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HYPERVALENT ORGANOANTIMONY COMPOUND 12-ARYL-TETRAHYDRODIBENZ[*c*,*f*][1,5]AZASTIBOCINE: NEW TRANSMETALLATING AGENT FOR PALLADIUM-CATALYZED ARYLATION OF ORGANIC HALIDES

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Abstract – Palladium-catalyzed cross-coupling reaction of 12-aryltetrahydrodibenz[*c*,*f*][1,5]azastibocines with acyl chlorides and aryl iodides was investigated. Although this type of arylation is hardly possible with non-activated triarylstibanes, the intramolecular N---Sb non-bonding interaction in the 1,5-azastibocine facilitates transmetallation of the aryl group in a Stille-type catalytic cycle, and a wide range of acyl chlorides and aryl iodides were arylated with the azastibocine in the presence of 5 mol% of $PdCl_2(PPh_3)_2$. Acceleration of the coupling reaction was also demonstrated under microwave irradiation.

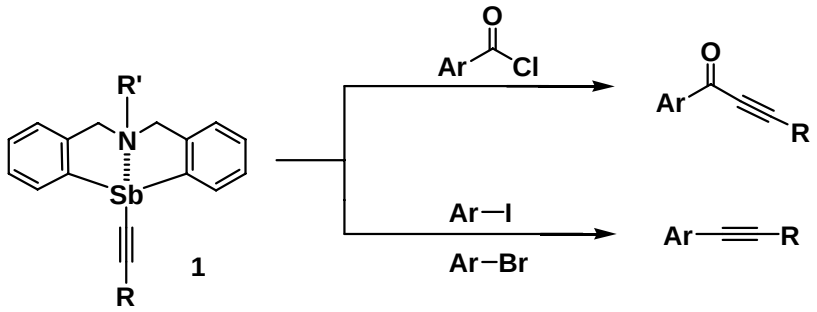
INTRODUCTION

The transition metal-catalyzed cross-coupling reaction is one of the most practical methods for C–C, C–N, and C–O bond formations in modern organic synthesis.[1] A number of attractive catalysts and transmetallating agents have been developed such that even inactive organic halides such as aryl chlorides and bromides having electron-donating groups are employed as electrophiles in various coupling reactions under mild conditions. Besides the progressive development of effective ligands for metal catalysts,[2] much attention has been directed toward developing highly reactive transmetallating agents involving typical heavier elements,[3-9] because versatile and high reactivity can be expected from the reagents including such heavier elements, which can not be found in typical lower elements. For example, incorporation of a highly reactive hypervalent heavier element in transmetallating agents is an attractive strategy to activate metal-catalyzed cross-coupling reactions.[10] Several hypervalent silicon-,[11] tin-,[12] and bismuth-composed[13] coupling reagents have already been known. However, the antimony counterpart still remains to be developed.

As a part of our continuing research on making use of organoantimony(III) compounds (stibanes) as a practical organic reagent,[14] we have previously reported the palladium (Pd)-catalyzed ethynylation of

organic halides by use of *Sb*-ethynyl-1,5-azastibocines (**1**) [15] (Scheme 1). The ethynyl group in **1** is activated by transannular non-bonding interaction between intramolecular antimony and nitrogen, which elongates the antimony–ethynyl carbon bond and facilitates transmetallation of the ethynyl group in a Stille-type catalytic cycle. For instance, the Pd-catalyzed cross-coupling reaction of **1** with acyl chlorides and aryl iodides proceeded at room temperature in a few minutes. Even less reactive aryl bromides could be applied for this cross-coupling reaction, although some heating of the reaction mixture was required. Thus, without air-unstable, expensive, and elaborated phosphine ligands and any additives, which sometimes cause waste disposal problems, the *Sb*-ethynyl-1,5-azastibocine could be used as an ethynylation reagent in Pd-catalyzed cross-coupling reaction under extremely mild conditions.

These results prompted us to investigate the generality of 1,5-azastibocine derivatives as a new transmetallating agent. So we attempted the Pd-catalyzed arylation of organic halides with *Sb*-aryl-1,5-azastibocine and the details are described here.

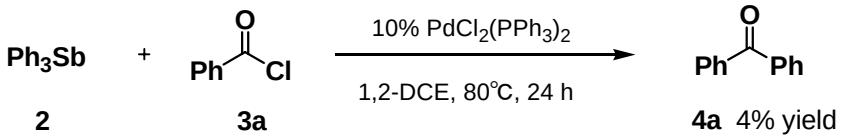


Scheme 1 Pd-catalyzed ethynylation of organic halides by *Sb*-ethynyl-1,5-azastibocine

RESULTS AND DISCUSSION

1. Preparation of *Sb*-Phenyl-1,5-oxa-, thia-, and aza-stibocines

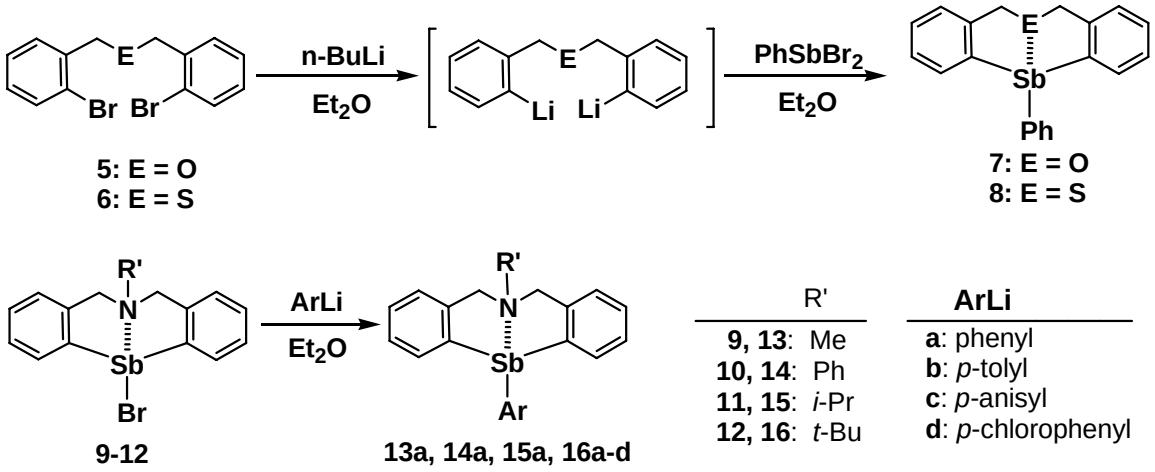
By using non-activated triphenylstibane (**2**), the Pd-catalyzed arylation of benzoyl chloride (**3a**) scarcely proceeded even with 10 mol% $PdCl_2(PPh_3)_2$ in 1,2-dichloroethane (1,2-DCE) at 80 ˚C for 24 h, resulting in only 4% yield of the expected coupling product (**4a**) (Scheme 2).



Scheme 2 Cross-coupling reaction of triphenylstibane (**2**) and benzoyl chloride (**3a**)

Then, we examined the activation of the aryl group on antimony by intramolecular non-bonding interaction between antimony and oxygen, or sulfur using *Sb*-phenyl-1,5-oxa- (**7**) and thiastibocines (**8**) (Scheme 3). The oxastibocine (**7**) was prepared from bis(2-bromobenzyl) ether (**5**)[15b] by treatment with butyllithium (BuLi), followed by addition of dibromophenylantimony ($PhSbBr_2$) prepared from

redistribution of a mixture (2:1) of triphenylstibane (**2**) and antimony tribromide ($SbBr_3$).[16] A similar method was applied to the preparation of thiastibocine (**8**) from bis(2-bromobenzyl) sulfide (**6**). In the synthesis of azastibocines, various *N*-substituted azastibocines (**13-16**) were prepared to test whether substituents on nitrogen show effective activation of the ligand (aryl group) on the antimony through N---Sb non-bonding interaction. Thus, *N*-methyl (**9**), *N*-phenyl (**10**), *N*-isopropyl (**11**), and *N*-*t*-butyl (**12**) derivatives of *Sb*-bromo-1,5-azastibocines were prepared[15b] and were treated with aryllithium reagents to afford the corresponding *Sb*-arylated 1,5-azastibocines (**13-16**) in excellent yields. All the compounds obtained here were isolated as an air-stable crystalline form.



Scheme 3 Preparation of 1,5-heterostibocines

2. Pd-catalyzed Cross-coupling Reaction of *Sb*-Phenyl-1,5-oxa-, thia-, and aza-stibocines with Aroyl Chlorides

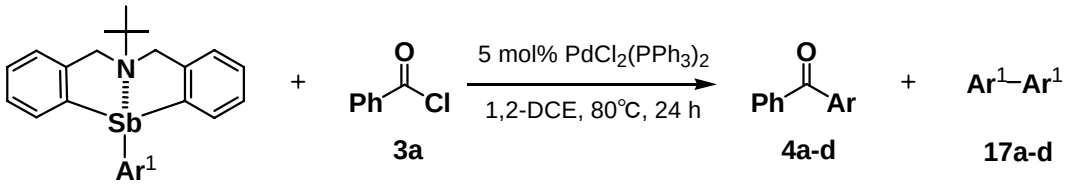
The O---Sb coordinated **7** was heated at 80 ˚C with **3a** in 1,2-DCE in the presence of 5 mol% $PdCl_2(PPh_3)_2$ as a catalyst. Even after heating the mixture for 96 h, no cross-coupling product was formed and almost all the starting material (**7**) was recovered. Generally, nucleophilicity of a thiol group is known to be stronger than that of a hydroxyl group, so interaction with sulfur is thought to be more advantageous than with oxygen, viz. the phenyl group on the antimony in **8** might be more activated by the sulfur than in **7** by the oxygen. However, the situation was not changed even when the S---Sb coordinated **8** was reacted with **3a** with prolonged heating and **8** remained unchanged.

Then, we altered the arylating agent from the O---Sb and S---Sb coordinated oxa- (**7**) and thia-stibocines (**8**) to N---Sb coordinated azastibocines (**13-16**). As expected from our previous results on the Pd-catalyzed ethynylation of organic halides, only the N---Sb coordinated stibocine showed high reactivity in arylation of benzoyl chloride. Thus, the reaction of *N*-*t*-butyl-*Sb*-phenyl-1,5-azastibocine (**16a**) with **3a** in the presence of 5 mol% $PdCl_2(PPh_3)_2$ gave benzophenone (**4a**) in 78 % yield. However, *N*-methyl (**13**), *N*-phenyl (**14**), and *N*-isopropyl (**15**) counterparts were ineffective in this type of coupling

reaction, and almost all starting materials were recovered unchanged, although the reason is not clear at present.

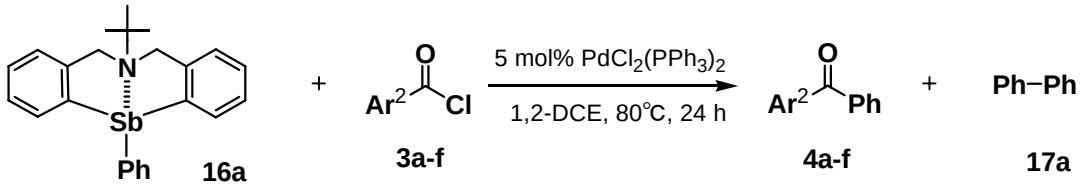
The aryl ligands such as *p*-tolyl, *p*-methoxyphenyl, and *p*-chlorophenyl on the antimony in **16b-d** underwent the cross-coupling reaction with **3a** to afford benzophenone derivatives (**4b-d**) in moderate yields, accompanied by homo-coupled biaryl derivatives (**17b-d**) (Table 1).

Table 1 Reaction of azastibocines (**16a-d**) with benzoyl chloride (**3a**)



Ar^1	Yield of **4** (%)	Yield of **17** (%)
16a: phenyl	78	20
16b: *p*-tolyl	60	37
16c: *p*-methoxyphenyl	57	38
16d: *p*-chlorophenyl	57	34

Table 2 Reaction of azastibocine (**16a**) with aroyl chlorides (**3a-f**)



Ar^2	Yield of **4** (%)	Yield of **17a** (%)
3a: phenyl	76	20
3b: *p*-tolyl	91	9
3c: *p*-methoxyphenyl	58	26
3d: *p*-chlorophenyl	67	13
3e: *p*-fluorophenyl	92	7
3f : *p*-nitrophenyl	61	10

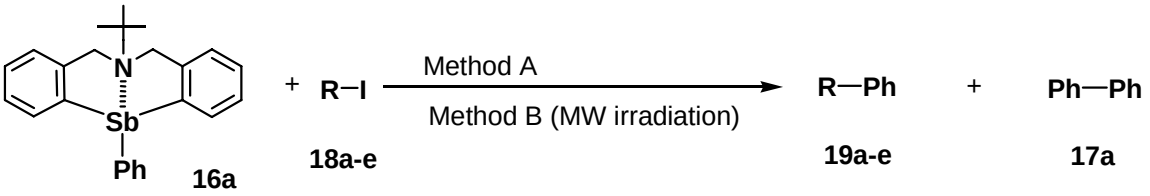
Reaction of **16a** with **3f** afforded 4-nitrobiphenyl (Ar^2-Ph) in 15 % yield along with **4f** and **17a**.

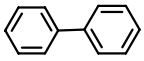
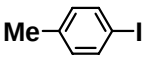
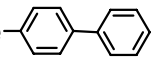
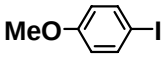
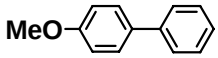
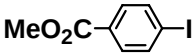
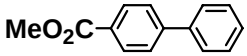
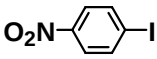
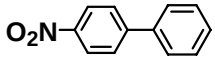
Several acyl chlorides (**3b-f**) were also subjected to the reaction with **16a** (Table 2). In all cases, it was required to heat the mixture at 80 ˚C for 24 h for completion of the reaction, and aroyl chlorides with electron-donating (**3b**, **c**) and -withdrawing (**3d**, **e**) substituents afforded the cross-coupling product in moderate to good yields. However, in the reaction of **16a** with the aroyl chloride (**3f**) bearing a strong electron-withdrawing nitro group, simultaneous decarbonylation[17] was induced to give rise to the unexpected 4-nitrobiphenyl in 15% yield in addition to the cross- (**4f**) and homo-coupling (**17a**) products.

3. Pd-catalyzed Cross-coupling Reaction of Azastibocine with Aryl Iodides

Next, cross-coupling of the azastibocine (**16a**) with aryl iodides (**18a-e**) was examined (Table 3). Electronically neutral and deficient aryl iodides (**18a**, **d**, **e**) underwent the cross-coupling reaction efficiently with 5 mol% $PdCl_2(PPh_3)_2$ in 1,2-DCE at 80 ˚C for 24 h (Method A). Aryl iodide (**18c**) with an electron-donating methoxy group gave the cross-coupling product (**19c**) in rather inferior yield (57%) and the yield of the undesirable homo-coupled product (**17a**) increased to 23 %. A similar substituent effect was observed in other heteroatom-mediated cross-coupling reactions in that the oxidative addition of electron-rich aryl halides to Pd(0) species is unfavorable compared with electron-deficient halides.[1, 2]

Table 3 Reaction of 1,5-azastibocine (**16a**) with aryl iodides (**18a-e**)



	Aryl iodide (**18**)	Cross-coupling product (**19**)	**19** (%)	**17a** (%)
a			93 (75)	
b			68 (62)	13 (23)
c			57 (54)	23 (36)
d			78 (61)	7 (28)
e			73	8

Method A: 5 mol% $PdCl_2(PPh_3)_2$, 1,2-DCE, 80 ℃, 24 h.
Method B: 1 mol% $PdCl_2(PPh_3)_2$, DMSO, MW(200 W), 100 ℃, 5 min, $C_{16}H_{33}NMe_3Br$.
Yields in parentheses were obtained by method B, and the values were determined by GLC analysis.

Because of the inevitable requirement of long reaction time for arylation of aryl iodides in Method A, we finally attempted acceleration of this cross-coupling with microwave (MW) irradiation[18] (Method B), and the results are shown in Table 3 in parentheses. Since DMSO was revealed to be suitable for the Pd-catalyzed ethynylation of aryl iodides with **1**,[19] the reaction of **16a** with **18** was also carried out in the same solvent. With MW heating (200 W, 100 ˚C) of the mixture only for 5 min, 66 % yield of biphenyl (**17a**, **19a**) was obtained in the presence of 1 mol% $PdCl_2(PPh_3)_2$. Further improvement was achieved by addition of cetyltrimethylammonium bromide with increasing the polarity of the reaction mixture[19, 20] and the yield of the product was improved to 75 %. Under these conditions, aryl iodides (**18b-e**) were subjected to the MW-assisted coupling reaction. In all cases, the reaction was completed within 5 min and the yields of the products (**19b-e**) were almost comparable to those of the conventional heating method

(Method A), although some increase of homo-coupling product (**17a**) was observed under these conditions. When the same mixture of **16a**, **18**a, $PdCl_2(PPh_3)_2$ (1 mol%), and the ammonium salt in DMSO was heated in an oil bah at 100 ˚C, the reaction mixture gave biphenyl (**19a**) in 90% yield, however, prolonged reaction time (24 h) was required under these reaction conditions.

This Sb-mediated arylation is thought to proceed in a similar pathway to that for Sb-mediated ethynylation reported previously.[14, 15] The initial step for the formation of the cross-coupling product (**19**) would be the oxidative addition of aryl iodide (**18**) to Pd(0) species generated *in situ* from $PdCl_2(PPh_3)_2$ and 2 eq of **16**. The Pd(II) complex (**20**) thus formed results in transmetallation with the aryl group on **16** to afford Pd(II) complex (**21**) which undergoes reductive elimination to give the product (**19**) with catalytic cycle A in Figure 1. The increase of the homo-coupling product (**17**) under MW-irradiation can be explained as follows. The oxidative addition of the halides (**18**) or azastibocine (**16**) to the Pd(0) may be competitive, and the latter reaction to form **17** with catalytic cycle B will be more thermally advantageous than the former one. It has been well documented that, in MW-assisted reactions, the molecules are provided powerful instantaneous energy which assists the formation of thermally favorable product.[18] A part of Sb-iodinated 1,5-azastibocine (**22**) was recovered from the reaction mixture, although bis(1,5-azastibocine) (**25**) could not be isolated yet.

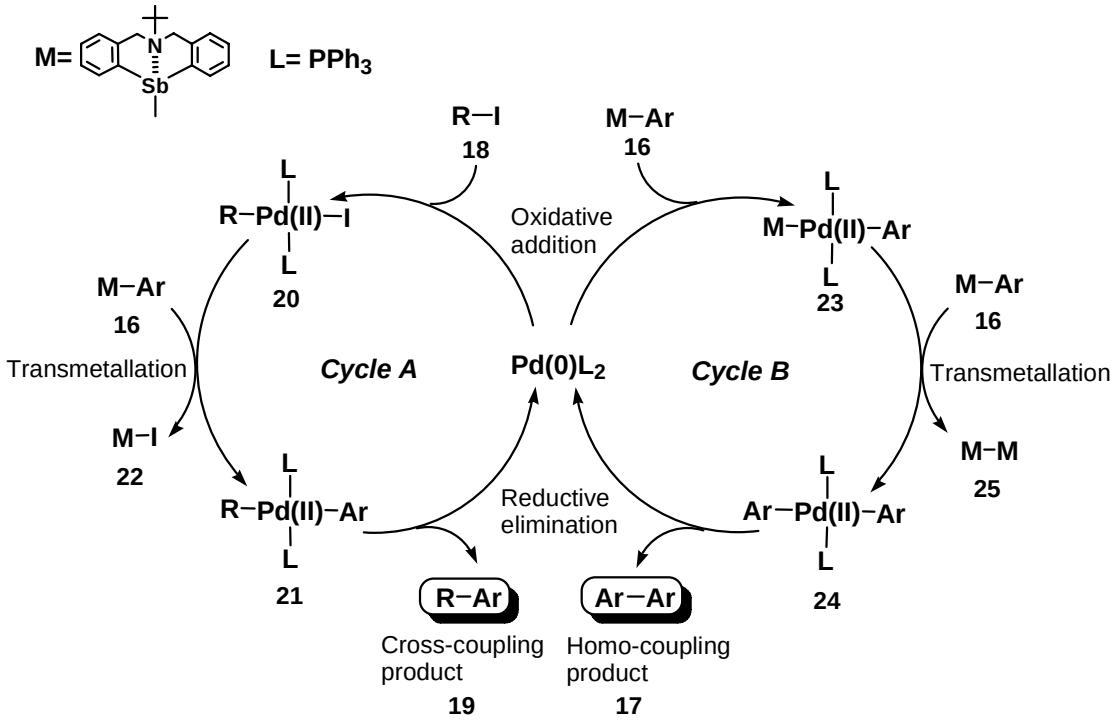


Figure 1 Possible catalytic cycles for cross- and homo-coupling product

In summary, Pd-catalyzed arylation of acyl chlorides and aryl iodides was achieved by using *Sb*-aryl-1,5-azastibocines under neutral conditions. Although this type of cross-coupling reaction is hardly

possible with non-activated triphenylstibane, the [5,5,0]-bicyclic transannular coordination between antimony and nitrogen atoms in *Sb*-aryldibenz[1,5]azastibocine facilitated transmetallation of an aryl group on the antimony with a Stille-type catalytic cycle. Generality of this transmetallating agent was also proved by a number of coupling reactions with acyl chlorides and aryl iodides. Under MW irradiation, the coupling reaction was promoted effectively to complete in only 5 min. Taking these new findings and our recent results[15] into account, we have disclosed that N---Sb coordinated 1,5-azastibocine derivatives have high ability as a coupling partner for Pd-catalyzed coupling reactions and can be utilized not only for ethynylation but also arylation of a variety of organic halides such as acid halides and aryl halides under mild conditions.

EXPERIMENTAL

General: Reactions requiring anhydrous conditions were performed in pre-dried glassware under an argon atmosphere with rigorous exclusion of air and moisture. 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 are not corrected. ^{1}H 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 MHz and 125 MHz) spectrometer in $CDCl_3$ unless otherwise stated. MS (EI) spectra were obtained on a JEOL JMS–SX 102A instrument and IR spectra were recorded on a HORIBA FT–720 instrument. GLC analysis of the products was made using Shimadzu GC–14B. All chromatographic separations were accomplished with either Kieselgel 60 (Merck) or Silica Gel 60N (Kanto Chemical Co., Inc.). TLC was performed with Macherey-Nagel Pre-coated TLC plates Sil G25 UV_{254}. Tetrahydrofuran (THF: anhydrous grade), butyllithium (BuLi: 1.51–1.60 M in hexane solution), and phenyllithium (PhLi: 0.98-1.05 M in cyclohexane–diethyl ether solution) was obtained from Kanto Chemical Co., Inc. Japan.

Reaction of triphenylstibane (2) with benzoyl chloride

A mixture of triphenylstibane (**2**, $SbPh_3$: 352 mg, 1.00 mmol), benzoyl chloride (**3a**: 211 mg, 1.50 mmol) and $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol) in 1,2-dicholoroethane (DCE: 10 mL) was heated at 80 ˚C for 24 h with stirring. After dilution of the reaction mixture with ether and water, the organic layer was separated, washed with saturated aqueous solution of sodium bicarbonate and brine. The organic solution was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated *in vacuo*. The residue was separated by silica gel column chromatography (hexane:ether = 10:1 as an eluent) to give **4a** (7.3 mg, 4%).

12-Phenyl-5*H*-7,12-dihydrodibenz[*c*,*f*][1,5]oxastibocine (7)

To a stirred solution of 2-bromobenzyl ether[15b] (**5**: 3.56 g, 10.0 mmol) in ether (50 mL), BuLi (1.58 M solution in hexane, 12.7 mL, 20.0 mmol) was added using a syringe through the rubber septa cap at –20 ˚C and the mixture was stirred for 1 h at this temperature. An ether (50 mL) solution of dibromophenylstibane ($PhSbBr_2$), prepared by heating a mixture of Ph_3Sb (1.17 g, 3.33 mmol) and antimony tribromide ($SbBr_3$: 2.40 g, 6.66 mmol) at 100 ˚C for 1 h, was added dropwise and stirring was continued for 40 min at –20 ˚C. The reaction mixture was diluted with ether and quenched with water. The ether layer was separated, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was separated by silica gel column chromatography (hexane:ether = 10:1) to give **7** (832 mg, 21%). Colorless prisms (mp 170–171 ˚C, from ethanol–chloroform). Anal. Calcd for $C_{20}H_{17}OSb$: C, 60.80; H, 4.34. Found: C, 61.03; H, 4.42. MS *m/z* (%): 394 (M^+, 100), 317 (96), 287 (58), 226 (13). ^{1}H NMR δ ppm: 4.72 (2H, d, J = 13.3 Hz), 4.96 (2H, d, J = 13.3 Hz), 7.10–7.12 (4H, m), 7.19–7.24 (4H, m), 7.43–7.45 (3H, m), 7.69–7.71 (2H, m). ^{13}C NMR δ ppm: 71.9 (t), 126.1 (d), 127.9 (d), 128.3 (d), 128.8 (d), 135.4 (s), 136.2 (d), 138.8 (d), 142.6 (s), 143.4 (s).

Bis(2-bromobenzyl) sulfide (6)

A mixture of *o*-bromobenzyl hydrosulfide[21] (9.83 g, 48.4 mmol), *o*-bromobenzyl bromide (12.1 g, 48.4 mmol) and sodium hydroxide (2.3 g, 53.5 mmol) in aqueous ethanol (ethanol/water = 80 mL/10 mL) was heated at 100 ˚C for 1 h. The solvent was concentrated in vacuo to half of the volume and the residue was diluted with ether. The organic layer was separated, washed with brine, dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was recrystallized from hexane to give **6** (16.7 g, 94%). Colorless needles (mp 69–70 ˚C, from hexane). Anal. Calcd for $C_{14}H_{12}Br_2S$: C, 45.19; H, 3.25. Found: C, 45.23; H, 3.19. MS *m/z* (%): 372 (M^+, 78), 293 (17), 212 (14), 169 (100). ^{1}H NMR δ ppm: 3.80 (4H, s), 7.09 (2H, dd, $J_{3,4} = J_{4.,5} = 7.8$ Hz), 7.24 (2H, dd, $J_{4,5} = J_{5,6} = 7.8$ Hz), 7.35 (2H, d, $J_{5,6} = 7.8$ Hz), 7.54 (2H, d, $J_{3,4} = 7.8$ Hz). ^{13}C NMR δ ppm: 36.4 (t), 126.4 (s), 127.4 (d), 128.6 (d), 130.7 (d), 133.1 (d), 137.3 (s).

12-Phenyl-5*H*-7,12-dihydrodibenz[*c*,*f*][1,5]thiastibocine (8)

To a stirred solution of **6** (5.00 g, 13.4 mmol) in ether (50 mL), BuLi (1.60 M solution in hexane, 16.8 mL, 26.9 mmol) was added at –20 ˚C and the mixture was stirred for 1 h at this temperature. An ether (50 mL) solution of $PhSbBr_2$ [prepared by heating the mixture of Ph_3Sb (1.57 g, 4.47 mmol) and $SbBr_3$ (3.23 g, 8.94 mmol) at 100 ˚C for 1 h] was added to the mixture and stirring was continued for 40 min at –20 ˚C. The reaction mixture was diluted with ether and quenched with water. The ether layer was separated, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was separated by silica gel column chromatography (hexane:ether = 10:1) to give **8** (1.82 g, 33%).

Colorless needles (mp 154–155 ˚C, from ethanol–chloroform). Anal. Calcd for $C_{20}H_{17}SSb$: C, 58.42; H, 4.17. Found: C, 58.49; H, 4.25. MS *m/z* (%): 410 (M^+, 12), 333 (100), 287 (7%), 243 (12). ^{1}H NMR δ ppm: 3.67 (2H, d, *J* = 14.2 Hz), 3.76 (2H, d, *J* = 14.2 Hz), 7.14–7.18 (2H, m), 7.29–7.34 (7H, m), 7.41–7.43 (2H, m), 7.55–7.56 (2H, m). ^{13}C NMR δ ppm: 34.5 (t), 127.1 (d), 128.7 (d), 128.9 (d), 129.6 (d), 130.4 (d), 135.9 (d), 136.8 (d), 139.7 (s), 140.1 (s), 143.9 (s).

6-Methyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (13a)

To a THF (100 mL) solution of 12-bromo-6-methyl-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine[15b] (**9**: 4.10 g, 10.0 mmol), a solution of PhLi (1.04 M in cyclohexane–ether solution, 14.4 mL, 15.0 mmol) was added at 0 ˚C, and the mixture was stirred for 1 h in an ice-bath. The mixture was diluted with ether, and quenched with water. The organic layer was separated, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was separated by silica gel column chromatography (hexane:ethyl acetate = 2:1) to give **13a** (3.75 g, 92%). Colorless prisms (mp 109–110 ˚C, from ethanol–ether). Anal. Calcd for $C_{20}H_{20}NSb$: C, 61.80; H, 4.94; N, 3.43. Found: C, 61.53; H, 4.89; N, 3.51. MS *m/z* (%): 407 (M^+, 7), 330(100), 316 (9), 239 (15), 208 (5), 118 (5). ^{1}H NMR δ ppm: 2.50 (3H, s), 3.68 (2H, d, *J* = 14.2 Hz), 3.97 (2H, d, *J* = 14.2 Hz), 7.06-7.08 (4H, m), 7.16–7.19 (4H, m), 7.39–7.40 (3H, m), 7.67–7.68 (2H, m). ^{13}C NMR δ ppm: 41.4 (q), 59.9 (t), 126.6 (d), 127.7 (d), 127.8 (d), 128.0 (d), 128.3 (d), 136.4 (d), 137.3 (s), 138.5 (d), 143.9 (s), 146.7 (s).

6,12-Diphenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (14a)

The same procedure for the preparation of **13a** using 12-bromo-6-phenyl-5,6,7,12-tetrahydrodibenz-[*c*,*f*][1,5]azastibocine[15b] (**10**: 3.78 g, 8.0 mmol) and PhLi (0.99 M, 9.7 mL, 9.60 mmol) gave **14a** (3.30 g, 88%). Colorless prisms (mp 218–220 ˚C, from benzene–hexane). Anal. Calcd for $C_{26}H_{22}NSb$: C, 66.41; H, 4.72; N, 2.98. Found: C, 66.31; H, 4.81; N, 3.03. MS *m/z* (%): 469 (M^+, 8), 392 (100), 301 (18). ^{1}H NMR δ ppm: 4.45 (2H, d, *J* = 15.1 Hz), 4.71 (2H, d, *J* = 15.1 Hz), 6.93 (1H, t, *J* = 7.0 Hz), 7.09–7.11 (4H, m), 7.19–7.25 (8H,m), 7.40–7.42 (3H, m), 7.65–7.67 (2H, m). ^{13}C NMR δ ppm: 57.4 (t), 117.4 (d), 121.3 (d), 126.8 (d), 127.9 (d), 128.2 (d), 128.3 (d), 128.6 (d), 128.9 (d), 135.6 (s), 136.5 (d), 138.9 (d), 143.2 (s), 144.2 (s), 148.4 (s).

6-Isopropyl-12-phenyl–5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (15a)

The same procedure for the preparation of **13a** using 6-isopropyl-12-bromo-5,6,7,12-tetrahydrodibenz [*c*,*f*][1,5]azastibocine[15b] (**11**: 3.66 g, 8.36 mmol) and PhLi (0.99 M, 10 mL, 10.0 mmol) gave **15a** (3.55 g, 98%). Colorless prisms (mp 121–122 ˚C, from benzene–hexane). Anal. Calcd for $C_{23}H_{24}NSb$: C, 63.33; H, 5.55; N, 3.21. Found: C, 63.20; H, 5.61; N, 3.23. MS *m/z* (%): 435 (M^+, 5), 392 (3), 358 (100), 316 (4%),

267 (5%), 225 (8%). ^{1}H NMR δ ppm: 1.20 (6H, d, J = 6.9 Hz), 3.17 (1H, m), 3.85 (2H, d, J = 14.9 Hz), 3.93 (2H, d, J = 14.9 Hz), 7.04–7.08 (4H, m), 7.14–7.18 (4H, m), 7.38–7.39 (3H, m), 7.66–7.68 (2H, m). ^{13}C NMR δ ppm: 18.4 (q), 51.7 (d), 53.8 (t), 126.7 (d), 127.5 (d), 127.8 (d), 128.0 (d), 128.3 (d), 136.3 (d), 136.7 (s), 138.7 (d), 145.0 (s), 146.6 (s).

6-*t*-Butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (16a)

The same procedure for the preparation of **13a** using 12-bromo-6-*t*-butyl-5,6,7,12-tetrahydrodibenz-[*c,f*][1,5]azastibocine[15b] (**12**: 4.52 g, 10.0 mmol) and PhLi (0.99 M, 10 mL, 10.0 mmol) gave **16a** (3.98 g, 88%). Colorless prisms (mp 134–135 ˚C, from ethanol–chloroform). Anal. Calcd for $C_{24}H_{26}NSb$: C, 64.02; H, 5.82; N, 3.11. Found: C, 64.11; H, 5.91; N, 3.13. MS *m/z* (%): 449 (M^+, 7), 392 (4), 372 (100), 316 (44), 225 (11). ^{1}H NMR δ ppm: 1.24 (9H, s), 3.86 (2H, d, J = 15.4 Hz), 4.17 (2H, d, J = 15.4 Hz), 7.01–7.06 (4H, m), 7.14–7.19 (4H, m), 7.40–7.41 (3H, m), 7.66–7.68 (2H, m). ^{13}C NMR δ ppm: 26.9 (q), 54.8 (t), 57.6 (s), 126.2 (d), 127.1 (d), 127.8 (d), 128.1 (d), 128.3 (d), 136.2 (d), 136.4 (s), 138.9 (d), 146.5 (s), 146.7 (s).

6-*t*-Butyl-12-*p*-tolyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (16b)

To a stirred solution of *p*-bromotoluene (1.13 g, 6.61 mmol) in ether (20 mL), BuLi (1.57 M, 4.2 mL, 6.59 mmol) was added using a syringe at 0 ˚C and the mixture was stirred for 1 h in an ice-bath. A THF (30 mL) solution of **12** (2.0 g, 4.42 mmol) was added dropwise at 0 ˚C and stirring was continued for 2 h. The reaction mixture was diluted with ether, and quenched with water, and separated. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was separated by silica gel column chromatography (hexane:ether =10:1) to give **16b** (1.71 g, 84%). Colorless prisms (mp 183–184 ˚C, from ethanol–chloroform). Anal. Calcd for $C_{25}H_{28}NSb$: C, 64.68; H, 6.08; N, 3.02. Found: C, 64.73; H, 6.11; N, 3.11. MS *m/z* (%): 463 (M^+, 9), 406 (4), 372 (100), 316 (43), 287 (3), 225 (12). ^{1}H NMR δ ppm: 1.23 (9H, s), 2.42 (3H, s), 3.85 (2H, d, J = 15.4 Hz), 4.16 (2H, d, J = 15.4 Hz), 7.01–7.06 (4H, m), 7.13–7.16 (2H, m), 7.19–7.24 (4H, m). ^{13}C NMR δ ppm: 21.5 (q), 26.9 (q), 54.8 (t), 57.5 (s), 126.1 (d), 127.0 (d), 127.8 (d), 129.2 (d), 136.2 (d), 136.5 (s), 137.7 (s), 138.9 (d), 142.4 (s), 146.7 (s).

6-*t*-Butyl-12-*p*-methoxyphenyl–5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (16c)

The same procedure for the preparation of **16b** using *p*-bromoanisole (1.86 g, 9.96 mmol), BuLi (1.57 M, 6.34 mL, 9.96 mmol), and **12** (3.00 g, 6.64 mmol) afforded **16c** (1.97 g, 62%). Colorless prisms (mp 142–143 ˚C, from ethanol–ether). Anal. Calcd for $C_{25}H_{28}NOSb$: C, 62.52; H, 5.88; N, 2.92. Found: C, 62.61; H, 5.89; N, 2.81. MS *m/z* (%): 479 (M^+, 12), 422 (7), 372 (100), 316 (44), 287 (4), 225 (11). ^{1}H

NMR δ ppm: 1.23 (9H, s), 3.60 (2H, d, J = 16.0 Hz), 3.87 (3H, s), 4.16 (2H, d, J = 16.0 Hz), 6.97 (2H, d, J = 8.3 Hz), 7.01–7.05 (4H, m), 7.13–7.16 (2H, m), 7.19–7.20 (2H, m), 7.57 (2H, d, J = 8.3 Hz). ^{13}C NMR δ ppm: 25.9 (q), 54.8 (t), 55.0 (q), 57.5 (s), 114.2 (d), 126.1 (d), 127.1 (d), 127.8 (d), 136.2 (d), 136.56 (s), 136.63 (s), 140.1 (d), 146.7 (s), 159.8 (s).

6-*t*-Butyl-12-*p*-chlorophenyl-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine (16d)

The same procedure for the preparation of **16b** using *p*-bromochlorobenzene (1.27 g, 6.64 mmol), BuLi (1.57 M, 4.20 mL, 6.64 mmol), and **12** (2.00 g, 4.42 mmol) afforded **16d** (1.55 g, 73%). Colorless prisms (mp 148–149 ˚C, from ethanol–chloroform). Anal. Calcd for $C_{24}H_{25}NClSb$: C, 59.47; H, 5.20; N, 2.89. Found: C, 59.42; H, 5.19; N, 2.77. MS *m/z* (%): 485 (M^+, 5), 428 (6), 372 (100), 316 (45), 225 (14). ^{1}H NMR δ ppm: 1.23 (9H, s), 3.86 (2H, d, J = 15.1 Hz), 4.17 (2H, d, J = 15.1 Hz), 7.02–7.07 (4H, m), 7.12–7.17 (4H, m), 7.37 (2H, d, J = 7.8 Hz), 7.59 (2H, d, J = 7.8 Hz). ^{13}C NMR δ ppm: 26.9 (q), 54.8 (t), 57.7 (s), 126.2 (d), 127.2 (d), 128.0 (d), 128.5 (d), 134.4 (s), 136.0 (d), 136.2 (s), 140.2 (d), 144.9 (s), 146.6 (s).

Reaction of 12-aryl-6-*t*-butyl-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocines (16a-d) with benzoyl chloride (3a)

General procedure: a mixture of **16a-d** (1.00 mmol), **3a** (211 mg, 1.50 mmol), and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in DCE (10 mL) was heated with stirring at 80 ˚C for 24 h under an argon atmosphere. After cooling, the mixture was diluted with ether and water. The ether layer was separated, washed with 5% aqueous sodium hydrogen carbonate and brine, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was separated by silica gel column chromatography (hexane:ether = 10:1) to give biphenyl derivatives (**17a-d**) and diaryl ketones (**4a-d**), successively. The results of these reactions are collected in Table 1.

Reaction of 12-phenyl–*N*-*t*-butyl-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine (16a) with aroyl chlorides (3b-f)

General procedure: a mixture of **16a** (450 mg, 1.00 mmol), **3b-f** (1.50 mmol), and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in DCE (10 mL) was heated at 80 ˚C for 24 h under an argon atmosphere. After cooling, the mixture was diluted with ether and water. The ether layer was separated, washed with 5% aqueous sodium hydrogen carbonate and brine, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was separated by silica gel column chromatography (hexane:ether = 10:1) to give biphenyl (**17a**) and diaryl ketones (**4b-f**), successively. The results of these reactions are collected in Table 2.

In the reaction of **16a** with 4-nitrobenzoyl chloride (**3f**), decarbonylated product, 4-nitrobiphenyl, was isolated in 15% yield along with **4f** and **17a**. 4-Nitrobiphenyl: Colorless prisms (mp 115–116 ˚C, from ethanol). MS *m/z* (%): 199 (M^+, 100), 152 (68). ^{1}H NMR δ ppm: 7.45 (1H, t, J = 7.3 Hz), 7.50 (2H, t, J = 7.3 Hz), 7.62 (2H, d, J = 7.3 Hz), 7.73 (2H, d, J = 8.7 Hz), 8.30 (2H, d, J = 8.7 Hz). ^{13}C NMR δ ppm: 124.1 (d), 127.4 (d), 127.8 (d), 128.9 (d), 129.1 (d), 138.7 (s), 147.1 (s), 147.6 (s). IR(cm^{-1}): 1512, 1351.

Reaction of 6-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (16a) with aryl iodides (18a-e)

General procedure: a mixture of **16a** (450 mg, 1.00 mmol), aryl iodides (**18a-e**: 1.50 mmol), and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in DCE (10 mL) was heated at 80 ˚C for 24 h under an argon atmosphere. After dilution of the reaction mixture with ether and water, the ether layer was separated, washed with 5% aqueous sodium hydrogen carbonate and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo.* The residue was separated by silica gel column chromatography (hexane) to afford biphenyl derivatives (**17a** and **19a-e**). The results of these reactions are collected in Table 3.

Microwave-assisted reaction of 6-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (16a) with aryl iodides (18a-e)

General procedure: The azastibocine (**16a**: 113 mg, 0.25 mmol), aryl iodides (**18a-e**: 0.375 mmol), $PdCl_2(PPh_3)_2$ (1.8 mg, 2.6 μmol), and cetyltrimethylammonium bromide (CTMAB: 90 mg, 0.25 mmol) were dissolved in 2 mL of DMSO. The vessel was sealed with silicon septa with aluminum cap and heated at 100 ˚C for 5 min under microwave irradiation (200 W). After dilution of the reaction mixture with ether and water, the solution was filtered through a bed of celite by suction filtration. The organic layer was separated, washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The yields of the products were determined by GLC analysis (5% SE-30, 1.6 M, column temp. 210 ˚C) of the residue using benzil (t_R=5.00 min) as an internal standard. Biphenyl (**18a**: t_R=1.22 min); 4-methylbiphenyl (**18b**: t_R=1.75 min); 4-methoxybiphenyl (**18c**: t_R=2.99 min); 4-methoxycarbonylbiphenyl (**18d**: t_R=5.96 min). The results of these MW-assisted reactions are collected in Table 3 in parentheses.

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