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RHODIUM-CATALYZED CONJUGATE ADDITION OF Sb-ARYL-1,5-AZASTIBOCINES TO α,β-UNSATURATED CARBONYL COMPOUNDS

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This paper is dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday

Abstract – Rhodium-catalyzed conjugate addition of *Sb*-aryl-1,5-azastibocines to α,β-unsaturated carbonyl compounds is described. The rhodium-catalyzed reaction was carried out in aqueous *N*-methy-2-pyrrolidinone (NMP) to give 1,4-conjugate adduct exclusively, while the palladium catalyzed reaction gave only Heck-type adduct. The 1,4-addition of various aryl groups such as substituted benzenes and thiophenes was achieved with various enones and enoates.

INTRODUCTION

Recent advancements in metal catalyzed C-C bond formation are remarkable,[1] because of the development of the sophisticated ligands of transition metals,[2] elaboration of effective transmetallating agents,[3] employment of ionic liquids as reaction medium,[4] and microwave irradiation technology.[5] Research into effective transmetallating agents is a field of attention. With these agents, the transition metal-catalyzed reactions can be carried out efficiently under mild conditions and the reactions become applicable to unstable compounds with labile functional groups.

Progress in chemistry of main group elements[6] contributes much to the development of efficient transmetallating agents because main group compounds exhibit suitable properties for the metal catalyzed reaction. Particularly, heavier element compounds below the third row show soft nucleophilic characteristics, and are considered to be reasonable partners for soft electrophiles such as α,β-unsaturated carbonyl compounds.

For 1,4-conjugate addition, one of the most conventional and prevailing methods is the use of soft copper reagents such as organocuprates.[7] However, because these reagents have to be prepared from moisture sensitive organolithiums,[8] Grignard reagents,[9] and organozinc reagents,[10] the reactions must be carried out in strict anhydrous conditions under an inert atmosphere.

Another method for 1,4-conjugate addition was pioneered by Miyaura and co-workers by use of boronic acid in the presence of rhodium catalysts.[11] Inspired by this work, a number of main group compounds were investigated for the transition metal catalyzed 1,4-conjugate addition including organo-aluminum,[12] -boron,[13] -tin,[14] -silicon,[15] -bismuth,[16] -indium,[17] -plumbum,[18] -zirconium,[19] and -zinc[20] compounds. Unlike copper reagents, these compounds exhibit a tolerance for hard electrophiles such as water and the reactions can be carried out in aqueous medium.

Over the past few years, we have investigated the chemistry of organoantimony compounds and revealed that 1,5-azastibocines (**1**) with N-Sb intramolecular interaction are excellent transmetallating agents in Pd-catalyzed cross-coupling reactions.[21] These results prompted us to investigate metal-catalyzed 1,4-conjugate addition using 1,5-azastibocines (**1**), and we now disclose that the reaction of α,β-unsaturated carbonyl compounds with **1** in the presence of rhodium catalyst resulted in 1,4-conjugated addition in aqueous media. It should be noted that the mode of the reaction is largely dependent on the nature of the transition metal catalyst employed, and the reaction by use of rhodium catalyst gave 1,4-conjugate adduct exclusively, while that of palladium catalyst afforded Heck-type adduct. Details are described here along with preliminary results.[22]

RESULTS AND DISCUSSION

1. Investigation of Metal Catalyst and Solvent

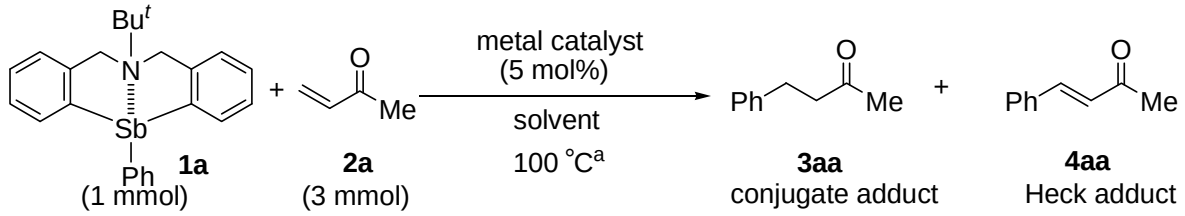
According to Pauling's electronegativity, antimony atom is more electronically positive than carbon atom (Sb, 1.9; C, 2.5).[23] Thus, phenyl carbon atom in 1,5-azastibocine is slightly negatively charged and is considered to exhibit a nucleophilic character. However, it was not reactive enough toward 1,4-conjugate addition without a metal catalyst. None of the reactions of 1,5-azastibocine occurred with methyl vinyl ketone even after prolonged heating at 100 ˚C for 24 h in 1,4-dioxane : H_2O (10 : 1).

So, we first investigated suitable metal catalysts (Table 1, entries 1-10). Nickel catalysts are reported to be effective for indium-mediated 1,4-conjugate addition,[17] however, neither $NiCl_2(PPh_3)_2$ nor $Ni(cod)_2$ promoted the reaction of 1,5-azastibocine (**1a**) with methyl vinyl ketone (**2a**) and all the starting stibocine (**1a**) was recovered unchanged (entries 1 and 2). In the presence of 5 mol% palladium catalyst, the reaction of 1,5-azastibocine (**1a**) and methyl vinyl ketone (**2a**) afforded Heck-type adduct (**4aa**) solely and no 1,4-conjugate adduct (**3aa**) was obtained (entries 3-5). Palladium-catalyzed reactions of organoantimony compounds to alkenes have already been reported, such as phenylantimony chlorides and

triarylantimony diacetates, to give Heck-type adduct.[24] Furthermore, palladium-catalyzed reactions of organoboron and silicon compounds with alkenes also gave the Heck-type adduct.[25] It is characteristic of palladium catalyst to undergo *β*-elimination with ease to give Heck-type adduct. Thus, it is reasonable for *Sb*-aryl-1,5-azastibocine to give Heck-type adduct efficiently in the presence of $Pd(OAc)_2$.

Under the rhodium catalysts, the reaction proceeded efficiently to afford the expected 1,4-adduct as the major product (entries 6-10). Especially, rhodium catalyst with diene ligand (cod: cyclooctadiene) worked effectively to suppress the competitive Heck reaction completely. In terms of yield and selectivity of the product, $[RhCl(cod)]_2$ was found to be a suitable catalyst (entry 10).

Table 1. Investigation of Catalyst and Solvent



Entry	Catalyst	Solvent	Time (h)	**3aa** (%)[b]	**4aa** (%)[b]
1	$NiCl_2(PPh_3)_2$		25	---	---
2	$Ni(cod)_2$		24	---	---
3	$Pd(OAc)_2$	dioxane : H_2O (10 : 1)	24	---	79
4	$PdCl_2$		24	---	43
5	$PdCl_2(PPh_3)_2$		24	---	14
6	$Rh(acac)(C_2H_4)_2$		24	36	36
7	$Rh(nbd)ClO_4$		16	55	11
8	$Rh(cod)BF_4$		14	78	---
9	$[Rh(OH)(cod)]_2$		16	80	11
10	$[RhCl(cod)]_2$		9	81	---
11	$[RhCl(cod)]_2$	THF : H_2O (10 : 1)	5.5	70	---
12		DME : H_2O (10 : 1)	3.5	84	---
13		C_2H_5OH	1	75	---
14		CH_3COOH	1.5	---	---
15		DMU : H_2O (10 : 1)	1	76	6
16		TMU : H_2O (10 : 1)	2.5	77	---
17		NMP : H_2O (10 : 1)	1	83	---
18		NMP	1	74	9

[a] Oil bath temperature.
[b] Isolated yield.

Next, the most suitable solvent for the reaction was investigated by use of $[RhCl(cod)]_2$ as the catalyst (Table 1, entries 10-18). When the reaction was attempted in aqueous ethereal solvents, the conjugate

adduct (**3aa**) was produced in good yield, although the reaction required a prolonged time for completion (entries 10-12). A neutral protic solvent like ethanol was a good alternative to aqueous ethereal solvents (entry 13), however, acidic protic solvents such as acetic acid were not suitable because of decomposition of 1,5-azastibocine (**1a**) in acidic media (entry 14). Aqueous dipolar solvents were appropriate for the reaction to give the conjugate adduct (**3aa**) in good yield in short time (entries 15-17). Among them, aqueous NMP was found to be the best choice of solvent giving the expected product (**3aa**) exclusively in 83% yield in 1 h and no Heck type adduct (**4aa**) was observed (entry 17). Also apparent was that water plays an important role in the present reaction. When the reaction was conducted in dehydrated NMP, Heck type adduct (**4aa**) was formed in 9% yield which was never observed in aqueous NMP (entry 18). The ratio of water in the reaction medium is one of the important factors in controlling the competing 1,4-conjugate reaction and Mizoroki-Heck reaction in other rhodium catalyzed reaction.[26]

2. The Reaction of Various *Sb*-Aryl-1,5-azastibocines with Methyl Vinyl Ketone (Table 2)

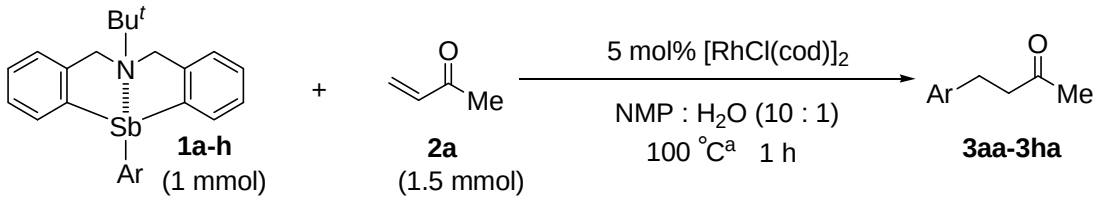
Under the optimized condition proved above, various *Sb*-aryl-1,5-azastibocines (**1a-h**) were reacted with methyl vinyl ketone (**2a**) and the results are summarized in Table 2. *Sb*-Aryl-1,5-azastibocine derivatives (**1a-d**) were prepared by the reported procedure.[21] Following this procedure, *Sb*-(*p*-fluorophenyl) (**1e**) and thienyl-1,5-azastibocine (**1f-h**) were also prepared. Thus, lithium or Grignard reagent of *p*-fluorophenyl- and thienyl- derivatives were reacted with *Sb*-bromo-1,5-azastibocine to give the *Sb*-(*p*-fluorophenyl) (**1e**) and thienyl-1,5-azastibocines (**1f-h**) in stable crystalline form (See experimental section). Regardless of the electronic nature of aryl groups, all the *Sb*-aryl-1,5-azastibocines gave the corresponding 1,4-conjugate adducts (**3aa-3ha**) in good yields in 1 h at 100 ˚C. From these results, *Sb*-aryl-1,5-azastibocines (**1**) are proved to be good aryl donors in the present 1,4-conjugate addition.

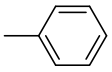
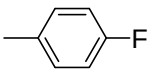
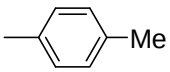
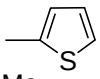
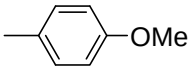
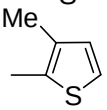
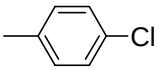
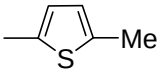
3. The Reaction of *Sb*-Phenyl-1,5-azastibocine with Various Enones and Enoates (Table 3)

The reactions of *Sb*-phenyl-1,5-azastibocine (**1a**) with various enones and enoates (**2b-k**) were investigated and the results are shown in Table 3. The reaction with enone unsubstituted at *β*-position and with cyclic enones gave the expected 1,4-adducts in good yield (entries 1-4). However, the yields of the 1,4-adduct were decreased in the reaction of enones with bulky substituent at *β*-position (entries 5 and 6). In the reaction of enoates, steric hindrance of ester moiety did not affect the reaction and methyl, butyl, and *t*-butyl esters gave the 1,4-adducts in high yield (entries 7-9). However, substituents on double bonds inhibited the 1,4-addition and the corresponding adducts were formed in moderate yields (entries 10, 11). In all cases, the 1,4-adducts were obtained exclusively and none of the Heck-type adduct was observed.

Under the $[RhCl(cod)]_2$ catalyst in aqueous NMP, methyl vinyl ketone (**2a**) also underwent 1,4-conjugate addition with triphenylstibane (Ph_3Sb) which was not activated by intramolecular N-Sb interaction.

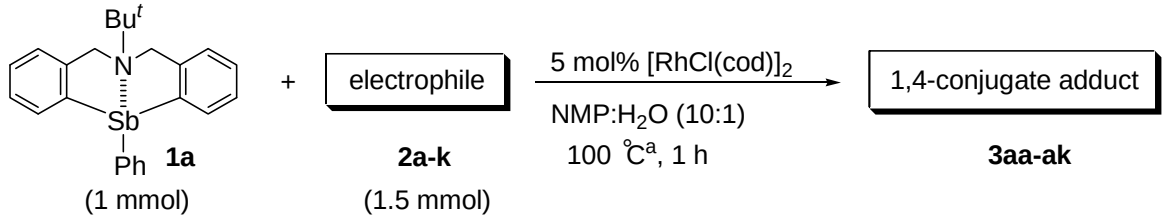
Table 2. Reaction of Various *Sb*-aryl-1,5-azastibocines (**1a-h**) with methyl vinyl ketone (**2a**)

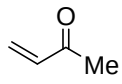
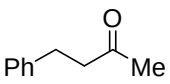
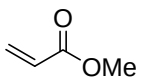
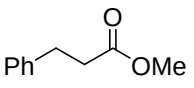
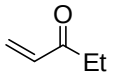
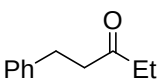
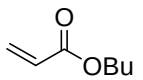
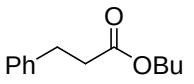
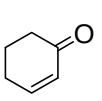
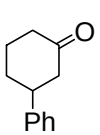
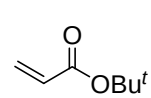
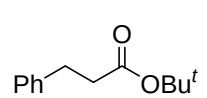
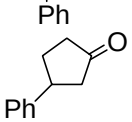
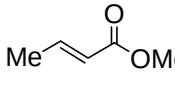
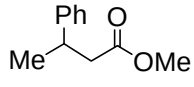
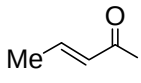
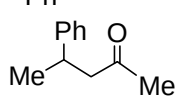
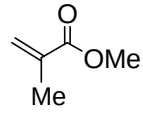
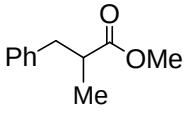
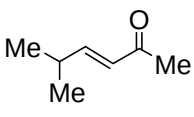
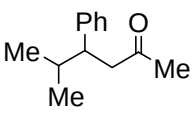


Entry	**1**	Ar	**3** (%)	Entry	**1**	Ar	**3** (%)
1	**a :**		80	5	**e :**		90
2	**b :**		74	6	**f :**		94
3	**c :**		87	7	**g :**		79
4	**d :**		87	8	**h :**		86

[a] Oil bath temperature

Table 3. Reaction of *Sb*-phenyl-1,5-azastibocines (**1a**) with various enones and enoates (**2**)



Entry	Electrophile **2**	Adduct **3**	Yield (%)[b]	Entry	Electrophile **2**	Adduct **3**	Yield (%)[b]
1	**a:** 		80	7	**g:** 		84
2	**b:** 		86	8	**h:** 		94
3	**c:** 		80	9	**i:** 		>99
4	**d:** 		92	10	**j:** 		66
5	**e:** 		59	11	**k:** 		51
6	**f:** 		57				

[a] Oil bath temperature.
[b] Isolated yield

However, the reaction required a much longer time (24 h). These results suggest that the intramolecular N-Sb interaction in 1,5-azastibocine (**1**) contributed to activation of the aryl group on antimony and reduction of the reaction time.

A possible mechanism of this reaction has already been proposed in the preliminary report,[22] which may be similar to the mechanism for 1,4-addition of organoboronic acid to enones.[27]

In summary, *Sb*-aryl-1,5-azastibocines were shown to be good aryl donors in the rhodium catalyzed 1,4-conjugate addition to α,β-unsaturated carbonyl compounds. In this reaction, high selectivity for the 1,4-conjugate adduct was achieved and the competing Heck-type reaction was completely suppressed which can be realized by use of a palladium catalyst.

EXPERIMENTAL

General information. Reactions requiring anhydrous conditions were performed in pre-dried glassware under an argon atomosphere. Elementary combustion analyses were determined with a Yanako CHN CORDER MT-5 and melting points were taken on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and are uncorrected. LRMS (EI) spectra were obtained on a JEOL JMS-SX 102A instrument and IR spectra were recorded on a HORIBA FT-720 instrument. ^{1}H NMR (TMS: δ 0.00 ppm as an internal standard) and ^{13}C NMR ($CDCl_3$: δ 77.0 ppm as an internal standard) spectra were recorded on a JEOL JNM-ECA-400 (400 MHz and 100 MHz) spectrometer in $CDCl_3$. All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). TLC was performed with Macherey-Nagel Pre-coated TLC plates Sil G25 UV_{254}. Dehydrated diethyl ether and THF were purchased from Kanto Chemical Co., Inc. (Cat. No. 14547-84 and 40993-85) and used without further distillation. *N*-*t*-Butyl-12-bromo-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine, *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine (**1a**), *N*-*t*-butyl-12-(4-tolyl)-5,6,7,12-tetrahydrodibenz-[*c*,*f*][1,5]azastibocine (**1b**), *N*-*t*-butyl-12-(4-methoxyphenyl)-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]-azastibocine (**1c**), *N*-*t*-butyl-12-(4-chlorophenyl)-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine (**1d**) were prepared from the reported procedure.[21]

Preparation of *N*-*t*-butyl-12-(4-fluorophenyl)-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine (1e)

n-Butyllithium (1.57 M, 3.82 mL, 6.00 mmol) was added dropwise to a solution of *p*-bromofluoro-benzene (1.05 g, 6.00 mmol) in Et_2O (20 mL) at 0 ˚C and the mixture was stirred at this temperature for 1 h. A THF solution (30 mL) of *N*-*t*-butyl-12-bromo-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocine (1.81 g, 4.00 mmol) was added slowly and the mixture was stirred at 0 ˚C for 2 h. The reaction mixture was diluted with an excess amount of Et_2O and quenched with water. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue

was recrystallized from $CHCl_3$-EtOH.

N-t-Butyl-12-(4-fluorophenyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (**1e**): 1.21 g (65%), colorless prisms, mp 146-147 ˚C. Anal. Calcd for $C_{24}H_{25}FNSb$: C, 61.56; H, 5.38; N, 2.99. Found: C, 61.61; H, 5.35; N, 2.81. LRMS (EI) *m/z*: 467 (M^+, 35%), 372 (100%), 316 (41%).225 (12%). ^{1}H NMR ($CDCl_3$) δ: 1.23 (9H, s), 3.86 (2H, d, *J* = 15.1 Hz), 4.17 (2H, d, *J* = 15.1 Hz), 7.02-7.17 (10H, m), 7.60-7.63 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 26.9 (q), 54.8 (t), 57.6 (s), 115.5 (d, ^2J_F = 19.1 Hz), 126.2 (d), 127.1 (d), 128.0 (d), 136.0 (d), 136.4 (s), 140.5 (d, ^3J_F = 6.75 Hz), 141.4 (s), 146.7 (s), 163.4 (d, ^1J_F = 262.5 Hz).

Preparation of *N-t*-butyl-12-(2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1f)

General procedure: To a suspension of magnesium (0.74 g, 30.7 mmol) in dry Et_2O (80 mL), 2-bromothiophene (5 g, 30.7 mmol) was added slowly at rt in the presence of a catalytic amount of iodine. After almost all magnesium metal was dissolved, a THF solution (80 mL) of *N-t*-butyl-12-bromo-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (13.9 g, 30.7 mmol) was added dropwise and the mixture was stirred at rt for 3 h. The mixture was diluted with Et_2O and quenched with water. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the crude residue was purified on a silica gel column chromatography (hexane : Et_2O = 10 : 1).

N-t-Butyl-12-(2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (**1f**): 10.8 g (77%), colorless prisms, mp 138-139 ˚C (from hexane-benzene). LRMS (EI) *m/z*: 455 (M^+, 17%), 398 (12%), 372 (93%), 316 (100%), 225 (16%), 165 (13%). Anal. Calcd for $C_{22}H_{24}NSSb$: C, 57.91; H, 5.30; N, 3.07. Found: C, 57.85; H, 5.35; N, 3.00. ^{1}H NMR ($CDCl_3$) δ: 1.24 (9H, s), 3.87 (2H, d, *J* = 15.3 Hz), 4.18 (2H, d, *J* = 15.3 Hz), 7.03-7.12 (4H, m), 7.15-7.21 (2H, m), 7.30 (1H, t, *J* = 3.43 Hz), 7.37 (2H, d, *J* = 7.33 Hz), 7.43 (1H, d, *J* = 3.21 Hz), 7.74 (1H, d, *J* = 5.04 Hz). ^{13}C NMR ($CDCl_3$) δ: 26.9 (q), 54.8 (t), 57.9 (s), 126.0 (d), 127.2 (d), 128.2 (d), 131.8 (d), 136.2 (s), 136.2 (d), 138.0 (d), 142.8 (s), 146.1 (s).

***N-t*-Butyl-12-(3-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1g)**

N-t-Butyl-12-(3-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (**1g**) was prepared from magnesium (432 mg, 18.0 mmol), 2-bromo-3-methylthiophene (3.19 g, 18.0 mmol) and *N-t*-butyl-12-bromo-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (6.78 g, 15 mmol) by the procedure described above.

N-t-Butyl-12-(3-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (**1g**): 5.91 g (84%), colorless prisms, mp 145-146 ˚C (from hexane-benzene). LRMS (EI) *m/z*: 469 (M^+, 8%), 412 (8%), 372 (68%), 316 (100%), 225 (14%). Anal. Calcd for $C_{23}H_{26}NSSb$: C, 58.74; H, 5.57; N, 2.98. Found: C, 58.89; H, 5.46; N, 2.86. ^{1}H NMR ($CDCl_3$) δ: 1.23 (9H, s), 1.26 (3H, br. s), 3.88 (2H, d, *J* = 15.3 Hz), 4.17

(2H, d, *J* = 15.3 Hz), 7.04-7.12 (5H, m), 7.14-7.19 (2H, m), 7.34 (2H, d, *J* = 7.80 Hz), 7.63 (2H, d, *J* = 5.04 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.0 (q), 26.9 (q), 54.9 (t), 57.8 (s), 126.0 (d), 127.1 (d), 128.1 (d), 130.3 (s), 131.1 (d), 135.4 (s), 136.2 (d), 136.7 (s), 146.2 (s).

***N*-*t*-Butyl-12-(5-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1h)**

N-*t*-Butyl-12-(5-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (**1h**) was prepared from magnesium (432 mg, 18.0 mmol), 2-bromo-5-methylthiophene (3.19 g, 18.0 mmol) and *N*-*t*-butyl-12-bromo-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (6.78 g, 15 mmol) by the procedure described above.

N-*t*-Butyl-12-(5-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (**1h**): 6.90 g (98%), colorless prisms, mp 166-167 ˚C (from hexane-benzene). LRMS (EI) *m/z*: 469 (M^+, 8%), 412 (7%), 372 (52%), 316 (100%), 225 (14%). Anal. Calcd for $C_{23}H_{26}NSSb$: C, 58.74; H, 5.57; N, 2.98. Found: C, 58.85; H, 5.40; N, 2.83. ^{1}H NMR ($CDCl_3$) δ: 1.23 (9H, s), 2.62 (3H, s), 3.85 (2H, d, *J* = 15.6 Hz), 4.17 (2H, d, *J* = 15.6 Hz), 6.92-7.24 (8H, m), 7.45 (2H, d, *J* = 6.90 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.4 (q), 26.9 (q), 54.8 (t), 57.8 (s), 125.9 (d), 126.8 (d), 127.2 (d), 128.1 (d), 136.2 (d), 136.3 (s), 138.4 (d), 140.7 (s), 146.1 (s), 146.7 (s).

Palladium-catalyzed reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with 3-butene-2-one (2a)

A mixture of 1,5-azastibocine (**1a**) (449 mg, 1.00 mmol), 3-butene-2-one (**2a**) (105 mg, 1.50 mmol) and $Pd(OAc)_2$ (23 mg, 0.1 mmol) in 1,4-dioxane : H_2O (10 : 1) was stirred at 100 ˚C for 1 h under argon atomosphere. The mixture was diluted with Et_2O and washed with brine. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the crude residue was purified on silica gel column chromatography (hexane : EtOAc = 9 : 1 as eluent). 4-Phenyl-3-butene-2-one (**4aa**): 114 mg (79%), colorless oil. LRMS (EI) *m/z*: 146 (M^+, 75%), 131 (100%), 103 (70%), 77 (26%). IR (KBr) ν: 1668 (C=O) cm $^{-1}$, 1610 (C=C) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.37 (3H, s), 6.72 (1H, d, *J* = 16.5 Hz), 7.37-7.40 (3H, m), 7.50 (1H, d, *J* = 16.5 Hz), 7.52-7.55 Hz (2H, m). ^{13}C NMR ($CDCl_3$) δ: 27.5 (t), 127.1 (d), 128.2 (d), 129.0 (d), 130.5 (d), 134.4 (s), 143.4 (d), 198.4 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with 3-butene-2-one (2a)

General procedure: A mixture of 1,5-azastibocine (**1a**) (449 mg, 1.00 mmol), 3-butene-2-one (**2a**) (105 mg, 1.50 mmol) and $[RhCl(cod)]_2$ (25 mg, 0.05 mmol) in NMP : H_2O (10 : 1) was stirred at 100 ˚C for 1 h under argon atomosphere. The mixture was diluted with Et_2O and washed with brine. The organic layer

was separated and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the crude residue was purified using silica gel column chromatography (hexane : EtOAc = 9 : 1 as eluent). 4-Phenyl-2-butanone (**3aa**): 118 mg (80%), colorless oil. LRMS (EI) *m/z*: 148 (M^+, 100%), 133 (16%), 105 (61%), 91 (43%), 77 (12%). IR (KBr) ν: 1712 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.10 (3H, s), 2.74 (2H, t, *J* = 7.79 Hz), 2.88 (2H, t, *J* = 7.79 Hz), 7.15 – 7.20 (3H, m), 7.25-7.28 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 29.7 (t), 30.0 (q), 45.1 (t), 126.0 (d), 128.2 (d), 128.4 (d), 207.8 (s).

Reaction of *N*-*t*-butyl-12-(4-tolyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1b) with 3-butene-2-one (2a)

4-(4-Tolyl)-2-butanone (**3ba**): 120 mg (74%), colorless oil. LRMS (EI) *m/z*: 162 (M^+, 100%), 147 (29%), 119 (45%), 105 (72%), 91 (16%), 77 (8%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.12 (3H, s), 2.31 (3H, s), 2.73 (2H, t, *J* = 7.78 Hz), 2.85 (2H, t, *J* = 7.78 Hz), 7.00 (2H, d, *J* = 7.50 Hz), 7.20 (2H, d, *J* = 7.50 Hz). ^{13}C NMR ($CDCl_3$) δ: 20.9 (q), 29.3 (t), 30.0 (q), 45.6 (t), 128.1 (d), 129.1 (d), 135.5 (s), 137.8 (s).

Reaction of *N*-*t*-butyl-12-(4-methoxyphenyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1c) with 3-butene-2-one (2a)

4-(4-Methoxyphenyl)-12-butanone (**3ca**): 154 mg (87%), colorless oil. LRMS (EI) *m/z*: 178 (M^+, 85%), 163 (8%), 135 (12%), 121 (100%), 108 (8%), 91 (11%). IR (KBr) ν: 1712 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.13 (3H, s), 2.74 (2H, t, *J* = 7.33 Hz), 3.77 (3H, s), 6.82 (2H, d, *J* = 8.70 Hz), 7.09 (2H, d, *J* = 8.70 Hz). ^{13}C NMR ($CDCl_3$) δ: 28.8 (t), 30.1(q), 45.4 (t), 55.2 (q), 113.8 (d), 129.2 (d), 132.9 (s), 157.9 (s), 208.1 (s).

Reaction of *N*-*t*-butyl-12-(4-chlorophenyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1d) with 3-butene-2-one (2a)

4-(4-Chlorophenyl)-2-butanone (**3da**): 158 mg (87%), colorless oil. LRMS (EI) *m/z*: 182 (M^+, 100%), 167 (23%), 147 (23%), 139 (32%), 125 (69%), 103 (27%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.13 (3H, s), 2.74 (2H, t, *J* = 7.33 Hz), 2.86 (2H, t, *J* = 7.33 Hz), 7.11 (2H, d, *J* = 8.24 Hz), 7.24 (2H, d, *J* = 8.24 Hz). ^{13}C NMR ($CDCl_3$) δ: 28.9 (t), 30.1 (q), 44.8 (t), 128.5 (d), 129.7 (d), 131.8 (s), 139.4 (s).

Reaction of *N*-*t*-butyl-12-(4-fluorophenyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1e) with 3-butene-2-one (2a)

4-(4-Fluorophenyl)-2-butanone (**3ea**): 150 mg (90%), colorless oil. LRMS (EI) *m/z*: 166 (M^+, 100%),

151(21%), 123 (27%), 109 (73%). IR (KBr) ν: 1718 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.13 (3H, s), 2.73 (2H, t, J = 7.56 Hz), 2.86 (2H, t, J = 7.56 Hz), 6.95 (2H, dd, $J_{2,3} = J_{3,F}$ = 8.47 Hz), 7.13 (2H, dd, $J_{2,3}$ = 8.47 Hz, $J_{2,F}$ = 5.50 Hz). ^{13}C NMR ($CDCl_3$) δ: 28.8 (t), 30.1 (q), 45.1 (t), 115.2 (d, $^{2}J_F$ = 21.1 Hz), 129.7 (d, $^{3}J_F$ = 7.67 Hz), 136.6 (s), 161.3 (d, $^{1}J_F$ = 243.5 Hz), 207. 6 (s).

Reaction of *N*-*t*-butyl-12-(2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1f) with 3-butene-2-one (2a)

A mixture of 12-(2-thienyl)-1,5-azastibocine (**1f**) (455 mg, 1.00 mmol), 3-butene-2-one (**2**) (105 mg, 1.50 mmol) and $[RhCl(cod)]_2$ (25 mg, 0.05 mmol) in NMP : H_2O (10 : 1) was stirred at 100 ˚C for 1 h under argon atomosphere. The mixture was diluted with Et_2O and washed with brine. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the crude residue was purified on silica gel column chromatography (hexane : EtOAc = 9 : 1 as eluent). 4-(2-Thienyl)-2-butanone (**3fa**): 145 mg (94%), colorless oil. LRMS (EI) *m/z*: 154 (M^+, 100%), 97 (87%), 84 (7%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.16 (3H, s), 2.18 (2H, t, J = 7.33 Hz), 3.11 (2H, t, J = 7.33 Hz), 6.79 (1H, dd, J = 3.66 Hz, J = 1.37 Hz), 6.90 (1H, dd, J = 5.04 Hz, J = 3.66 Hz), 7.11 (1H, dd, J = 5.04 Hz, J = 1.37 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.8 (q), 30.0 (q), 45.2 (t), 123.3 (d), 124.5 (d), 126.8 (d), 143.6 (s), 207.2 (s).

Reaction of *N*-*t*-butyl-12-(3-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1g) with 3-butene-2-one (2a)

4-(3-Methyl-2-thienyl)-2-butanone (**3ga**): 133 mg (79%), colorless oil. LRMS (EI) *m/z*: 168 (M^+, 35%), 125 (20%), 111 (100%), 97 (8%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.15 (3H, s), 2.16 (3H, s), 2.76 (2H, d, J = 7.56 Hz), 3.00 (2H, d, J = 7.56 Hz), 6.76 (1H, d, J = 5.04 Hz), 7.01 (1H, d, J = 5.04 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.5 (q), 21.7 (t), 30.0 (q), 44.7 (t), 121.2 (d), 130.0 (d), 133.0 (s), 136.5 (s), 207.3 (s).

Reaction of *N*-*t*-butyl-12-(5-methyl-2-thienyl)-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1h) with 3-butene-2-one (2a)

4-(5-Methyl-2-thienyl)-2-butanone (**3ha**): 144 mg (86%), colorless oil. LRMS (EI) *m/z*: 168 (M^+, 100%), 125 (32%), 111 (66%), 97 (5%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.16 (3H, s), 2.42 (3H,s), 2.78 (2H, t, J = 7.33 Hz), 3.02 (2H, t, J = 7.33 Hz), 6.53 (1H, d, J = 2.75 Hz), 6.55 (1H, d, J = 2.75 Hz), ^{13}C NMR ($CDCl_3$) δ: 15.2 (q), 24.0 (t), 30.0 (q), 45.2 (t), 124.2 (d), 124.6 (d), 137.7 (s), 141.2(s), 207.4 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with 1-pentene-3-one (2b) (Table 3, entry 2)

1-Phenyl-3-pentanone (**3ab**): 139 mg (86%), colorless oil. LRMS (EI) *m/z*: 162 (M^+, 100%), 133 (48%), 105 (95%), 91 (86%), 77 (20%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 1.04 (3H, t, *J* = 7.33 Hz), 2.40 (2H, q, *J* = 7.33 Hz), 2.72 (2H, t, *J* = 7.79 Hz), 2.90 (2H, t, *J* = 7.79 Hz), 7.14-7.20 (3H, m), 7.23-7.30 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 7.7 (t), 29.8 (t), 36.1 (t), 43.8 (t), 126.0 (d), 128.2 (d), 128.4 (d), 141.1 (s), 210.6 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with 2-cyclohexene-1-one (2c) (Table 3, entry 3)

3-Phenylcyclohexanone (**3ac**): 139 mg (80%), colorless oil. LRMS (EI) *m/z*: 174 (M^+, 100%), 131 (52%), 117 (62%), 104 (56%), 91 (23%). IR (KBr) ν: 1712 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 1.70-1.82 (2H, m), 2.05-2.20 (2H, m), 2.35-2.65 (4H, m), 2.95-3.05 (1H, m), 7.20-7.27 (3H, m), 7.31-7.37 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 25.5 (t), 32.7 (t), 41.1 (t), 44.7 (d), 48.9 (t), 126.5 (d), 126.6 (d), 129.5 (d), 144.3 (s), 211.1 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with 2-cyclopentene-1-one (2d) (Table 3, entry 4)

3-Phenylcyclopentanone (**3ad**): 147 mg (92%), colorless oil. LRMS (EI) *m/z*: 160 (M^+, 100%), 131 (26%), 117(44%), 104 (94%), 91 (19%), 77 (10%). IR (KBr) ν: 1739 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 1.91-2.05 (1H, m), 2.25-2.50 (4H, m), 2.61-2.72 (1H, m), 3.35-3.47 (1H, m), 7.23-7.27 (3H, m), 7.31-7.36 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 31.1 (t), 38.8 (t), 42.1 (d), 45.7 (t), 126.5 (d), 126.6 (d), 128.6 (d), 143.0 (s), 218.3 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with 3-pentene-2-one (2e) (Table 3, entry 5)

4-Phenyl-2-pentanone (**3ae**): 95 mg (59%), colorless oil. LRMS (EI) *m/z*: 162 (M^+, 79%), 147 (92%), 105 (100%), 91 (40%), 77 (21%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 1.26 (3H, d, *J* = 6.87 Hz), 2.05 (3H, s), 2.61-2.78 (2H, m), 3.29 (1H, m), 7.15-7.23 (3H, m), 7.26-7.33 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 22.0 (q), 30.5 (q), 35.4 (d), 52.0 (t), 126.3 (d), 126.8 (d), 128.5 (d), 146.1 (s), 207.8 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with 5-methyl-3-hexene-2-one (2f) (Table 3, entry 6)

5-Methyl-4-phenyl-2-hexanone (**3af**): 101 mg (57%), colorless oil. LRMS (EI) *m/z*: 191 (M^++1, 12%),

190 (M^+, 6%), 147 (20%), 132 (100%), 105 (20%), 91 (25%), 77 (10%). IR (KBr) ν: 1716 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 0.74 (3H, d, *J* = 6.64 Hz), 0.92 (3H, d, *J* = 6.64 Hz), 2.00 (3H, s), 2.76-2.81 (2H, m), 2.91 (1H, m), 7.11-7.20 (3H, m), 7.24-7.29 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 20.3 (q), 20.7 (q), 30.5 (q), 33.3 (d), 47.6 (t), 48.0 (d), 126.2 (d), 128.1 (d), 128.2 (d), 143.2 (s), 208.3 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with methyl acrylate (2g) (Table 3, entry 7)

Methyl 3-phenylpropanoate (**3ag**): 139 mg (82%), colorless oil. LRMS (EI) *m/z*: 164 (M^+, 64%), 131 (58%), 91 (100%), 77 (28%). IR (KBr) ν: 1735 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 2.55 (2H, t, *J* = 7.76 Hz), 2.87 (2H, t, *J* = 7.76 Hz), 3.58 (3H, s), 7.08-7.16 (3H, m), 7.18-7.24 (2 H, m). ^{13}C NMR ($CDCl_3$) δ: 30.9 (t), 35.6 (t), 51.5 (q), 126.2 (d), 128.4 (d), 140.4 (s), 173.3 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with *n*-butyl acrylate (2h) (Table 3, entry 8)

n-Butyl 3-phenylpropanoate (**3ah**): 195 mg (94%), colorless oil. LRMS (EI) *m/z*: 206 (M^+, 95%), 150 (35%), 133 (30%), 104 (100%), 91 (60%). IR (KBr) ν: 1735 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 0.91 (3H, t, *J* = 7.33 Hz), 1.33 (2H, sextet, *J* = 7.33 Hz), 1.57 (2H, quintet, *J* = 7.33 Hz), 2.62 (2H, t, *J* = 8.01 Hz), 2.95 (2H, t, *J* = 8.01 Hz), 7.15-7.22 (3H, m), 7.25-7.31 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 13.7 (q), 19.1 (t), 30.6 (t), 31.0 (t), 35.9 (t), 64.3 (t), 126.2 (d), 128.2 (d), 128.4 (d), 140.5 (s), 172.9 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with *t*-butyl acrylate (2i) (Table 3, entry 9)

t-Butyl 3-phenylpropanoate (**3ai**): 204 mg (99%), colorless oil. LRMS (EI) *m/z*: 207 (M^++1, 36%), 206 (M^+, 23%), 150 (100%), 133 (45%), 104 (45%), 91 (40%). IR (KBr) ν: 1710 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 1.41 (9H, s), 2.53 (2H, d, *J* = 7.79 Hz), 2.90 (2H, d, *J* = 7.79 Hz), 7.14-7.21 (3H, m), 7.24-7.30 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 28.0 (q), 28.1 (s), 31.1 (t), 37.0 (t), 126.0 (t), 128.2 (d), 128.3 (d), 140.7 (s), 172.1 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with methyl crotonate (2j) (Table 3, entry 10)

Methyl 3-phenylbutanoate (**3aj**): 118 mg (66%), colorless oil. LRMS (EI) *m/z*: 179 (M^+, 36%). IR (KBr) ν: 1739 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 1.29 (3H, d, *J* = 7.33 Hz), 2.57 (2H, m), 3.27 (1H, m), 3.61 (3H, s), 7.17-7.23 (3H, m), 7.27-7.32 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 21.7 (q), 36.4 (d), 42.7 (t), 51.4 (q), 126.7 (d), 128.5 (d), 145.7 (s), 172.8 (s).

Reaction of *N*-*t*-butyl-12-phenyl-5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azastibocine (1a) with methyl methacrylate (2k) (Table 3, entry 11)

Methyl 2-methyl-3-phenylpropanoate (**3ak**): 91 mg (51%), colorless oil. LRMS (EI) *m/z*: 178 (M^+, 52%), 118 (100%). IR (KBr) ν: 1735 (C=O) cm $^{-1}$. ^{1}H NMR ($CDCl_3$) δ: 1.15 (3H, d, *J* = 6.87 Hz), 2.68 (2H, m), 3.02 (1H, m), 7.13-7.22 (3H, m), 7.24-7.30 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 16.7 (q), 39.7 (t), 41.4 (d), 51.5 (q), 126.3 (d), 128.3 (d), 128.9 (d), 139.3 (s), 176.5 (s).

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