separated, washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified on silica gel column chromatography (hexane:benzene = 4:1) to give **7g** (840 mg, 78% yield). Colorless needles (m.p. 149–150 °C, from EtOH). Elemental analysis: Calcd. for $C_{20}H_{17}Br_2N$: C, 55.71; H, 3.97; N, 3.25. Found: C, 55.68; H, 4.05; N, 3.30. EI-MS *m*/*z*: 433 [$(M + 2)^+$, 52%], 431 (M^+, 100%), 350 (12%), 294 (27%), 180 (28%). ^{1}H NMR δ ppm: 4.66 (4H, s), 6.56 (2H, d, $J = 7.33$ Hz), 6.72 (1H, t, $J = 7.33$ Hz), 7.12–7.19 (4H, m), 7.22–7.30 (4H, m), 7.59 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 55.3 (t), 112.0 (d), 117.1 (d), 122.7 (s), 127.6 (d), 127.8 (d), 128.5 (d), 129.3 (d), 133.0 (d), 136.4 (s), 148.0 (s).

4.3. Preparation of 12-bromo-N-alkyl- and N-phenyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocines

4.3.1. 12-Bromo-N-methyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (8a)

N,*N*-bis(2-bromobenzyl)-*N*-methylamine (**7a**: 30.0 g, 0.081 mol) was dissolved in ether (300 ml) and was cooled in methanol–ice bath (−15 to −20 °C). To this solution, BuLi (1.52 M in hexane, 107 ml, 0.163 mol) was added using syringe through septum cup, and the mixture was stirred for 1 h. An ethereal solution (50 ml) of antimony(III) bromide [$SbBr_3$: 32.6 g (90% purity), 0.081 mol] was added and stirring was continued for 12 h at room temperature. The reaction mixture was quenched with water and diluted with large excess of chloroform ($CHCl_3$). The organic layer was separated, washed with saturated aqueous solution of sodium bicarbonate and brine. The organic layer was dried over anhydrous magnesium sulfate and removed in vacuo. The residue was recrystallized from $CHCl_3$–EtOH to give **8a** (29.7 g, 88% yield). Colorless prisms (m.p. 171–174 °C). Elemental analysis: Calcd. for $C_{15}H_{15}BrNSb$: C, 43.84; H, 3.68; N, 3.41. Found: C, 44.83; H, 3.77; N, 3.42. EI-MS *m*/*z*: 411 (M^+, 4%), 367 (28%), 330 (66%), 276 (34%), 239 (18%), 208 (100%). ^{1}H NMR δ ppm: 2.76 (3H, s), 3.94 (2H, d, $J = 14.66$ Hz), 4.14 (2H, d, $J = 14.66$ Hz), 7.11 (2H, d, $J = 7.33$ Hz), 7.28 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.36 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 8.36 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 43.6 (q), 62.7 (t), 125.3 (d), 129.1 (d), 129.2 (d), 136.9 (d), 138.6 (s), 142.4 (s).

4.3.2. 12-Bromo-N-ethyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (8b)

The bromo-azastibocine (**8b**) was prepared according to the procedure described for **8a** in Section 4.3.1. The crude product obtained from **7b** (12.57 g, 32.8 mmol), BuLi (73 mmol), and $SbBr_3$ [13.2 g (90% purity), 32.8 mmol] was purified on silica gel column chromatography [CH_2Cl_2:ethyl acetate (AcOEt) = 4:1] to give **8b** (10.12 g, 73% yield). Colorless plates (m.p. 157–158 °C, from $CHCl_3$–EtOH). Elemental analysis: Calcd. for $C_{16}H_{17}BrNSb$: C, 45.22; H, 4.03; N, 3.30. Found: C, 45.10; H, 4.10; N, 3.28. EI-MS *m*/*z*: 425 (M^+, 4%), 381 (33%), 344 (90%), 290 (31%), 222 (100%). ^{1}H NMR δ ppm: 1.24 (3H, t, $J = 7.33$ Hz), 3.07 (2H, q, $J = 7.33$ Hz), 4.03 (2H, d, $J = 15.58$ Hz), 4.06 (2H, d, $J = 15.58$ Hz), 7.12 (2H, d, $J = 7.33$), 7.27 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.37 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 8.26 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 11.3 (q), 50.4 (t), 59.5 (t), 125.1 (d), 128.9 (d), 129.0 (d), 135.5 (d), 140.2 (s), 142.9 (s).

4.3.3. 12-Bromo-N-(2-methylpropyl)-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (8c)

The bromo-azastibocine (**8c**) was prepared according to the procedure described for **8a** in Section 4.3.1. The crude product obtained from **7c** (20.5 g, 50 mmol), BuLi (110 mmol), and $SbBr_3$ [20 g (90% purity), 50 mmol] was purified on silica gel column chromatography (CH_2Cl_2:AcOEt = 4:1) to give **8c** (21.47 g, 95% yield). Colorless needles (m.p. 202–204 °C, from $CHCl_3$–EtOH). Elemental analysis: Calcd. for $C_{18}H_{21}BrNSb$: C, 47.72; H, 4.67; N, 3.09. Found: C, 47.80; H, 4.59; N, 3.15. EI-MS *m*/*z*: 453 (M^+, 5%), 409 (33%), 372 (100%), 366 (51%), 316 (16%), 250 (53%). ^{1}H NMR δ ppm: 1.00 (6H, d, $J = 6.87$ Hz), 2.09 (1H, m), 2.82 (2H, d, $J = 5.96$ Hz), 4.05 (2H, d, $J = 16.00$ Hz), 4.09 (2H, d, $J = 16.00$ Hz), 7.08 (2H, d, $J = 7.33$ Hz), 7.24 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.33 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 8.23 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 23.2 (q), 25.9 (d), 59.8 (t), 63.2 (t), 125.3 (d), 128.9 (d), 129.1 (d), 136.8 (d), 138.0 (s), 142.9 (s).

4.3.4. 12-Bromo-N-isopropyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (8d)

The bromo-azastibocine (**8d**) was prepared according to the procedure described for **8a** in Section 4.3.1. The crude product obtained from **7d** (2 g, 5.0 mmol), BuLi (11 mmol), and $SbBr_3$ [2 g (90% purity), 5 mmol] was purified on silica gel column chromatography (CH_2Cl_2:AcOEt = 4:1) to give **8d** (1.75 g, 80% yield). Colorless prisms (m.p. 177–179 °C, from $CHCl_3$–EtOH). Elemental analysis: Calcd. for $C_{17}H_{19}BrNSb$: C, 46.15; H, 4.36; N, 3.19. Found: C, 46.77; H, 4.19; N, 3.20. EI-MS *m*/*z*: 439 (M^+, 6%), 395 (6%), 358 (100%), 236 (16%). ^{1}H NMR δ ppm: 1.24 (6H, d, $J = 6.42$ Hz), 3.47 (1H, septet, $J = 6.42$ Hz), 4.01 (2H, d, $J = 15.12$ Hz), 4.15 (2H, d, $J = 15.12$ Hz), 7.09 (2H, d, $J = 7.33$ Hz), 7.25 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.33 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 8.35 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 19.4 (q), 56.4 (d), 124.7 (d), 128.8 (d), 129.0 (d), 136.5 (d), 138.1 (s), 143.8 (s).

4.3.5. 12-Bromo-N-cyclohexyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**8e**)

The bromo-azastibocine (**8e**) was prepared according to the procedure described for **8a** in Section 4.3.1. The crude product obtained from **7e** (6.07 g, 13.9 mmol), BuLi (31 mmol), and $SbBr_3$ [5.50 g (90% purity), 13.7 mmol] was purified on silica gel column chromatography (CH_2Cl_2:AcOEt = 4:1) to give **8e** (6.11 g, 92% yield). Colorless prisms (m.p. 256–258 °C, from $CHCl_3$–EtOH). Elemental analysis: Calcd. for $C_{20}H_{23}BrNSb$: C, 50.14; H, 4.84; N, 2.92. Found: C, 50.63; H, 4.92; N, 2.99. EI-MS *m*/*z*: 479 (M^+, 3%), 435 (16%), 398 (100%), 344 (20%), 316 (18%), 276 (66%). ^1H NMR δ ppm: 1.05–1.13 (1H, m), 1.24–1.40 (4H, m), 1.64 (1H, d, $J = 12.83$ Hz), 1.84 (2H, d, $J = 12.83$ Hz), 2.01 (2H, d, $J = 12.83$ Hz), 3.04 (1H, m), 4.03 (2H, d, $J = 15.12$ Hz), 4.18 (2H, d, $J = 15.12$ Hz), 7.08 (2H, d, $J = 7.33$ Hz), 7.26 (2H, dd, $J_{3,4} = J_{2,3} = 7.33$ Hz), 7.32 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 8.35 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 25.4 (t), 25.5 (t), 29.6 (t), 57.8 (t), 65.5 (d), 124.7 (d), 128.7 (d), 129.0 (d), 136.4 (d), 138.0(s), 144.0 (s).

4.3.6. 12-Bromo-N-t-butyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**8f**)

The bromo-azastibocine (**8f**) was prepared according to the procedure described for **8a** in Section 4.3.1. The crude product obtained from **7f** (8.27 g, 20 mmol), BuLi (45 mmol), and $SbBr_3$ [8.2 g (90% purity), 20 mmol] was purified on silica gel column chromatography (CH_2Cl_2:AcOEt = 4:1) to give **8f** (8.18 g, 90% yield). Colorless prisms (m.p. 216–218 °C, from $CHCl_3$–EtOH). Elemental analysis: Calcd. for $C_{18}H_{21}BrNSb$: C, 47.72; H, 4.67; N, 3.09. Found: C, 47.68; H, 4.59; N, 3.21. EI-MS *m*/*z*: 453 (M^+, 10%), 409 (25%), 372 (100%), 316 (59%), 250 (34%), 194 (28%). ^1H NMR δ ppm: 1.32 (9H, s), 3.96 (2H, d, $J = 15.12$ Hz), 4.36 (2H, d, $J = 15.12$ Hz), 7.07 (2H, d, $J = 7.33$ Hz), 7.23 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.30 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 8.25 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 27.1 (q), 57.3 (t), 60.6 (s), 124.5 (d), 128.6 (d), 129.1 (d), 136.5 (d), 137.9 (s), 145.1 (s).

4.3.7. 12-Bromo-N-phenyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**8g**)

The bromo-azastibocine (**8g**) was prepared according to the procedure described for **8a** in Section 4.3.1. The crude product obtained from **7g** (9.84 g, 22.8 mmol), BuLi (51 mmol), and $SbBr_3$ [9.14 g (90% purity), 22.7 mmol] was purified on silica gel column chromatography (CH_2Cl_2:AcOEt = 4:1) to give **8g** (8.44 g, 79% yield). Colorless prisms (m.p. 227–228 °C, from $CHCl_3$–EtOH). Elemental analysis: Calcd. for $C_{20}H_{17}BrNSb$: C, 50.78; H, 3.62; N, 2.96. Found: C, 50.55; H, 3.71; N, 3.02. EI-MS *m*/*z*: 473 (M^+, 5%), 392 (100%), 301 (25%), 270 (28%), 180 (20%). ^1H NMR δ ppm: 4.53 (2H, d, $J = 15.12$ Hz), 4.69 (2H, d, $J = 15.12$ Hz), 7.14–7.43 (11H, m), 8.23 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 61.2 (t), 119.7 (d), 125.3 (d), 129.3 (d), 129.6 (d), 135.2 (d), 136.7 (d), 138.2 (d), 140.5 (s), 143.0 (s).

4.4. Preparation of 12-phenylethynyl-N-alkyl- (**9a–f**) and N-phenyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocines (**9g**)

4.4.1. 12-Phenylethynyl-N-methyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**9a**)

To a stirring solution of ethynylbenzene (2.24 g, 22 mmol) in ether (50 ml), BuLi (1.58 M in hexane, 14.0 ml, 22.1 mmol) was added using syringe through septum cup at 0 °C and the mixture was stirred for 1 h. To this solution, a THF (50 ml) solution of **8a** (9.04 g, 22 mmol) was added dropwise at 0 °C and stirring was continued for 4 h. The reaction mixture was diluted with ether and quenched with water. The ether layer was separated, washed with brine, dried over anhydrous magnesium sulfate, and then concentrated in vacuo. The residue was recrystallized from a mixture of benzene–hexane to give **9a** (8.7 g, 92% yield). Colorless prisms (m.p. 131–133 °C). Elemental analysis: Calcd. for $C_{23}H_{20}NSb$: C, 63.92; H, 4.66; N, 3.24. Found: C, 63.90; H, 4.76; N, 3.26. EI-MS *m*/*z*: 431 (M^+, 4%), 329 (100%), 208 (32%). ^1H NMR δ ppm: 2.53 (3H, s), 3.70 (2H,d, $J = 14.66$ Hz), 3.90 (2H, d, $J = 14.66$ Hz), 7.06 (2H, d, $J = 7.33$ Hz), 7.20–7.36 (7H, m), 7.59 (2H, m), 8.33 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 41.9 (q), 60.2 (t), 97.9 (s), 110.0 (s), 124.7 (s), 126.2 (d), 127.6 (d), 128.2 (d), 128.3 (d), 128.6 (d), 131.9 (d), 136.1 (s), 136.7 (d), 142.6 (s). IR cm^{-1}: 2117 (C≡C).

4.4.2. 12-Phenylethynyl-N-ethyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**9b**)

The ethynyl-azastibocine (**9b**) was prepared according to the procedure described for **9a** in Section 4.4.1. The crude product obtained from ethynylbenzene (765 mg, 7.5 mmol), BuLi (7.5 mmol), and **8b** (2.12 g, 5.0 mmol) was recrystallized from a mixture of benzene–hexane to give **9b** (2.23 g, quant.). Colorless prisms (m.p. 130–131 °C). Elemental analysis: Calcd. for $C_{24}H_{22}NSb$: C, 64.60; H, 4.97; N, 3.14. Found: C, 64.48; H, 4.99; N, 3.10. EI-MS *m*/*z*: 445 (M^+, 3%), 343 (100%), 314 (11%), 254 (12%), 222 (14%). ^1H NMR δ ppm: 1.16 (3H, t), 2.87 (2H, q), 3.82 (4H, s), 7.06 (2H, d, $J = 7.10$ Hz), 7.21–7.35 (7H, m), 7.59 (2H, d, $J = 8.25$ Hz), 8.33 (2H, d, $J = 7.10$ Hz). ^{13}C NMR δ ppm: 10.4 (q), 48.2 (t), 56.8 (t), 97.9 (s), 110.1 (s), 124.7 (s), 126.1 (d), 127.6 (d), 128.2 (d), 128.3 (d), 128.4 (d), 131.9 (d), 135.7 (s), 136.6 (d). IR (cm^{-1}): 2121 (C≡C).

4.4.3. 12-Phenylethynyl-N-(2-methylpropyl)-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**9c**)

The ethynyl-azastibocine (**9c**) was prepared according to the procedure described for **9a** in Section 4.4.1. The crude product obtained from ethynylbenzene (703 mg, 6.9 mmol), BuLi (6.9 mmol), and **8c** (2.08 g, 4.6 mmol) was purified on silica gel column chromatography (hexane:AcOEt = 1:1) to give **9c** (1.78 g, 82% yield). Colorless prisms (m.p. 86–88 °C, from benzene–hexane). Elemental analysis: Calcd. for $C_{26}H_{26}NSb$: C, 65.85; H, 5.53; N, 2.95. Found: C, 65.92; H,

5.49; N, 3.01. EI-MS *m/z*: 472 (M^+, 2%), 430 (10%), 371 (100%), 328 (46%). ^{1}H NMR δ ppm: 0.99 (6H, d, $J = 6.42$ Hz), 2.11 (1H, m), 2.66 (2H, d, $J = 6.42$ Hz), 3.90 (2H, d, $J = 16.00$ Hz), 3.94 (2H, d, $J = 16.00$ Hz), 7.06 (2H, d, $J = 7.33$ Hz), 7.22–7.35 (7H, m), 7.59 (2H, d, $J = 8.24$ Hz), 8.32 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 22.9 (q), 25.8 (d), 57.4 (t), 61.4 (t), 97.1 (s), 110.3 (s), 124.7 (s), 126.3 (d), 127.7 (d), 128.2 (d), 128.3 (d), 128.5 (d), 131.9 (d), 135.4 (s), 136.6 (d), 143.0 (s). IR (cm^{-1}): 2119 (C≡C).

4.4.4. 12-Phenylethynyl-N-isopropyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**9d**)

The ethynyl-azastibocine (**9d**) was prepared according to the procedure described for **9a** in Section 4.4.1. The crude product obtained from ethynylbenzene (1.02 g, 10 mmol), BuLi (10 mmol), and **8d** (4.38 g, 10 mmol) was purified on silica gel column chromatography (hexane:AcOEt = 1:1) to give **9d** (4.50 g, 98% yield). Colorless prisms (m.p. 139–140 °C, from benzene–hexane). Elemental analysis: Calcd. for $C_{25}H_{24}NSb$: C, 65.24; H, 5.26; N, 3.04. Found: C, 65.29; H, 5.30; N, 3.10. EI-MS *m/z*: 459 (M^+, 4%), 418 (7%), 357 (100%), 314 (66%). ^{1}H NMR δ ppm: 1.18 (6H, d, $J = 6.88$ Hz), 3.26 (1H, septet, $J = 6.88$ Hz), 3.78 (2H, d, $J = 15.13$ Hz), 3.94 (2H, d, $J = 15.13$ Hz), 7.06 (2H, d, $J = 7.33$ Hz), 7.20–7.35 (7H, m), 7.59 (2H, d, $J = 7.56$ Hz), 8.32 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 18.7 (q), 53.5 (d), 54.6 (t), 97.6 (s), 110.5 (s), 124.8 (s), 126.0 (d), 127.6 (d), 128.2 (d), 128.3 (d), 128.3 (d), 131.9 (d), 135.5 (s), 136.5 (d), 143.8 (s). IR cm^{-1}: 2123 (C≡C).

4.4.5. 12-Phenylethynyl-N-cyclohexyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**9e**)

The ethynyl-azastibocine (**9e**) was prepared according to the procedure described for **9a** in Section 4.4.1. The crude product obtained from ethynylbenzene (612 mg, 6.0 mmol), BuLi (6.0 mmol), and **8e** (1.91 g, 4.0 mmol) was purified on silica gel column chromatography (hexane:AcOEt = 1:1) to give **9e** (1.09 g, 55% yield). Colorless prisms (m.p. 125–126 °C, from benzene–hexane). Elemental analysis: Calcd. for $C_{28}H_{28}NSb$: C, 67.22; H, 5.64; N, 2.80. Found: C, 67.36; H, 5.52; N, 2.95. EI-MS *m/z*: 499 (M^+, 3%), 416 (8%), 397 (100%), 314 (54%). ^{1}H NMR δ ppm: 1.01–1.13 (1H, m), 1.18–1.36 (4H, m), 1.63 (1H, d, $J = 12.83$ Hz), 1.78 (2H, d, $J = 12.83$ Hz), 2.02 (2H, d, $J = 12.83$ Hz), 2.85 (1H, m), 3.81 (2H, d, $J = 15.12$ Hz), 3.97 (2H, d, $J = 15.12$ Hz), 7.03 (2H, d, $J = 7.33$ Hz), 7.59 (2H, d, $J = 8.25$ Hz), 8.32 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 25.9 (t), 26.0 (t), 29.0 (t), 55.2 (t), 63.1 (d), 97.8 (s), 110.5 (s), 124.8 (s), 125.9 (d), 127.6 (d), 128.1 (d), 128.2 (d), 128.3 (d), 131.9 (d), 135.5 (s), 136.4 (d), 144.0 (s). IR cm^{-1}: 2115 (C≡C).

4.4.6. 12-Phenylethynyl-N-t-butyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**9f**)

The ethynyl-azastibocine (**9f**) was prepared according to the procedure described for **9a** in Section 4.4.1. The crude product obtained from ethynylbenzene (765 mg, 7.5 mmol), BuLi (7.5 mmol), and **8f** (2.26 g, 5.0 mmol) was purified on silica gel column chromatography (hexane:AcOEt = 1:1) to give **9f** (3.17 g, 89% yield). Colorless prisms (m.p. 163–164 °C, from benzene–hexane). Elemental analysis: Calcd. for $C_{26}H_{26}NSb$: C, 65.85; H, 5.53; N, 2.95. Found: C, 65.89; H, 5.59; N, 3.03. EI-MS *m/z*: 473 (M^+, 4%), 416 (5%), 371 (13%), 314 (100%). ^{1}H NMR δ ppm: 1.26 (9H, s), 3.76 (2H, d, $J = 15.12$ Hz), 4.18 (2H, d, $J = 15.12$ Hz), 7.04 (2H, d, $J = 7.33$ Hz), 7.17–7.25 (4H, m), 7.28–7.36 (3H, m), 7.60 (2H, d, $J = 8.25$ Hz), 8.33 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 26.8 (q), 54.9 (t), 58.2 (s), 97.5 (s), 110.8 (s), 124.8 (s), 125.6 (d), 127.6 (d), 127.9 (d), 128.2 (d), 128.3 (d), 131.8 (d), 135.3 (s), 136.5 (d), 145.2 (s). IR cm^{-1}: 2127 (C≡C).

4.4.7. 12-Phenylethynyl-N-phenyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**9g**)

The ethynyl-azastibocine (**9g**) was prepared according to the procedure described for **9a** in Section 4.4.1. The crude product obtained from ethynylbenzene (510 mg, 5.0 mmol), BuLi (5.0 mmol), and **8g** (2.36 g, 5.0 mmol) was purified on silica gel column chromatography (hexane:AcOEt = 1:1) to give **9g** (2.17 g, 88% yield). Colorless prisms (m.p. 177–180 °C, from benzene–hexane). Elemental analysis: Calcd. for $C_{28}H_{22}NSb$: C, 68.04; H, 4.49; N, 2.83. Found: C, 68.14; H, 4.81; N, 2.95. EI-MS *m/z*: 493 (M^+, 2%), 391 (100%), 301 (16%), 269 (49%), 213 (29%), 179 (41%). ^{1}H NMR δ ppm: 4.34 (2H, d, $J = 15.13$ Hz), 4.64 (2H, d, $J = 15.13$ Hz), 6.99 (1H, t, $J = 7.33$ Hz), 7.09 (2H, d, $J = 7.82$ Hz), 7.17 (2H, d, $J = 6.87$ Hz), 7.22–7.35 (9H, m), 7.58 (2H, d, $J = 7.82$ Hz), 8.29 (2H, d, $J = 6.87$ Hz). ^{13}C NMR δ ppm: 58.0 (t), 94.0 (s), 111.6 (s), 118.1 (d), 122.5 (d), 124.3 (s), 126.2 (d), 128.0 (d), 128.2 (d), 128.6 (d), 128.7 (d), 129.1 (d), 131.9 (d), 134.9 (s), 136.9 (d), 143.0 (s), 148.6 (s). IR cm^{-1}: 2121 (C≡C).

4.4.8. 12-p-Tolylethynyl-N-methyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**10a**)

The same procedure as for the preparation of **9a** using **8a** and *p*-tolylacetylene gave **10a** (91% yield). Colorless prisms (m.p. 142–145 °C, from ether–EtOH). Elemental analysis: Calcd. for $C_{24}H_{22}NSb$: C, 64.60; H, 4.97; N, 3.14. Found: C, 64.23; H, 5.36; N, 2.90. EI-MS *m/z*: 445 (M^+, 6%), 329 (100%), 208 (26%), 179 (26%). ^{1}H NMR δ ppm: 2.36 (3H, s), 2.52 (3H, s), 3.69 (2H, d, $J = 14.29$ Hz), 3.89 (2H, d, $J = 14.29$ Hz), 7.05 (2H, d, $J = 7.33$ Hz), 7.13 (2H, d, $J = 8.06$ Hz), 7.22 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.29 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 7.49 (2H,d, $J = 8.06$ Hz), 8.33 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 21.5 (q), 41.9 (q), 60.2 (t), 96.8 (s), 110.2 (s), 121.7 (s), 126.2 (d), 128.3 (d), 128.5 (d), 128.9 (d), 131.8 (d), 136.2 (s), 136.7 (d), 137.6 (s). IR cm^{-1}: 2107 (C≡C).

4.4.9. 12-p-Fluorophenylethynyl-N-methyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine (**11a**)

The same procedure as for the preparation of **9a** using **8a** and *p*-fluorophenylacetylene gave **11a** (86% yield). Col-

orless prisms (m.p. 143–145 °C, from hexane–benzene). Elemental analysis: Calcd. for $C_{23}H_{19}FNSb$: C, 61.37; H, 4.25; N, 3.11. Found: C, 60.24; H, 4.44; N, 3.20. EI-MS *m/z*: 449 (M^+, 6%), 329 (100%), 208 (33%), 179 (25%). ^{1}H NMR δ ppm: 2.54 (3H, s), 3.71 (2H, d, $J = 14.77$ Hz), 3.91 (2H, d, $J = 14.77$ Hz), 7.02 (2H, dd, $J_{16,17} = J_{17,F} = 8.79$ Hz), 7.07 (2H, d, $J = 7.33$ Hz), 7.24 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.30 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 7.56 (2H, dd, $J_{16,17} = 8.79$ Hz, $J_{16,F} = 5.50$ Hz), 8.30 (2H, d, $J_{1,2} = 7.33$ Hz). ^{13}C NMR δ ppm: 41.9 (q), 60.2 (t), 97.5 (s), 108.8 (s), 115.3 (dd, $^2J_F = 21.8$ Hz), 120.8 (s), 126.2 (d), 128.4 (d), 128.6 (d), 133.7 (d, $^3J_F = 7.2$ Hz), 136.0 (s), 136.6 (d), 142.6 (s), 162.1 (d, $^1J_F = 248.1$ Hz). IR cm^{-1}: 2129 (C≡C).

4.5. Preparation of 12-arylethynyl-5H-7,12-dihydrodibenz[c,f][1,5]oxastibocine (**15**–**17**)

4.5.1. Bis(2-bromobenzyl) ether (**13**)

To a suspension of NaH (2.40 g, 60% oil dispersion, 0.06 mol) in THF (50 ml), 2-bromobenzylalcohol (**12**) (9.35 g, 0.05 mol) was added at 0 °C during 30 min and stirring was continued for 1.5 h. To this solution, a THF (25 ml) solution of 2-bromobenzyl bromide (**6**) (12.5 g, 0.05 mmol) was added dropwise at 0 °C. The mixture was warmed to 60 °C and stirred for 2.5 h at this temperature. After cooling, the reaction mixture was diluted with ether and quenched with water. The ether layer was separated, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was recrystallized from hexane to give **13** (13.02 g, 73% yield). Colorless needles (m.p. 63–65 °C, lit. m.p. 61–62 °C [29]). Elemental analysis: Calcd. for $C_{14}H_{12}Br_2O$: C, 47.23; H, 3.40. Found: C, 47.31; H, 3.51. EI-MS *m/z*: 356 (M^+, 4%), 275 (4%), 198 (6%), 185 (32%), 170 (86%), 157 (22%), 91 (100%). ^{1}H NMR δ ppm: 4.70 (4H, s), 7.14 (2H, dd, $J_{3,4} = J_{4,5} = 7.33$ Hz), 7.32 (2H, dd, $J_{4,5} = J_{5,6} = 7.33$ Hz), 7.53 (2H, d, $J_{3,4} = 7.33$ Hz), 7.55 (2H, d, $J_{5,6} = 7.33$ Hz). ^{13}C NMR δ ppm: 72.0 (t), 122.6 (s), 127.4 (d), 128.9, (d), 129.0 (d), 132.5 (d), 137.4 (s).

4.5.2. 12-Bromo-5H-7,12-dihydrodibenz[c,f][1,5]oxastibocine (**14**)

To an ethereal (60 ml) solution of **13** (4.00 g, 11.2 mmol), BuLi (24.7 mmol) was added by using syringe at 0 °C and stirring was continued for 1 h. A THF (50 ml) solution of $SbBr_3$ (4.49 g, 90%, 11.2 mmol) was added dropwise at 0 °C and the mixture was stirred for 4 h at room temperature. The reaction mixture was diluted with ether and quenched with water. The organic layer was separated, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was recrystallized from $CHCl_3$–EtOH to give **14** (800 mg, 18% yield). Colorless prisms (m.p. 152–155 °C). Elemental analysis: Calcd. for $C_{14}H_{12}BrOSb$: C, 42.26; H, 3.04. Found: C, 42.74; H, 3.30. EI-MS *m/z*: 398 (M^+, 4%), 354 (9%), 317 (8%), 287 (7%), 263 (8%), 195 (100%). ^{1}H NMR δ ppm: 4.76 (2H, d, $J = 13.55$ Hz), 5.16 (2H, d, $J = 13.55$ Hz), 7.10 (2H, d, $J = 7.33$ Hz), 7.25 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.36 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 8.13 (2H, d, $J_{1,2} = 7.33$ Hz). ^{13}C NMR δ ppm: 75.4 (t), 124.4 (d), 128.8 (d), 129.3 (d), 134.3 (d), 139.7 (s), 141.2 (s).

4.5.3. 12-Phenylethynyl-5H-7,12-dihydrodibenz[c,f][1,5]oxastibocine (**15**)

Ethynylbenzene (51 mg, 0.50 mmol) was dissolved in 5 ml of ether and cooled in ice bath. BuLi (0.50 mmol) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h. A THF (10 ml) solution of **14** (200 mg, 0.50 mmol) was added at 0 °C and stirring was continued for 1.5 h. The reaction mixture was diluted with ether and quenched with water. The ether layer was separated, washed with brine, and dried over anhydrous magnesium sulfate. The organic solution was concentrated in vacuo, and the residue was purified by passing through a short silica gel column (hexane:benzene = 2:1) to give **15** (198 mg, 94% yield). Colorless prisms (m.p. 127–128 °C, benzene–hexane). Elemental analysis: Calcd. for $C_{22}H_{17}OSb$: C, 63.05; H, 4.09. Found: C, 62.96; H, 4.28. EI-MS *m/z*: 418 (M^+, 86%), 279 (37%), 222 (45%), 191 (100%), 167 (50%), 105 (40%). ^{1}H NMR δ ppm: 4.62 (2H, d, $J = 13.55$ Hz), 4.99 (2H, d, $J = 13.55$ Hz), 7.07 (2H, d, $J = 7.33$ Hz), 7.20–7.38 (7H, m), 7.62 (2H, d, $J = 8.06$ Hz), 8.29 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 72.7 (t), 92.8 (s), 112.0 (s), 124.0 (s), 125.4 (d), 128.2 (d), 128.3 (d), 128.9 (d), 132.0 (d), 134.1 (s), 136.3 (d), 142.0 (s). IR cm^{-1}: 2133 (C≡C).

4.5.4. 12-p-Tolylethynyl-5H-7,12-dihydrodibenz[c,f][1,5]oxastibocine (**16**)

The same procedure as for the preparation of **15** using **14** and *p*-tolylacetylene gave **16** (99% yield). Colorless prisms (m.p. 143–144 °C, from benzene–hexane). Elemental analysis: Calcd. for $C_{23}H_{19}OSb$: C, 63.78; H, 4.42. Found: C, 63.74; H, 4.54. EI-MS *m/z*: 432 (M^+, 48%), 293 (21%), 236 (38%), 205 (100%), 195 (73%), 105 (32%). ^{1}H NMR δ ppm: 2.38 (3H, s), 4.64 (2H, d, $J =$ 13.56 Hz), 5.02 (2H, d, $J = 13.56$ Hz), 7.09 (2H, d, $J = 7.33$ Hz), 7.17 (2H, d, $J = 7.69$ Hz), 7.24 (2H, dd, $J_{1,2} = J_{2,3} = 7.33$ Hz), 7.31 (2H, dd, $J_{2,3} = J_{3,4} = 7.33$ Hz), 7.51 (2H, d, $J = 7.69$ Hz), 8.29 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 21.5 (q), 72.7 (t), 91.8 (s), 112.2 (s), 120.9 (s), 125.4 (d), 128.2 (d), 128.9 (d), 129.0 (d), 131.9 (d), 134.2 (s), 136.4 (d), 138.4 (s), 142.0 (s). IR cm^{-1}: 2123 (C≡C).

4.5.5. 12-p-Fluorophenylethynyl-5H-7,12-dihydrodibenz[c,f][1,5]oxastibocine (**17**)

The same procedure as for the preparation of **15** using **14** and *p*-fluorophenylacetylene gave **17** (86% yield). Colorless prisms (m.p. 98–100 °C, benzene–hexane). Elemental analysis: Calcd. for $C_{22}H_{16}FOSb$: C, 60.45; H, 3.69. Found: C, 60.62; H, 3.84. EI-MS *m/z*: 436 (M^+, 46%), 297 (22%), 227 (45%), 195 (100%), 105 (40%). ^{1}H NMR δ

ppm: 4.65 (2H, d, $J = 13.55$ Hz), 5.02 (2H, d, $J = 13.55$ Hz), 7.00–7.10 (4H, m), 7.24–7.36 (4H, m), 7.57–7.61 (2H, m), 8.26 (2H, d, $J = 7.33$ Hz). ^{13}C NMR δ ppm: 72.7 (t), 92.5 (s), 110.8 (s), 115.5 (dd, $^2J_F = 21.9$ Hz), 120.1 (s), 125.4 (d), 128.3 (d), 128.9 (d), 133.8 (dd, $^3J_F = 7.3$ Hz), 134.0 (s), 136.3 (d), 142.0 (s), 162.5 (d, $^1J_F = 249.5$ Hz). IR cm^{-1}: 2129 (C≡C).

4.6. Reaction of ethynyl-1,5-aza- and oxastibocines with acyl chlorides

A mixture of ethynyl-1,5-azastibocine (**9a**, **10a**, **11a**: 1.00 mmol) or ethynyl-1,5-oxastibocine (**15**: 1.00 mmol), acyl chloride (**18a**–**e**: 1.50 mmol), and $PdCl_2(PPh_3)_2$ (0.03 mmol) in 1,2-dichloroethane (5.0 ml) was stirred at room temperature for 1.0 h under an argon atmosphere. After dilution of the reaction mixture with ether (50 ml), a saturated aqueous solution of sodium bicarbonate (30 ml) was added and stirring was continued for another 10 min at room temperature. The ether layer was separated and aqueous layer was extracted with ether. The organic layer was combined and washed with brine, dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified on silica gel column chromatography (hexane:ether = 1:1) to give the cross-coupling product (**19**). Yields of the coupling product were listed in Table 1.

4.7. Reaction of ethynyl-1,5-azastibocine with aryl iodides

A mixture of ethynyl-1,5-azastibocine (**9a**, **d**, **f**: 1.00 mmol), aryl iodide (**22a**–**i**: 1.50 mmol), and $PhCH_2PdCl(PPh_3)_2$ (0.03 mmol) in 1,2-dichloroethane (5.0 ml) was stirred at room temperature under an argon atmosphere. Yields of the cross-coupling (**23**) and homo-coupling products (**21**) were calculated by GLC analysis (5% SE-30 1.5 m, column temperature 180 °C) using biphenyl ($t_R = 1.2$ min) as an internal standard, and the results were listed in Tables 2 and 3.

4.8. Reaction of ethynyl-1,5-azastibocine with aryl bromides

A mixture of ethynyl-1,5-azastibocine (**9f**: 1.00 mmol), aryl bromide (**24a**–**f**: 1.50 mmol), and $PhCH_2PdCl(PPh_3)_2$ (0.03 mmol) in 1,2-dichloroethane (5.0 ml) was stirred under an argon atmosphere. Yields of the cross-coupling (**23**) and homo-coupling products (**21**) were calculated by GLC analysis noted above in Section 4.7, and the results were listed in Table 4.

5. Supplementary materials

Crystallographic data for the aza- and oxastibocines reported in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Number CCDC No. 220330 for **9a** and CCDC No. 602712 for **15**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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