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Palladium-catalyzed cross-coupling reaction of ethynylstibanes with organic halides

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Abstract

The reaction of ethynylstibanes (**1a–g**) with vinyl halides or triflate in the presence of a palladium catalyst led to the formation of cross-coupling products (**5a–g**, **10–12**) in good to moderate yield, along with homo-coupling products (**6a–g**). A similar reaction of ethynyldiphenylstibane **(1a)** with aryl iodides (**13a–i**) also gave cross-coupling products (**14a–i**), although the yields were relatively low. The yields of the cross-coupling products were highly dependent on the nature of the solvent employed, and good results were obtained when the reaction was carried out in HMPA or amines such as diethylamine and morpholine. The results imply that HMPA and amine used as solvents facilitate transmetallation of the ethynyl group on **1** to the palladium by intermolecular coordination between antimony and oxygen (for HMPA) or nitrogen (for amine).

Keywords: Antimony; Cross-coupling; Intermolecular coordination; Ethynylstibane; Vinyl halide; Aryl halide

1. Introduction

Recent researches on typical heavier elements have disclosed a variety of reactions which so far are believed to be extraordinary to synthetic organic chemists [1]. Different from the typical lower elements such as carbon, nitrogen, and oxygen, the heavier elements have lower electronegativity and relatively larger atomic radii which form longer and weaker bonds between them and other elements [2]. These properties make it facile for these compounds to form highly reactive hypervalent species with hetero atoms such as nitrogen, oxygen, sulfur and so on. Taking advantage of these characters, much attention has been directed toward utilization of these compounds as novel synthetic reagents, and a variety of hetero atoms are now commonly employed in transition-metal catalyzed coupling reactions [3]. Many attempts to apply organoantimony compounds to a synthetic reagent are also reported [4]. However, contrary to the prevailing use of inorganic antimony compounds for Lewis acid, super acid, antimony metal alloy, and anti-flammable materials, studies on organoantimony compounds as a novel synthetic reagent are relatively underdeveloped. Most of them dealt with highly reactive but less stable pentavalent or hypervalent antimony compounds [5]. From the viewpoint of practical use of organoantimony compounds as a synthetic reagent, it is desirable for them to be relatively stable, easy to prepare and to handle. Trivalent organoantimony compounds (stibanes) are stable enough to tolerate practical handling, less harmful, and not so expensive. So it is worth investigating stibanes as novel practical organic reagents [6].

As a part of our continuing research on making use of stibanes as practical organic reagents, we have previously reported the palladium-catalyzed ethynylation of acyl chloride using ethynylstibanes [7]. Thus, acyl chlorides and ethynyldiphenylstibanes were coupled by use of 5 mol% of commercially available palladium reagents to give ethynylketones in good to excellent yields. The

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reaction was thought to proceed by the classical Stille-type catalytic cycle [8]. In order to improve the generality of the reaction, cross-coupling with aryl and vinyl iodides was investigated, and full details of these reactions including preparation of ethynylstibanes are described here.

2. Results and discussion

2.1. Preparation of ethynylstibanes

Highly reactive pentavalent organoantimony compounds easily underwent either reductive homo-coupling or cross-coupling reaction with organic halides under transition metals [5]. However, trivalent stibanes have been thought to be less reactive in these classes of reaction. Asano et al. [9] have first reported that treatment of triphenylantimony with styrene resulted in cross-coupling reaction to afford *trans*-stilbene, but their reaction required a stoichiometric amount of the palladium reagent. Barton et al. [10] have also performed a ligand coupling reaction of triarylstibanes with acyl halides using a stoichiometric amount of palladium. Uemura and coworkers [6b] have first demonstrated a catalytic cross-coupling reaction of triarylstibanes with enones to produce β-arylated ketones in the presence of a palladium catalyst, although the reaction required 2 equimolar amounts (on the bases of $SbPh_3$) of AgOAc as an oxidant and an acidic condition. They also developed the same type of reaction using phenylantimony chlorides instead of the triarylstibane under an aerobic condition [6a].

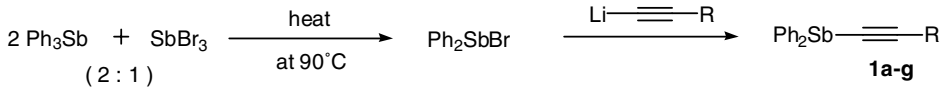
We have recently reported that ethynylstibanes could be isolated as air-stable compounds [7]. Taking the high reactivity of the ethynyl group in the Stille reaction and other cross-coupling reaction into consideration [8d], ethynylation of organic halides under palladium catalyst might be possible even by use of the so-called less reactive trivalent stibanes. From this point of view, ethynylstibanes were prepared by the condensation of diphenylantimony bromide [11] with appropriate lithium acetylides [12]. Thus, diphenylantimony bromide, prepared from redistribution of a 2:1 mixture of triphenylantimony and tribromoantimony, was reacted with lithium acetylides generated from the corresponding acetylene derivatives and butyllithium. Arylethynyl, alkylethynyl, and silylethynyl compounds (**1a**–**g**) were obtained in moderate to good yields (Table 1). Each compound was so stable such that it could be purified on silica gel column chromatography and kept in a refrigerator for over several years.

2.2. Cross-coupling reaction of ethynylstibanes with vinyl halides

It is well documented that 1,3-enynes and aryl acetylenes are an important building-block for a variety of biologically active substances, medicinals, liquid crystals and conductive polymers, and various methods to prepare them have been investigated [13,14]. We considered that cross-coupling reaction of ethynylstibanes with vinyl halides and aryl halides should be another synthetic approach to these compounds.

In this context, we initially performed the reaction of ethynylstibanes (**1**) and cyclopentenyl derivatives, such as cyclopentenyl iodide (**2**), bromide (**3**) and triflate (**4**), to compare the reactivity of the leaving group using 5 mol% of dichlorobis(triphenylphosphine)palladium [$PdCl_2(PPh_3)_2$] as a catalyst in hexamethylphosphoramide (HMPA) at 80 °C, (Table 2, entry 1–3). The expected enyne compound (**5a**) was obtained in good yields when the iodide (**2**) and triflate (**4**) were employed as a coupling partner. However, the vinyl bromide (**3**) was found to be unreactive toward the cross-coupling reaction and the major product was 1,3-diyne (**6a**) derived from homo-coupling reaction of the ethynyl group on **1**. A survey of solvents revealed that the reaction took place

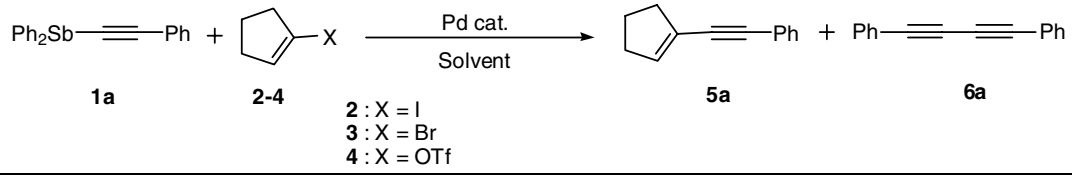
Table 1
Preparation of ethynyldiphenylstibanes **1a**–**g**



R	Yield of **1** (%)[a]	Appearance
a: Phenyl	73	m.p. 53–55 °C[b,c]
b: *p*-Tolyl	64	m.p. 63–64 °C[c]
c: *p*-Anisyl	74	m.p. 62–63 °C[c]
d: *p*-Fluorophenyl	64	m.p. 42–43 °C[c]
e: *n*-Butyl	78	Colorless oil
f: *t*-Butyl	69	Colorless oil
g: TMS	78	Colorless oil

[a] Isolated yield.
[b] Literature [11], m.p. 84–86 °C.
[c] Recrystallized from ether–ethanol.

Table 2
Reaction of diphenylphenylethynylstibane **1a** with cyclopentene derivatives **2**–**4** using a variety of Pd-catalysts and solvents[a]



Entry	Cyclopentene deriv. (X)	Pd-Cat.	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]	
						5a	**6a**
1	**2**: I	$PdCl_2(PPh_3)_2$	HMPA	80	1.0	90	9
2	**3**: Br				3.5	0.3	40
3	**4**: OTf				1.0	80	9
4	**2**: I	$PdCl_2(PPh_3)_2$	HMPA	25	20.0	87	9
5			1,2-Dichloroethane	80	1.5	15	42
6			Acetonitril	80	2.0	5	66
7			Benzene	80	3.0	24	41
8			1,4-Dioxane	80	2.0	28	39
9			Diethylamine	55	21.0	78	11
10			Morpholine	80	1.0	87	9
11			NMP	80	1.0	64	24
12			TMU	80	1.0	52	37
13			DMPU	80	1.0	54	27
14	**2**: I	$PdCl_2(PhCN)_2$	HMPA	80	1.0	60	38
15		$Pd(OAc)_2$				53	43
16		$PdCl_2(CH_2 = CHCH_3)_2$				29	41
17		$PdCl_2$				53	44

[a] **1a** (1 mmol), **2**–**4** (1.5 mmol), Pd-Cat. (5 mol%), solvent (10 ml).
[b] Determined by GLC. The yield of **6a** was calculated on the bases of that 0.5 equimolar amounts of **6a** to **1a** correspond to 100% yield.

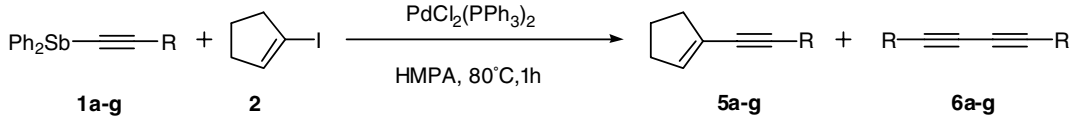
efficiently in amines and HMPA, whereas halogenated solvents, ethereal solvents, hydrocarbons, and aprotic polar solvents such as 1-methyl-2-pyrrolidinone (NMP), tetramethylurea (TMU), and *N*,*N*′-dimethylpropyleneurea (DMPU) gave inferior results (Table 2, entry 5–13). Several easily available palladium catalysts were also screened (Table 2, entry 14–17). The results showed that the palladium with a phosphine ligand was preferable for effective transmetallation of the ethynyl group from antimony to palladium. Without phosphine ligands, palladium might coordinate with stibane which can act as a mild palladium ligand [15]. A tightly-coordinated phosphine ligand stabilizes the palladium and might prevent it from undesirable coordination with antimony. These reactions were highly substituent-selective and only the ethynyl group was transferred from **1a** to form 1,3-enynes (**5a**) and aryl acetylenes (**6a**), indicating that the phenyl groups on **1a** work as dummy ligands in the present reaction. These results are comparable with that the ethynyl moiety in ethynylstannanes is more reactive than aryl, vinyl and alkyl groups in Stille-coupling reaction [8a]. Consequently, the best result was obtained up to now when the reaction was carried out in HMPA with $PdCl_2(PPh_3)_2$.

In order to prove the generality of this cross-coupling reaction, ethynyldiphenylstibanes (**1b**–**g**) were reacted with 1-iodocyclopentene (**2**) and the results are shown in Table 3. The iodine function was displaced effectively with an arylethynyl, alkylethynyl and silylethynyl group to afford the corresponding 1,3-enyne compounds (**5b**–**g**) in good to moderate yields. Reaction of phenylethynyldiphenylstibane (**1a**) with several vinyl iodides (**7**–**9**) also brought about the expected cyclic (**10**) and acyclic enyne compounds (**11**, **12**) as major products in moderate yields (Table 4).

2.3. Cross-coupling reaction of ethynylstibanes with aryl halides

Next, the reaction of the ethynylstibane (**1a**) with a variety of aryl halides was investigated to disclose the difference in the reactivity between vinyl halides and aryl halides, and the results are summarized in Table 5. Phenylethynylstibane (**1a**) and iodobenzene (**13a**) were reacted using $PdCl_2(PPh_3)_2$ catalyst in various solvents (Table 5, entry 1–8). In the reaction with **13a**, longer reaction time was required to complete the reaction even in the presence of 10 mol% of the palladium catalyst. These results showed that the reactivity of **13a** was lower

Table 3
Reaction of ethynyldiphenylstibanes **1a–g** with 1-iodocyclopentene **2**[a]

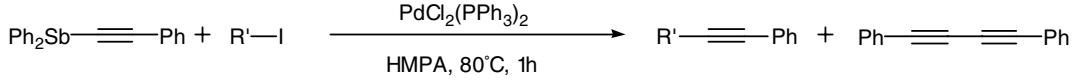


1a-g **2** **5a-g** **6a-g**

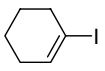
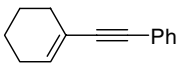
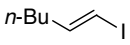
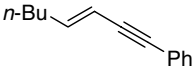
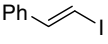
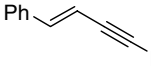
R	Yield (%)[b]	
	5	**6**
a: Phenyl	90	9
b: *p*-Tolyl	87	9
c: *p*-Anisyl	69	21
d: *p*-Fluorophenyl	85	8
e: *n*-Butyl	70	9
f: *t*-Butyl	75	13
g: TMS	64	15

[a] **1a–g** (1 mmol), **2** (1.5 mmol), Pd-Cat. (5 mol%), HMPA (10 ml).
[b] Determined by GLC. The yield of **6** was calculated on the bases of that 0.5 equimolar amounts of **6a–g** to **1a–g** correspond to 100% yield.

Table 4
Reaction of ethynylstibanes **1a** with vinyl iodides **7–9**[a]



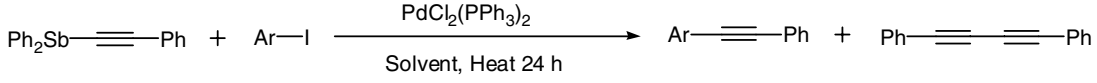
1a **7-9** **10-12** **6a**

Vinyl halide R′–I	Product **10–12**	Yield (%)[b]	
		10–12	**6a**
7 	**10** 	67	30
8 	**11** 	41	39
9 	**12** 	63	30

[a] **1a** (1 mmol), **7–9** (1.5 mmol), Pd-Cat. (5 mol%), HMPA (10 ml).
[b] Determined by GLC. The yield of **6a** was calculated on the bases of that 0.5 equimolar amounts of **6a** to **1a** correspond to 100% yield.

than that of the vinyl iodides. A remarkable solvent effect, namely amines and HPMA were superior to other solvents, was observed as in the case of the former reaction with vinyl halides. We considered that amine and HMPA used as solvents would activate the Sb–$C_{(sp)}$ bond by intermolecular coordination between the unshared electron pair on nitrogen or oxygen and the antimony atom on **1a**. We have already reported that intramolecular interaction between the nitrogen and antimony in 12-arylethynyl-6-methyl-5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azastibocines led to an elongation of the Sb–$C_{(sp)}$ bond and facilitated easier cross-coupling reaction between the ethynyl group on antimony and organic halides [16]. The following evidence should also support this interpretation. We have recently reported that several triarylstibanes bearing amine moiety, e.g., 2-(*N*,*N*-dimethylaminobenzyl)diphenylstibane, have Sb–N intramolecular coordination and the coordination brings about marked lowering of oxidation potential of the antimony atom. Similar effect on decreasing the potential was observed in a mixture of triphenylstibane and *N*,*N*-dimethylbenzylamine, which was never detected in a solution of triphenylstibane or *N*,*N*-dimethylbenzylamine alone [17]. These results indicate the existence of intermolecular interaction between the antimony and nitrogen atoms in this system. Similar Sb–N and Sb–O intermolecular coordinations which bring about Sb–$C_{(sp)}$ bond activation may occur when amine

Table 5
Reaction of ethynylstibane **1a** with aryl iodides **13a–i**[a]



1a **13a-i** **14a-i** **6a**

Entry	Ar: **13a–i**	Solvent	Temp. (°C)[b]	Yield (%)[c]	
				14	**6a**
1	**13a**: Phenyl	1,2-Dichloroethane	80	16	47
2		THF	60	20	60
3		Acetonitrile	80	32	54
4		Benzene	80	24	32
5		Diisopropylamine	80	33	23
6		Diethylamine	55	49	21
7		Morpholine	80	46	31
8		HMPA	80	37	51
9	**13b**: *p*-Anisyl	Diethylamine	55	35	25
10	**13c**: *o*-Tolyl			30	20
11	**13d**: *p*-Tolyl			34	20
12	**13e**: *p*-Fluorophenyl			43	7
13	**13f**: *p*-Acetylphenyl			46	7
14	**13g**: *o*-Nitrophenyl			77	11
15	**13h**: *m*-Nitrophenyl			73	20
16	**13i**: *p*-Nitrophenyl			87	5

[a] **1a** (1 mmol), **13a–i** (1.5 mmol), Pd-Cat. (10 mol%), solvent (5 ml), 24 h.
[b] Bath temperature.
[c] Determined by GLC. The yield of **6a** was calculated on the bases of that 0.5 equimolar amounts of **6a** to **1a** correspond to 100% yield.

and HMPA is employed as solvent in the present reaction, although no evidence of the Sb–O coordination in the stibane–HMPA system has not been obtained at present. Also apparent is that substituents on aryl iodides (**13**) exhibit a distinctive effect in the coupling reaction. Aryl iodides with electron-withdrawing groups gave better results than those with electron-donating groups similar to other palladium-catalyzed coupling reactions (Table 5, entry 9–16). The electron-withdrawing group should assist the oxidative addition of aryl halides to the phosphine-ligated, electron-rich palladium(0) [8].

The palladium-catalyzed alkynylation is thought to be initiated by oxidative addition of organic halides and related electrophiles to Pd(0). The pathways of the cross-coupling reaction of ethynylstibanes (**1**) with vinyl iodides and the homo-coupling reaction of **1** itself in the

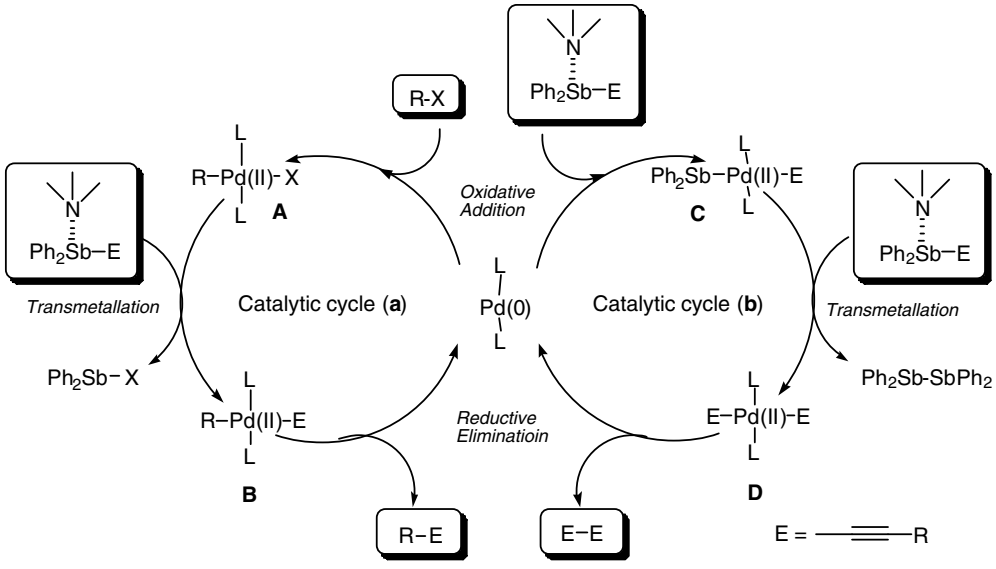


Fig. 1.

present reaction are depicted in Fig. 1. When the reactivity of the halide (R–X) is sufficiently higher than that of the stibanes, oxidative addition of the halides to Pd(0) may take place in preference to the reaction with ethynylstibane, as shown in the reaction with vinyl iodides and aryl iodides bearing electron withdrawing groups. The Pd(II) complex (**A**) thus formed results in transmetallation with the ethynyl group (E) on **1** to afford Pd(II) complex (**B**) which undergoes reductive elimination to give the cross-coupling product (R–E) via a catalytic cycle (**a**). The intermolecular coordination of the amine moiety used as a solvent to the antimony on **1** would activate the Sb–$C_{(sp)}$ bond and assist the transmetallation as noted above. When the reactivity of the halides is relatively low, however, competition for oxidative addition to Pd(0) will arise between the halides and the ethynylstibanes, such that the latter should bring about the homo-coupling product (E–E) via a catalytic cycle **(b)**, although the evidence for the formation of Ph_2Sb–$SbPh_2$ has so far not been obtained from the reaction mixture.

3. Conclusion

In summary, we have developed a simple and useful preparative method for trivalent ethynylstibanes (**1a**–**g**) which are air-stable, easy to handle and can be stored with no special care. In palladium-catalyzed cross-coupling of the ethynyldiphenylstibane with vinyl and aryl iodides, only the ethynyl group on the ethynylstibanes reacted to form 1,3-enynes and aryl acetylenes, and phenyl groups functioned as dummy ligands. As for a practical ethynylation technique of organic halides, a variety of useful methods have been published [3a,18]. Further improvements including reactivity enhancement of antimony-mediated coupling reactions with heteroatom–antimony nonbonding interaction are now in progress and will be reported by us in due course.

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 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 and 125 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Mass spectra (MS) and high-resolution mass spectra (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 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel Pre-coated TLC plates Sil G25 UV_{254}. All of HMPA including the aqueous solution of HMPA arose from working up of the reaction mixture should be collected in a fixed glass bottle and the contents will be treated by an appropriate company specialized in the disposal of chemical waste, because HMPA has been known to be a cancer suspect agent.

4.2. Preparation of ethynyldiphenylstibanes (*1a*–*g*)

General procedure. An ether solution (100 ml) of diphenylantimony(III) bromide [12], synthesized from redistribution of triphenylstibane (23.5 g, 67 mmol) and tribromoantimony (12.0 g, 33 mmol) was added dropwise at 0 °C to an ether solution (100 ml) of lithium acetylide, prepared from the appropriate acetylene derivatives (100 mmol) and butyllithium (1.53–1.48 M solution in hexane, 100 mmol). After stirring the mixture at the same temperature for 2 h, the reaction mixture was diluted with ether (100 ml) and quenched with water. The reaction mixture was separated and the aqueous layer was extracted with ether (50 ml). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography using a mixture of *n*-hexane and dichloromethane as eluent to afford ethynyldiphenylstibanes (**1a**–**g**). The ethynyldiphenylstibanes (**1a**–**g**) thus obtained are listed together with their yields and appearances in Table 1.

4.2.1. Diphenylphenylethynylstibane (*1a*)

Anal. Calc. for $C_{20}H_{15}Sb$: C, 63.70; H, 4.01. Found: C, 63.82; H, 4.18. ^{1}H NMR (δ ppm): 7.29–7.35 (9H, m), 7.50–7.52 (2H, m), 7.71–7.34 (4H, m). ^{13}C NMR (δ ppm): 85.6 (s), 111.4 (s), 123.3 (s), 128.2 (d), 128.6 (d), 128.8 (d), 129.0 (d), 132.0 (d), 135.5 (d), 138.1 (s). MS (EI) *m/z*: 376 (M^+, 77%), 299 (8%), 198 (100%), 178 (96%). IR (cm^{-1}): 2137 (C≡C).

4.2.2. Diphenyl(*p*-tolylethynyl)stibane (*1b*)

Anal. Calc. for $C_{21}H_{17}Sb$: C, 64.49; H, 4.38. Found: C, 64.52; H, 4.41. ^{1}H NMR (δ ppm): 2.34 (3H, s), 7.11 (2H, d, $J_{p\text{-tol}}$ = 7.79 Hz), 7.29–7.35 (6H, m), 7.41 (2H, d, $J_{p\text{-tol}}$ = 7.79 Hz), 7.71–7.73 (4H, m). ^{13}C NMR (δ ppm): 21.5 (q), 84.9 (s), 111.6 (s), 120.2 (s), 128.8 (d), 128.9 (d), 129.0 (d), 131.9 (d), 135.5(d), 138.2 (s), 138.8

(s). MS (EI) *m/z*: 390 (M^+, 67%), 313 (7%), 236 (14%), 198 (78%), 192 (100%). IR (cm^{-1}): 2132 (C≡C).

4.2.3. p-Anisylethynyldiphenylstibane (1c)

Anal. Calc. for $C_{21}H_{17}OSb$: C, 61.96; H, 4.21. Found: C, 62.14; H, 4.37. ^1H NMR (δ ppm): 3.79 (3H, s), 6.83 (2H, d, $J_{p\text{-anisyl}}$ = 8.70 Hz), 7.31–7.35 (6H, m), 7.46 (2H, d, $J_{p\text{-anisyl}}$ = 8.70 Hz), 7.71–7.73 (4H, m). ^{13}C NMR (δ ppm): 55.3 (q), 84.0 (s), 111.5 (s), 113.9 (d), 115.4 (d), 128.8 (d), 128.9 (d), 133.5 (d), 135.5 (d), 138.3 (s), 159.8 (d). MS (EI) *m/z*: 406 (M^+, 53%), 329 (5%), 252 (8%), 208 (100%), 198 (33%). IR (cm^{-1}): 2140 (C≡C).

4.2.4. p-Fluorophenylethynylldiphenylstibane (1d)

Anal. Calc. for $C_{20}H_{14}FSb$: C, 60.80; H, 3.57. Found: C, 60.72; H, 3.72. ^1H NMR (δ ppm): 7.00 (2H, dd, $J_{H,H}$ = 8.70 Hz, $^{1,2}J_{H,F}$ = 8.70 Hz), 7.32–7.37 (6H, m), 7.49 (2H, dd, $J_{H,H}$ = 8.70 Hz, $^{1,3}J_{H,F}$ = 5.50 Hz), 7.70–7.72 (4H, m). ^{13}C NMR (δ ppm): 85.6 (s), 110.2 (s), 115.5 (dd, ^2J_F = 21.9 Hz), 119.4 (s), 128.9 (dd, ^3J_F = 13.4 Hz), 129.0 (d), 133.9 (d, ^4J_F = 8.6 Hz), 135.5 (d), 138.0 (s), 162.6 (d, ^1J_F = 248.0 Hz). MS (EI) *m/z*: 394 (M^+, 46%), 317 (5%), 273 (42%), 198 (100%). IR (cm^{-1}): 2144 (C≡C).

4.2.5. 1-Hexynyldiphenylstibane (1e)

HR-MS *m/z*: 356.0446 (Calc. for $C_{18}H_{19}Sb$: 356.0523). ^1H NMR (δ ppm): 0.90 (3H, t, J = 6.96 Hz), 1.42–1.58 (4H, m), 2.38 (2H, t, J = 6.96 Hz), 7.29–7.30 (6H, m), 7.66–7.67 (4H, m). ^{13}C NMR (δ ppm): 13.6 (q), 20.1 (t), 21.9 (t), 30.9 (t), 74.6 (s), 113.7 (s), 128.6 (d), 128.8 (d), 135.4 (d), 138.5 (s). MS (EI) *m/z*: 356 (M^+, 22%), 299 (5%), 279 (7%), 198 (100%). IR (cm^{-1}): 2152 (C≡C).

4.2.6. 3,3-Dimethyl-1-butynyldiphenylstibane (1f)

HR-MS *m/z*: 356.0530 (Calc. for $C_{18}H_{19}Sb$: 356.0525). ^1H NMR (δ ppm): 1.30 (9H, s), 7.28–7.33 (6H, m), 7.64–7.69 (4H, m). ^{13}C NMR (δ ppm): 31.0 (s), 31.2 (q), 73.1 (s), 122.2 (s), 128.6 (d), 128.8 (d), 135.2 (d), 138.7 (s). MS (EI) *m/z*: 356 (M^+, 29%), 300 (14%), 278 (6%), 198 (100%). IR (cm^{-1}): 2132 (C≡C).

4.2.7. Trimethylsilylethynyldiphenylstibane (1g)

HR-MS *m/z*: 372.0284 (Calc. for $C_{17}H_{19}SiSb$: 372.0293). ^1H NMR (δ ppm): 0.24 (9H, s), 7.30–7.33 (6H, m), 7.67–7.69 (4H, m). ^{13}C NMR (δ ppm): 0.02 (q), 104.3 (s), 120.4 (s), 128.9 (d), 135.4 (d), 136.2 (d), 138.0 (s). MS (EI) *m/z*: 372 (M^+, 31%), 357 (5%), 275 (8%), 198 (61%). IR (cm^{-1}): 2084 (C≡C).

4.3. Reaction of ethynyldiphenylstibane (1a–g) with vinyl halides (2, 3, 7–9) or triflate (4)

General procedure. A solution of ethynylstibane (**1a–g**, 1.00 mmol), vinyl halides (**2**, **3**, **7–9**, 1.50 mmol) [or triflate (**4**), 1.50 mmol] and dichlorobis(triphenylphosphine)palladium (35 mg, 0.05 mmol) in HMPA (10 ml) was heated at 80 °C for 1 h under an argon atmosphere. After dilution with ether (100 ml) and water (100 ml), the reaction mixture was separated and the aqueous layer was extracted with ether (30 ml). The combined organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by passing through SiO_2 short column using a mixture of *n*-hexane and benzene as eluent to give enyne derivatives (**5a–g**, **10–12**) and 1,3-butadiyne derivatives (**6a–g**). Yields of the products were analyzed by GLC (5% SE30, 1.6 M, column temperature 230 °C) based on benzil (t_R = 2.66 min) as an internal standard.

4.3.1. Reaction of diphenylphenylethynylstibane (1a) with 1-iodocyclopentene (2) [19]

1-Phenylethynylcyclopentene (**5a**); (t_R = 1.27 min), 152.2 mg (91%). Colorless needles (m.p. 82–84 °C, from ethanol). ^1H NMR (δ ppm): 1.94 (2H, m), 2.47 (2H, m), 2.54 (2H, m), 6.13 (1H, m), 7.26–7.30 (3H, m), 7.42–7.44 (2H, m). ^{13}C NMR (δ ppm): 23.4 (t), 33.4 (t), 36.4 (t), 86.8 (s), 90.4 (s), 123.6 (s), 124.6 (s), 127.9 (d), 128.2 (d), 131.4 (d), 138.1 (d). MS (EI) *m/z*: 168 (M^+, 100%), 153 (32%), 139 (18%), 115 (13%). IR (cm^{-1}): 2202 (C≡C), 1671 (C=C). 1,4-Diphenyl-1,3-butadiyne (**6a**); (t_R = 5.36 min), 18.2 mg (9%). Colorless needles (m.p. 87–88 °C, from ethanol [4] 84–86 °C). ^1H NMR (δ ppm): 7.31–7.38 (6H, m), 7.51–7.53 (4H, m). ^{13}C NMR (δ ppm): 73.9 (s), 81.5 (s), 121.8 (s), 128.4 (d), 129.2 (d), 132.5 (d). MS (EI) *m/z*: 202 (M^+, 100%), 174 (4%), 150 (7%), 126 (2%). IR (cm^{-1}): 2148 (C≡C).

4.3.2. Reaction of diphenylphenylethynylstibane (1a) with 1-bromocyclopentene (3) [20]

5a, 0.43 mg (0.3%); **6a**, 40 mg (40%).

4.3.3. Reaction of diphenylphenylethynylstibane (1a) with 1-trifluoromethanesulfonylcyclopentene (4) [21]

5a, 131.9 mg (79%); **6a**, 9.5 mg (9.5%).

4.3.4. Reaction of diphenyl(p-tolylethynyl)stibane (1b) with 1-iodocyclopentene (2)

1-(*p*-Tolylethynyl)cyclopentene (**5b**); (t_R = 1.80 min), 158 mg (87%). Colorless needles (m.p. 92–93 °C, from ethanol). ^1H NMR (δ ppm): 1.94 (2H, m), 2.32 (3H, s), 2.46 (2H, m), 2.54 (2H, m), 6.10 (1H, m), 7.10 (2H, d, $J_{p\text{-tol}}$ = 7.70 Hz), 7.32 (2H, d, $J_{p\text{-tol}}$ = 7.70 Hz). ^{13}C NMR (δ ppm): 21.4 (q), 23.4 (t), 33.3 (t), 36.5 (t), 86.1 (s), 90.6 (s), 120.5 (s), 124.7 (s), 129.0 (d), 131.3 (d), 137.6 (d), 138.0 (s). MS (EI) *m/z*: 182 (M^+, 100%), 167 (79%), 152 (29%), 139 (18%), 115 (17%). IR (cm^{-1}): 2204 (C≡C), 1658 (C=C). 1,4-Di(*p*-tolyl)-1,3-butadiyne (**6b**); (t_R = 12.28 min), 11 mg (9%). Colorless needles (m.p. 187–188 °C, from ethanol). ^1H NMR (δ ppm):

2.35 (6H, s), 7.12 (4H, d, $J_{p\text{-tol}}$ = 7.79 Hz), 7.40 (4H, d, $J_{p\text{-tol}}$ = 7.79 Hz). ^{13}C NMR (δ ppm): 21.6 (q), 73.4 (s), 81.5 (s), 118.8 (s), 129.2 (d), 132.4 (d), 139.5 (s). MS (EI) *m/z*: 230 (M^+, 100%), 215 (18%), 202 (7%), 189 (5%), 115 (5%). IR (cm^{-1}): 2135 (C≡C).

4.3.5. Reaction of p-anisylethynyldiphenylstibane (*1c*) with 1-iodocyclopentene (*2*)

1-(*p*-Anisyl)cyclopentene (**5c**); (t_R = 1.35 min), 137 mg (69%). Colorless needles (m.p. 43–44 °C, from ethanol). ^{1}H NMR (δ ppm): 1.99 (2H, m), 2.44 (2H, m), 2.52 (2H, m), 3.79 (3H, s), 6.09 (1H, m), 6.82 (2H, d, $J_{p\text{-anisyl}}$ = 8.71 Hz), 7.37 (2H, d, $J_{p\text{-anisyl}}$ = 8.71 Hz). ^{13}C NMR (δ ppm): 23.3 (t), 33.3 (t), 36.5 (t), 55.2 (q), 85.4 (s), 90.3 (s), 113.9 (d), 115.7 (s), 124.7 (s), 132.8 (d), 137.2 (d), 159.3 (s). MS (EI) *m/z*: 198 (M^+, 100%), 183 (14%), 167 (25%), 155 (36%). IR (cm^{-1}): 2194 (C≡C), 1664 (C=C). 1,4-Di(*p*-anisyl)-1,3-butadiyne (**6c**); (t_R = 11.47 min), 28 mg (21%). Colorless needles (m.p. 144–145 °C, from ethanol). ^{1}H NMR (δ ppm): 3.81 (6H, s), 6.85 (4H, d, J = 8.71 Hz), 7.45 (4H, d, J = 8.71 Hz). ^{13}C NMR (δ ppm); 55.3 (q), 72.9 (s), 81.2 (s), 113.9 (s), 114.1 (d), 134.0 (d), 160.2 (s). MS (EI) *m/z*: 262 (M^+, 100%), 247 (45%), 232 (3%), 219 (8%), 204 (5%), 131 (8%). IR (cm^{-1}): 2139 (C≡C).

4.3.6. Reaction of p-fluorophenylethynyldiphenylstibane (*1d*) with 1-iodocyclopentene (*2*)

1-(*p*-Fluorophenylethynyl)cyclopentene (**5d**); (t_R = 2.27 min), 158 mg (85%). Colorless prisms (m.p. 51–53 °C, from ethanol). ^{1}H NMR (δ ppm): 1.94 (2H, m), 2.45–2.49 (2H, m), 2.52–2.55 (2H, m), 6.13 (1H, m), 6.99 (2H, dd, $J_{2',3'} = J_{3',F}$ = 8.71 Hz), 7.41 (2H, dd, $J_{2',3'}$ = 8.71 Hz, $J_{2',F}$ = 5.50 Hz). ^{13}C NMR (δ ppm): 23.3 (t), 33.4 (t), 36.4 (t), 86.4 (s), 89.3 (s), 115.5 (dd, ^2J_F = 22.0 Hz), 119.7 (d, ^4J_F = 3.9 Hz), 124.4 (s), 133.3 (dd, ^3J_F = 8.6 Hz), 138.2 (d), 162.3 (d, ^1J_F = 247.1 Hz). MS (EI) *m/z*: 186 (M^+, 100%), 171 (28%), 165 (57%), 157 (18%), 144 (10%), 133 (13%). IR (cm^{-1}): 2204 (C≡C), 1656 (C=C). 1,4-Bis(*p*-fluorophenyl)-1,3-butadiyne (**6d**); (t_R = 4.46 min), 10 mg (8%). Colorless plates (m.p. 195–197 °C, from ethanol). ^{1}H NMR (δ ppm): 7.04 (4H, dd, $J_{2,3} = J_{3,F}$ = 8.71 Hz), 7.51 (4H, dd, $J_{2,3}$ = 8.71 Hz, $J_{2,F}$ = 5.50 Hz). ^{13}C NMR (δ ppm): 73.6 (s), 80.4 (s), 115.9 (dd, ^2J_F = 21.9 Hz), 117.8 (s), 134.5 (dd, ^3J_F = 8.50 Hz), 163.1 (d, ^1J_F = 249.9 Hz). MS (EI) *m/z*: 238 (M^+, 100%), 218 (12%), 119 (15%). IR (cm^{-1}): 2144 (C≡C).

4.3.7. Reaction of 1-hexynyldiphenylstibane (*1e*) with 1-iodocyclopentene (*2*)

1-(1-Hexynyl)cyclopentene (**5e**); (t_R = 0.54 min), 104 mg (70%). Colorless oil. ^{1}H NMR (δ ppm): 0.92 (3H, t, J = 7.33 Hz), 1.43 (2H, tq, J = 7.33 Hz), 1.50 (2H, tt, J = 7.33 Hz), 1.88 (2H, m), 2.32 (2H, t, J = 7.33 Hz), 2.39–2.43 (4H, m). ^{13}C NMR (δ ppm): 13.6 (q), 19.1 (t), 22.0 (t), 23.3 (t), 30.9 (t), 33.0 (t), 36.6 (t), 77.7 (s), 91.4 (s), 125.0 (s), 135.8 (d). MS (EI) *m/z*: 148 (M^+, 38%), 133 (13%), 119 (35%), 105 (76%), 91 (100%). IR (cm^{-1}): 2213 (C≡C), 1675 (C=C). 5,7-Dodecadiyne (**6e**); (t_R = 0.815 min), 7.1 mg (9%). Colorless oil. ^{1}H NMR (δ ppm): 0.91 (6H, t, J = 7.33 Hz), 1.41 (4H, sextet, J = 7.33 Hz), 1.50 (4H, quintet, J = 7.33 Hz), 2.25 (4H, t, J = 7.33 Hz). ^{13}C NMR (δ ppm): 13.5 (q), 18.9 (t), 21.9 (t), 30.4 (t), 65.3 (s), 77.4 (s). MS (EI) *m/z*: 162 (M^+, 83%), 147 (8%), 133 (11%), 119 (27%), 105 (81%), 91 (100%). IR (cm^{-1}): 2233 (C≡C).

4.3.8. Reaction of 3 3-dimethyl-1-butynyldiphenylstibane (*1f*) with 1-iodocyclopentene (*2*)

1-(3,3-Dimethyl-1-butynyl)cyclopentene (**5f**); (t_R = 0.933 min), 111 mg (75%). Colorless oil. ^{1}H NMR (δ ppm): 1.23 (9H, s), 1.52 (2H, m), 1.86 (2H, m), 2.37 (2H, m), 5.80 (1H, m). ^{13}C NMR (δ ppm): 23.2 (t), 27.7 (s), 30.5 (q), 32.9 (t), 36.6 (t), 76.0 (s), 99.1 (s), 125.0 (s), 135.3 (d). MS (EI) *m/z*: 148 (M^+, 71%), 133 (100%), 119 (32%), 105 (61%), 91 (32%). IR (cm^{-1}): 2144 (C≡C), 1677 (C=C). 2,2,7,7-Tetramethyl-3,5-octadiyne (**6f**); (t_R = 0.392 min), 10.3 mg (13%). Colorless plates (m.p. 105–110 °C, subl., from ethanol). ^{1}H NMR (δ ppm): 1.23 (18H, s). ^{13}C NMR (δ ppm): 27.9 (s), 30.6 (q), 63.7 (s), 86.2 (s). MS (EI) *m/z*: 162 (M^+, 100%), 147 (55%), 132 (18%), 119 (71%), 105 (59%), 91 (49%). IR (cm^{-1}): 2184 (C≡C).

4.3.9. Reaction of trimethylsilylethynyldiphenylstibane (*1g*) with 1-iodocyclopentene (*2*)

1-(2-Trimethylsilylethynyl)cyclopentene (**5g**); (t_R = 0.542 min), 105 mg (64%). Colorless oil. ^{1}H NMR (δ ppm): 0.14 (9H, s), 1.85 (2H, m), 2.34–2.42 (4H, m), 6.05 (1H, m). ^{13}C NMR (δ ppm): 0.21 (q), 23.3 (t), 33.2 (t), 36.3 (t), 95.2 (s), 102.5 (s), 124.6 (s), 139.2 (d). MS (EI) *m/z*: 164 (M^+, 33%), 149 (100%), 133 (4%), 121 (3%). IR (cm^{-1}): 2148 (C≡C), 1648 (C=C). 1,4-Bis(trimethylsilyl)-1,3-butadiyne (**6g**); (t_R = 0.425 min), 15 mg (15%). Colorless plates (m.p. 112–113 °C subl., from ethanol). ^{1}H NMR (δ ppm): 0.189 (18H, s). ^{13}C NMR (δ ppm): −0.5 (q), 85.9 (s), 88.0 (s). MS (EI) *m/z*: 194 (M^+, 20%), 179 (100%), 163 (2%), 149 (2%), 135 (2%), 121 (4%). IR (cm^{-1}): 2067 (C≡C).

4.3.10. Reaction of diphenylphenylethynylstibane (*1a*) with 1-iodocyclohexene (7) [19]

1-Phenylethynylcyclohexene (**10**); (t_R = 1.90 min), 121.1 mg (67%). Colorless oil. ^{1}H NMR (δ ppm): 1.51–1.69 (4H, m), 2.13–2.22 (4H, m), 6.20 (1H, m), 7.23–7.33 (3H, m), 7.40–7.51 (2H, m). ^{13}C NMR (δ ppm): 21.5 (t), 22.3 (t), 25.7 (t), 29.2 (t), 86.8 (s), 91.2 (s), 120.7 (s), 123.7 (s), 127.6 (d), 128.2 (d), 131.4 (d), 135.1 (d). MS (EI) *m/z*: 182 (M^+, 100%), 167 (62%), 154 (55%), 141 (22%), 126 (20%), 115 (31%). IR (cm^{-1}): 2202 (C≡C), 1592 (C=C). **6a**; 30 mg (30%).

*4.3.11. Reaction of diphenylphenylethynylstibane (**1a**) with trans-1-iodohexene (**8**) [22]*

trans-1-Phenyl-3-octene-1-yne (**11**); (t_R = 1.49 min), 75.2 mg (41%). Colorless oil. ^{1}H NMR (δ ppm): 0.91 (3H, t, $J_{7,8}$ = 7.33 Hz), 1.32–1.43 (4H, m), 2.16 (2H, dt, $J_{5,6}$ = $J_{4,5}$ = 7.33 Hz), 5.69 (1H, d, $J_{3,4}$ = 16.04 Hz), 6.24 (1H, dt, $J_{3,4}$ = 16.04 Hz, $J_{4,5}$ = 7.33 Hz), 7.24–7.30 (3H, m), 7.40–7.42 (2H, m). ^{13}C NMR (δ ppm): 13.8 (q), 22.2 (t), 30.9 (t), 32.9 (t), 87.8 (s), 88.3 (s), 109.5 (d), 123.7 (s), 127.8 (d), 128.2 (d), 131.4 (d), 145.2 (d). MS (EI) *m/z*: 184 (M^+, 100%), 169 (10%), 155 (55%), 141 (82%), 128 (78%), 115 (68%). IR (cm^{-1}): 2202 (C≡C), 1596 (C=C). **6a**; 39.4 mg (39%).

*4.3.12. Reaction of diphenylphenylethynylstibane (**1a**) with trans-β-iodostyrene (**9**) [23]*

trans-1,4-Diphenyl-1-butene-3-yne (**12**); (t_R = 4.88 min), 126.3 mg (62%). Colorless needles (m.p. 99–100 °C, from ethanol). ^{1}H NMR (δ ppm): 6.38 (1H, d, $J_{1,2}$ = 16.5 Hz), 7.04 (1H, d, $J_{1,2}$ = 16.5 Hz), 7.25–7.34 (6H, m), 7.39–7.42 (2H, m), 7.46–7.48 (2H, m). ^{13}C NMR (δ ppm): 88.9 (s), 91.8 (s), 108.1 (d), 123.4 (d), 126.3 (d), 128.2 (d), 128.3 (d), 128.6 (d), 128.7 (d), 131.5 (d), 136.3 (s), 141.2 (d). MS (EI) *m/z* : 204 (M^+, 100%), 189 (4%), 176 (5%), 163 (3%), 150 (3%). IR (cm^{-1}): 2192 (C≡C), 1592 (C=C). **6a**; 30.5 mg (30%).

*4.4. Reaction of diphenylphenylethynylstibane (**1a**) with aryl iodides (**13a–i**)*

General procedure. A mixture of diphenylphenylethynylstibane (**1a**, 376 mg, 1.00 mol) and aryl iodides (**13a–i**, 1.50 mmol) and dichloro(bistriphenylphosphine)palladium (70.0 mg, 0.10 mmol) in diethylamine (5 ml) was heated at 55 °C for 24 h under nitrogen atmosphere. After removal of the solvent under reduced pressure, the crude residue was purified on silica gel column chromatography using a mixture of *n*-hexane and benzene to afforded cross-coupling products (**14a–i**) and 1,4-diphenylbutadiyne (**6a**). Yields of the products were analyzed by GLC (5% SE30, 1.6 M, column temperature 210 °C) based on biphenyl (t_R = 1.17 min) as an internal standard.

*4.4.1. Reaction of diphenylphenylethynylstibane (**1a**) with iodobenzene (**13a**)*

1,2-Diphenylacetylene (**14a**); (t_R = 3.01 min), 81 mg (46%). Colorless prisms (m.p. 59–61 °C, from ethanol). ^{1}H NMR (δ ppm): 7.33–7.38 (6H, m), 7.53–7.57 (4H, m). ^{13}C NMR (δ ppm): 89.4 (s), 96.1 (s), 123.3 (s), 128.2 (d), 128.3 (d), 131.6 (d). MS (EI) *m/z*: 178 (M^+, 100%), 152 (27%), 126 (7%). **6a**; (t_R = 10.55 min), 21.4 mg (21%).

*4.4.2. Reaction of diphenylphenylethynylstibane (**1a**) with p-iodoanisole (**13b**)*

p-Anisylphenylacetylene (**14b**); (t_R = 8.17 min), 73 mg (35%). Colorless prisms (m.p. 59–60 °C, from ethanol). ^{1}H NMR (δ ppm): 3.80 (3H, s), 6.86 (2H, d, J = 8.71 Hz), 7.31–7.43 (3H, m), 7.46 (2H, d, J = 8.71 Hz), 7.49–7.52 (2H, m). ^{13}C NMR (δ ppm): 55.2 (q), 88.0 (s), 89.4 (s), 114.0 (d), 115.4 (s), 123.6 (s), 127.9 (d), 128.3 (d), 131.4 (d), 133.0 (d), 159.6 (s). MS (EI) *m/z*: 208 (M^+, 100%), 193 (60%), 176 (4%), 165 (40%). IR (cm^{-1}): 2214 (C≡C). **6a**; 25 mg (25%).

*4.4.3. Reaction of diphenylphenylethynylstibane (**1a**) with o-iodotoluene (**13c**)*

Phenyl(*o*-tolyl)acetylene (**14c**); (t_R = 4.00 min), 57.6 mg (30%). Colorless oil. ^{1}H NMR (δ ppm): 2.54 (3H, s), 7.18 (1H, dd, $J_{5',6'}$ = 7.79 Hz, $J_{4',5'}$ = 4.58 Hz), 7.24–7.25 (2H, m), 7.34–7.38 (3H, m), 7.52 (1H, d, $J_{5',6'}$ = 7.79 Hz), 7.55–7.56 (2H, m). ^{13}C NMR (δ ppm): 20.7 (q), 88.3 (s), 93.3 (s), 123.0 (s), 123.5 (s), 125.6 (d), 128.1 (d), 128.28 (d), 128.33 (d), 129.4 (d), 131.5 (d), 131.8 (d), 140.2 (s). MS (EI) *m/z*: 192 (M^+, 100%), 165 (25%), 139 (5%), 115 (11%). IR (cm^{-1}): 2215 (C≡C). **6a**; 20.2 mg (20%).

*4.4.4. Reaction of diphenylphenylethynylstibane (**1a**) with p-iodotoluene (**13d**)*

Phenyl(*p*-tolyl)acetylene (**14d**); (t_R = 4.58 min), 65.3 mg (34%). Colorless prisms (m.p. 69–71 °C, from ethanol). ^{1}H NMR (δ ppm): 2.35 (3H, s), 7.14 (2H, d, J = 7.79 Hz), 7.30–7.34 (3H, m), 7.42 (2H, d, J = 7.79 Hz), 7.50–7.52 (2H, m). ^{13}C NMR (δ ppm): 21.5 (q), 88.7 (s), 89.6 (s), 120.2 (s), 123.5 (s), 128.0 (d), 128.3 (d), 129.1 (d), 131.475 (d), 131.529 (d), 138.3 (s). MS (EI) *m/z*: 192 (M^+, 100%), 177 (5%), 165 (12%), 139 (5%), 115 (4%). IR (cm^{-1}): 2216 (C≡C). **6a**; 20.2 mg (20%).

*4.4.5. Reaction of diphenylphenylethynylstibane (**1a**) with 4-fluoro-1-iodobenzene (**13e**)*

p-Fluorophenylphenylacetylene (**14e**); (t_R = 2.96 min), 84.4 mg (43%). Colorless prisms (m.p. 113–114 °C, from ethanol). ^{1}H NMR (δ ppm): 7.03 (2H, dd, $J_{2',3'}$ = $J_{3',F}$ = 8.70 Hz), 7.32–7.35 (3H, m), 7.49–7.52 (4H, m). ^{13}C NMR (δ ppm): 88.3 (s), 89.0 (s), 115.6 (dd, ^2J_F = 22.0 Hz), 119.4 (s), 123.1 (s), 128.3 (d), 128.4 (d), 131.5 (d), 133.5 (dd, ^3J_F = 8.63 Hz), 162.5 (d, ^1J_F = 245 Hz). MS (EI) *m/z*: 196 (M^+, 100%), 170 (8%), 144 (4%). IR (cm^{-1}): 2222 (C≡C). **6a**; 7 mg (7%).

*4.4.6. Reaction of diphenylphenylethynylstibane (**1a**) with p-iodoacetophenone (**13f**)*

p-Acetylphenylphenylacetylene (**14f**); (t_R = 12.04 min), 101 mg (46%). Colorless needles (m.p. 99–100 °C, from ethanol). ^{1}H NMR (δ ppm): 2.60 (3H, s), 7.36–7.37 (3H, m), 7.54–7.56 (2H, m), 7.60 (2H, d, J = 8.25 Hz), 7.93 (2H, d, J = 8.25 Hz). ^{13}C NMR (δ ppm): 26.6 (q), 88.6 (s), 92.7 (s), 122.6 (s), 128.1 (s), 128.2 (d), 128.4 (d), 128.8 (d), 131.6 (d), 131.7 (d), 136.1 (s), 197.2 (s). MS (EI) *m/z*: 220 (M^+, 92%), 205

(100%), 189 (4%), 176 (45%), 151 (15%). IR (cm^{-1}): 2218 (C≡C), 1680 (C═O). **6a**; 7.1 mg (7%).

*4.4.7. Reaction of diphenylphenylethynylstibane (**1a**) with o-iodonitrobenzene (**13g**)*

o-Nitrophenylphenylacetylene (**14g**); (t_R = 11.05 min), 171 mg (77%). Orange plates (m.p. 192–194 °C, from ethanol). ^{1}H NMR (δ ppm): 7.46–7.55 (4H, m), 7.63 (1H, d, J = 6.88 Hz), 7.67–7.69 (2H, m), 8.63–8.65 (2H, m). ^{13}C NMR (δ ppm): 114.2 (d), 121.6 (d), 122.8 (s), 125.8 (s), 127.8 (d), 128.5 (d), 130.7 (d), 131.1 (d), 132.1 (s), 134.8 (d), 147.8 (s), 186.9 (s). MS (EI) *m/z*: 223 (M^+, 100%), 206 (59%), 195 (7%), 179 (12%), 167 (20%). **6a**; 11.1 mg (11%).

*4.4.8. Reaction of diphenylphenylethynylstibane (**1a**) with m-iodonitrobenzene (**13h**)*

m-Nitrophenylphenylacetylene (**14h**); (t_R = 13.01 min), 163 mg (73%). Colorless prisms (m.p. 71–72°, from ethanol). ^{1}H NMR (δ ppm): 7.37–7.39 (3H, m), 7.52 (1H, dd, $J_{4',5'} = J_{5',6'}$ = 7.79 Hz), 7.54–7.56 (2H, m), 7.81 (1H, d, $J_{5',6'}$ = 7.79 Hz), 8.17 (1H, d, $J_{4',5'}$ = 7.79 Hz), 8.36 (1H, s). ^{13}C NMR (δ ppm): 86.8 (s), 91.9 (s), 122.2 (s), 122.8 (d), 125.1 (s), 126.3 (d), 128.5 (d), 129.0 (d), 129.3 (d), 131.7 (d), 137.2 (d), 148.1 (s). MS (EI) *m/z*: 223 (M^+, 100%), 176 (43%), 165 (6%), 151 (16%),. IR (cm^{-1}): 2210 (C═C). **6a**; 20.2 mg (20%).

*4.4.9. Reaction of diphenylphenylethynylstibane (**1a**) with p-iodonitrobenzene (**13i**)*

p-Nitrophenylphenylacetylene (**14i**); (t_R = 12.64 min), 194 mg (87%). Colorless needles (m.p. 121–123 °C, from ethanol). ^{1}H NMR (δ ppm): 7.37–7.40 (3H, m), 7.55–7.57 (2H, m), 7.66 (2H, J = 8.71 Hz), 8.21 (2H, d, J = 8.71 Hz). ^{13}C NMR (δ ppm): 87.5 (s), 94.7 (s), 122.1 (s), 123.6 (d), 128.55 (d), 129.2 (d), 130.2 (s), 131.8 (d), 132.2 (d), 146.9 (s). MS (EI) *m/z*: 223 (M^+, 100%), 207 (2%), 193 (30%), 176 (72%), 165 (24%), 151 (26%). IR (cm^{-1}): 2215 (C≡C). **6a**; 5.1 mg (5%).

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