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Note

Pd-catalyzed oxidative Heck-type arylation of vinyl ketones, alkenes, and acrylates with *Sb*-aryl-tetrahydrodibenz[*c*,*f*][1,5]azastibocines

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ABSTRACT

The Pd-catalyzed cross-coupling reactions of *Sb*-aryl-1,5-azastibocines with alkenes are described. The reactions of azastibocines with alkenes such as vinyl ketones, alkenes, and acrylates in the presence of 10 mol% $PdCl_2$ at 80 °C in DMA under aerobic conditions produced Heck adducts in moderate-to-excellent yields. Single-crystal X-ray and NMR analysis revealed that the aryl donors in this reaction, the *Sb*-aryl-1,5-azastibocines, are hypervalent compounds that display N–Sb intramolecular non-bonding interaction. These are the first examples of Pd-catalyzed Heck-type arylations using heterocyclic hypervalent organoantimony compounds. Although the reactions proceeded efficiently with the azastibocines, they hardly progressed with trivalent and pentavalent triarylantimony reagents.

1. Introduction

Organoantimony compounds are not only important reagents for organic and inorganic chemistry, but are also widely used in biological and pharmaceutical research [1–4]. Among these compounds, *Sb*-substituted-tetrahydrodibenz[*c*,*f*] [1,5] azastibocines–eight-membered heterocycles containing antimony and nitrogen atoms–have garnered attention as bioactive substances as well as in organic synthesis and structural chemistry (Fig. 1). In 1989, Akiba et al. reported the first synthesis of an azastibocine with halogen, phenyl, and alkyne ligand substituents on the antimony center [5]; since then, many derivatives have been prepared. In the structural analyses of these compounds, the presence of a hypervalent bond between antimony and nitrogen is often observed [6,7]. Azastibocines have demonstrated anti-proliferation activity in human alveolar adenocarcinoma and human liver hepatocellular carcinoma cell lines, and have also shown toxicity to vascular endothelial cells [8–11]. We reported that *Sb*-alkynyl and -aryl azastibocines act as efficient transmetallation agents in the transition-metal-catalyzed reactions [6,12,13]. Pd-catalyzed cross-coupling reactions of *Sb*-alkynyl and aryl-azastibocines with acyl, vinyl, and aryl halides afford ethynyl ketones, diarylacetylenes, 1,3-enynes, diaryl ketones, and biaryls under mild reaction conditions without using bases. Moreover, Rh-catalyzed additions of *Sb*-aryl azastibocines to enones, enoates, and aldehydes also proceed to give 1,4-conjugate adducts and aryl alcohols [14–16]. It has recently been reported that an organoantimony triflate containing an azastibocine ring and *Sb*-fluoroazastibocine can be used as Lewis acid catalysts for the three component cyclization-aromatization of amines, aldehydes, and alkynes; the aminolysis reaction of epoxides with amines; the Mannich reaction of aldehydes, aniline, and ketones; and the allylation of aldehydes with tetraallyltin [7,17,18].

Antitumor activity
Aryl source of transition metal-catalyzed reaction
Lewis acid catalyst

R^1 = Halogen, Alkynyl, Aryl
R^2 = Alkyl, Phenyl

Fig. 1. Utilization of *Sb*-substituted-tetrahydrodibenz[*c*,*f*][1,5]azastibocines.

The Mizoroki-Heck reaction–i.e., the Pd-catalyzed coupling reaction of alkenes with aryl halides or triflates–has become a standard method for C(sp^2)–C(Ar) bond formation in organic synthesis [19]. The typical reaction conventionally requires high

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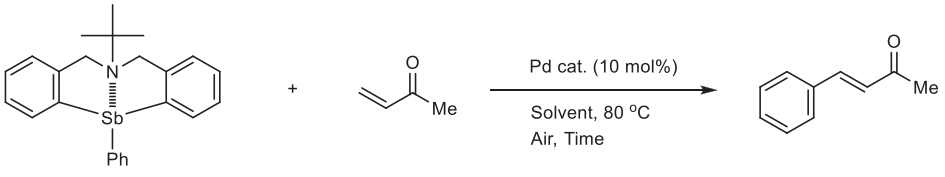
temperature and prolonged heating in the presence of a bases. To avoid these harsh conditions, various surrogates for aryl halides have been investigated, including highly reactive organometallic agents containing main group elements such as boron, silicon, tin, phosphorus, antimony, bismuth, and tellurium [20,21]. It is known that pentavalent organoantimony compounds, such as triarylantimony dicarboxylates {$Ar_3Sb[OC(O)R]_2$} and tetraphenylantimony carboxylates {$Ph_4Sb[OC(O)R]$}, can serve as aryl donors in oxidative Heck-type reactions [22–27]. Moreover, Uemura et al. reported that the Heck-type reaction of trivalent organoantimony compounds, diphenylantimony chloride (Ph_2SbCl), and triphenylstibane (Ph_3Sb) with various alkenes such as styrene, allyl acetate, and methyl acrylate gave the corresponding arylated products [28,29]. However, these reactions have several drawbacks, such as requiring acidic solutions and an oxidant, and delivering poor utilization efficiency for the multiple aryl groups. Furthermore, oxidative Heck-type reactions using heterocyclic compounds having hypervalent bonds have not been reported, to our knowledge. As part of our continuing studies on organoantimony compounds [6,12,13], we investigated the Pd-catalyzed oxidative Heck-type arylation of alkenes with *Sb*-aryl-1,5-azastibocines, which are highly reactive hypervalent organoantimony compounds with intramolecular N–Sb interactions.

2. Results and discussion

2.1. Reaction of azastibocine with vinyl ketones, alkenes, and acrylates

We previously reported that *N*-*t*-butyl-*Sb*-phenyl-1,5-azastibocine **1a** functions as an aryl donor in Pd-catalyzed reactions with acyl and aryl halides to afford the corresponding ketones and biaryls [13]. Uemura et al., described the Pd-catalyzed reaction between methyl vinyl ketone and Ph_2SbCl, which afforded only the conjugate addition product, 4-phenylbutan-2-one, rather than the Heck type product, (*E*)-4-phenylbut-3-en-2-one [29]. Therefore, we initially focused our attention on determining the optimal conditions for the Heck-type reaction of 1,5-azastibocine **1a** (0.25 mmol) with methyl vinyl ketone **2a** (0.75 mmol). The results are summarized in Table 1. We first screened several available Pd(0) and Pd(II) catalysts (0.025 mmol) under aerobic conditions in DMA at 80 °C without base. $Pd(OAc)_2$, $PdCl_2$, $PdCl_2(MeCN)_2$, and $PdCl_2(PPh_3)_2$ gave Heck adduct **3** in good-to-excellent yields (72–94%) without any byproducts (entries 1–6), and $PdCl_2$ was identified as the best catalyst in terms of the yield of product **3** (94%) (entry 2). The reaction did not proceed in the absence of a Pd catalyst (entry 8). Solvent screening showed that the reaction proceeded effectively in DMA, EtOH, MeCN, 1,4-dioxane and toluene (entries 2, 9–16), with DMA offering the best performance in terms of yield and reaction time (6 h, 94%; entry 2). On the other hand, DMF, DMSO, 1,2-DCE, and THF were inefficient reaction solvents. Significant decreases in the yield of **3** were observed under O_2 and Ar atmospheres (entries 17, 18). Decreasing the loading of $PdCl_2$ from 10 to 5 mol% reduced the yield of **3**, even with increased reaction time (entry 19). The reaction of **1a** with **2a** in the presence of one equivalent of galvinoxyl as a radical scavenger gave coupling product **3** in satisfactory yield (72%; entry 20). Table 2 shows the results for the reaction of methyl vinyl ketone **2a** with other trivalent and pentavalent antimony reagents **4–7** instead of azastibocine **1a** under optimized conditions. Poor selectivity was observed with these reagents, which produced mixtures of **3, 8**, and **9** in various ratios.

Table 1
Pd-catalyzed reaction of 1,5-azastibocine **1a** with methyl vinyl ketone **2a**.[a]

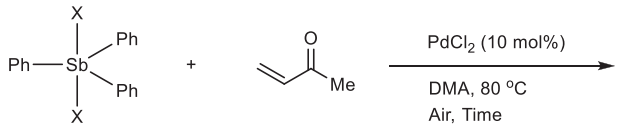


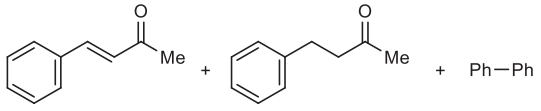
1a **2a** **3**

Entry	Pd cat.	Solvent	Time (h)	Yield of **3** (%)[b]
1	$Pd(OAc)_2$	DMA	24	72
2	$PdCl_2$	DMA	6	94
3	$PdCl_2(MeCN)_2$	DMA	24	74
4	$PdCl_2(PPh_3)_2$	DMA	6	75
5	$Pd(dba)_2$	DMA	24	49
6	$Pd(PPh_3)_4$	DMA	24	54
7	10% Pd-C	DMA	24	27
8	–	DMA	24	–
9	$PdCl_2$	DMF	6	56
10	$PdCl_2$	DMSO	6	58
11	$PdCl_2$	EtOH	24	90
12	$PdCl_2$	MeCN	24	79
13	$PdCl_2$	1,4-dioxane	24	71
14	$PdCl_2$	toluene	24	69
15	$PdCl_2$	1,2-DCE	24	58
16	$PdCl_2$	THF	24	41
17[c]	$PdCl_2$	DMA	4	32
18[d]	$PdCl_2$	DMA	24	36
19[e]	$PdCl_2$	DMA	24	56
20[f]	$PdCl_2$	DMA	6	72

[a] Reaction conditions: **1a** (0.25 mol), **2a** (0.75 mmol), Pd catalyst (0.025 mmol), Solvent (1.5 mL).
[b] Isolated yield.
[c] Under O_2.
[d] Under Ar.
[e] $PdCl_2$ (5 mol%).
[f] Added galvinoxyl (1 eq).

Table 2
Pd-catalyzed reaction of organoantimony compounds **4–7** with **2a**.[a]



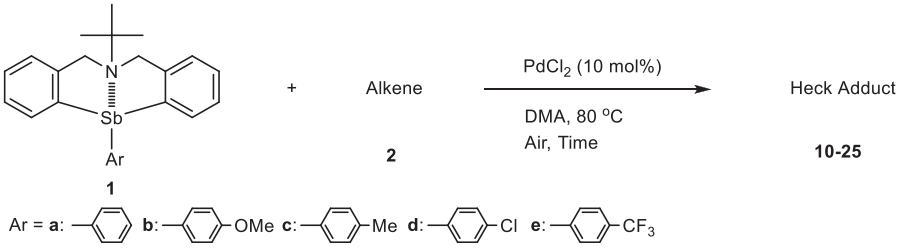


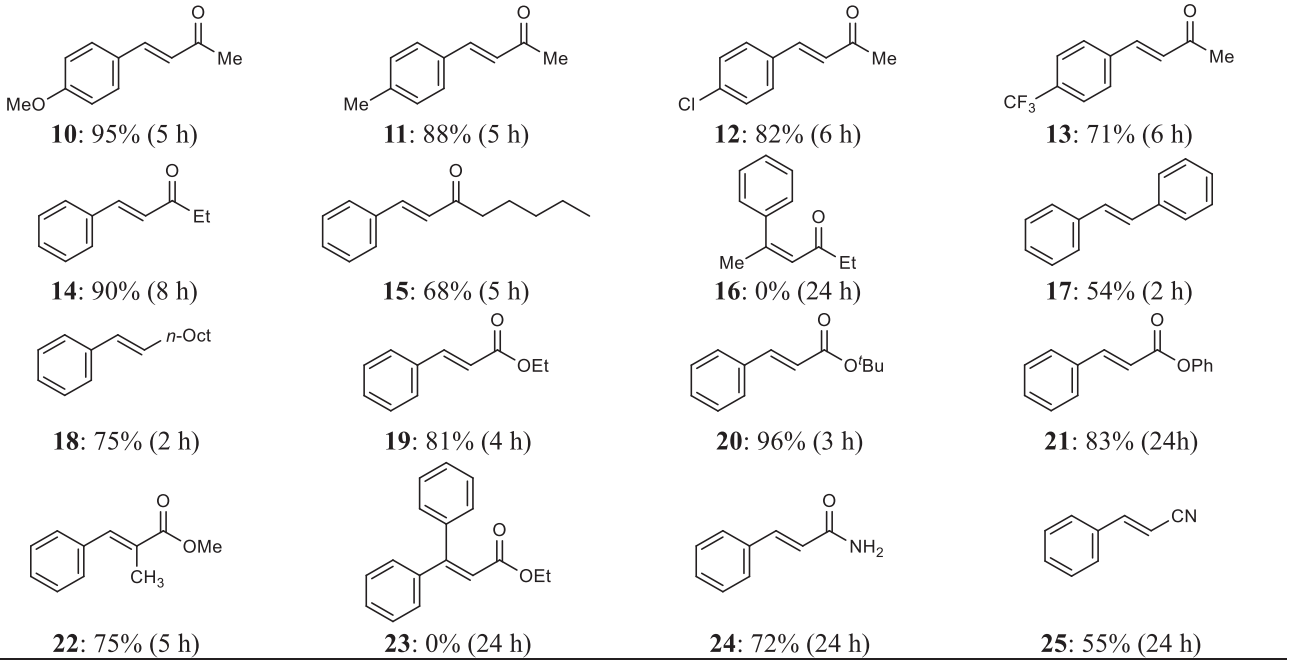
Entry	Reagent	Time (h)	Yield (%)[b]		
			3	**8**	**9**
1	Ph_3SbF_2 **4**	2	13	37	22
2	Ph_3SbCl_2 **5**	6	11	28	18
3	$Ph_3Sb(OAc)_2$ **6**	1	20	16	10
4	Ph_3Sb **7**	2	3	9	6

[a] Reaction conditions: **4–7** (0.25 mol), **2a** (0.75 mmol).
[b] GC yield.

To study of the scope of this arylation reaction, we coupled azastibocines **1** (1 mmol) with various alkenes **2** (3 mmol) using $PdCl_2$ (10 mol%) at 80 °C in DMA under aerobic conditions. The key starting materials, *Sb*-aryl-1,5-azastibocines **1**, were prepared according to the general method reported previously [5,13]. Briefly, *N,N*-bis(2-bromobenzyl)-2-methylpropan-2-amine was treated with *n*-butyllithium at −20 °C in dry ether under an argon atmosphere, and addition of antimony tribromide resulted in ring closure, giving rise to *Sb*-bromo-1,5-azastibocine. The obtained azastibocine was treated with aryllithium reagents to afford *Sb*-aryl-1,5-azastibocines **1a–e** in good yields (61–95%). The results of the coupling reactions are summarized in Table 3. Compounds **1b–e** reacted with **2a** to give corresponding Heck adducts **10–13** in good-to-excellent yields (71–95%). *Sb*-Aryl-azastibocines having electron-donating group such as methoxy and methyl at the *para* substituent of the benzene ring on antimony tended to give coupling products in higher yield. The reaction of **1a** with enones such as pent- **2b** and oct-1-en-3-one **2c** smoothly gave rise to compounds **14** and **15**, and aromatic and aliphatic alkenes **2e** and **2f** also applicable, affording **17** and **18** in 54% and 75% yields, respectively. Enoates **2g–j** also underwent arylation to give adducts **19–22** in good-to–excellent yields (75–96%). However, β-substituted α,β-unsaturated carbonyl compounds, such as (*E*)-hex-4-en-3-one **2d** and ethyl cinnamate **2k**, failed to react, and **16** and **23** were not obtained. The reaction of **1a** with cyclic enone such as 2-cyclohexen-1-one also did not proceed. Finally, the reaction

Table 3
Reaction of 1,5-azastibocines **1** with alkenes **2**.[a,b]

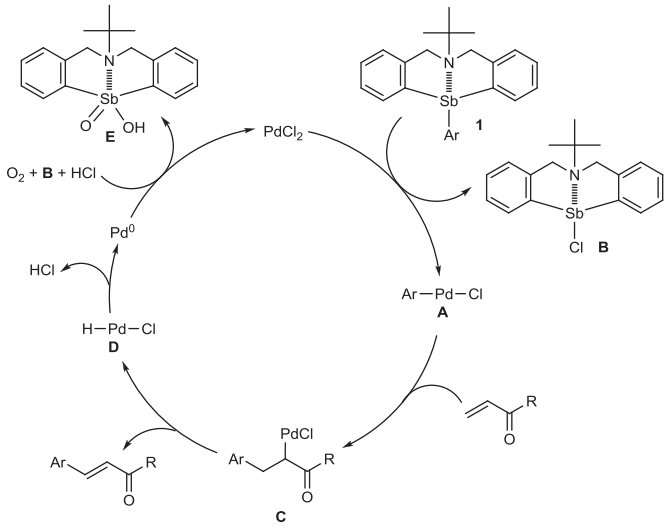




[a] Condition: **1** (1 mmol), **2** (3 mmol), $PdCl_2$ (0.1 mmol).
[b] Isolated yields.

of **1a** with acrylamide **2l** and acrylonitrile **2 m** gave corresponding coupling products **24** and **25** in 72% and 55% yields, respectively.

At present, the reaction mechanism for this coupling reaction is unclear. We consider that the mechanism would be similar to that of the Heck-type reaction of alkenes with Ph_2SbCl proposed by Uemura et al. [29]. The initial step is likely transmetallation of the azastibocine aryl group by $PdCl_2$ to form ArPdCl complex **A** with liberation of **B**. After coordination of the alkene to **A**, an insertion process proceeds to form σ complex **C**, which subsequently undergoes β-hydride elimination to produce the coupling adduct and HPdCl **D**. By reductive elimination, **D** is converted to Pd^0 and HCl, and $PdCl_2$ is regenerated by the transformation of Pd^0 with O_2, azastibocine **B**, and HCl. The $PdCl_2$ regeneration process may have a radical mechanism [29], but under the reaction conditions, the reaction was observed to progress even in the presence of a radical scavenger (Table 1, entry 20). On the other hand, the azastibocine **B** and stibonic acid **E** that are expected to be produced in this process have not be confirmed or isolated at this point.



Scheme 1. Proposed mechanism.

2.2. Molecular structure of 1,5-azastibocine

To better understand the chemistry of the *Sb*-aryldibenz[1,5]azastibocines, the molecular structure of **1a** was investigated. A single crystal of **1a** suitable for X-ray analysis was grown by repeating recrystallization. Fig. 2 shows the crystal structure of azastibocine **1a**, and Table 4 lists the selected bond lengths and angles. Single-crystal X-ray analysis of **1a** reveals the presence of an intramolecular interaction between the antimony and nitrogen atoms. The Sb–N distance is 2.746(2) Å, which is consistent with 73% of the sum of the van der Waals radii (3.74 Å) for both elements in the solid state [30]. The central antimony atom exhibits a pseudo trigonal bipyramidal (TBP) structure. The C3 of the phenyl group and nitrogen in the eight-membered ring are approximately *trans* to each other, with N–Sb–C3 bond angle of 159.31(6)°. This result indicates that the C1–Sb and C2–Sb bonds on the eight-membered ring occupy equatorial positions with a pair of electrons on antimony and the N···Sb and C3–Sb bonds occupying apical positions (Table 4). It is known that the apical bond is longer than the equatorial bond in the TBP structure of *Sb*-ethynyl-dibenz[1,5]azastibocine [6]. The bond distance between antimony and C3 [2.182(2) Å] occupying an apical position is also longer than those of Sb–C1 [2.161(2) Å] and Sb–C2 [2.166(2) Å]. These results indicate that *Sb*-phenyl-1,5-azastibocine is a hypervalent compound having an intramolecular N–Sb interaction similar to reported azastibocines [6,7]. Moreover, in the heteronuclear multiple bond correlation (HMBC) spectrum of azastibocine **1a**, a long-range coupling correlation is observed between the benzylic proton (δ = 3.86 and 4.17 ppm) and C3 carbon (δ = 146.5 ppm) in $CDCl_3$ solution. This indicates the possibility of a four-bond correlation *via* the N–Sb bond, suggesting that an intramolecular interaction exists between the antimony and nitrogen atoms even in solution on the NMR time scale [31].

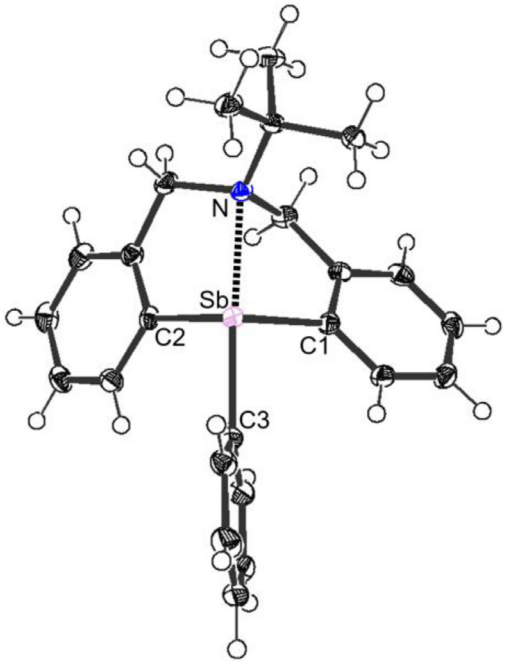


Fig. 2. ORTEP drawing of azastibocine **1a** with 50% probability.

Table 4
Selected bond lengths (Å) and bond angles (°) for azastibocine **1a**.

	1a
Bond lengths (Å)	
Sb–C1	2.161(2)
Sb–C2	2.166(3)
Sb–C3	2.182(2)
Sb–N	2.746(2)
Bond angles (°)	
C1–Sb–C2	100.03(7)
C1–Sb–C3	96.97(7)
C2–Sb–C3	93.97(7)
N–Sb–C1	71.41(6)
N–Sb–C2	72.09(6)
N–Sb–C3	159.31(6)

3. Conclusion

We have developed a simple Pd-catalyzed oxidative Heck-type arylation of alkenes, including vinyl ketones, alkenes, and acrylates, with *Sb*-aryl-1,5-azastibocines without the need for any additive. The azastibocines were superior aryl group donors and showed higher reactivity than other trivalent and pentavalent organoantimony reagents under the optimized conditions. The molecular structures of the *Sb*-phenyl-1,5-azastibocine was analyzed using single-crystal X-ray analysis and NMR, and was found to be hypervalent compounds having N–Sb intramolecular non-bonding interactions in both the solid and solution states. Further applications of *Sb*-aryl-1,5-azastibocines as aryl donors for the synthesis of functional materials, and reactions such as C(Ar)–heteroatom bond

formation using other coupling partners in the presence of the catalytic system, are under investigation.

4. Experimental

4.1. General

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. ^{1}H NMR ($CHCl_3$: δ: 7.26 ppm as an internal standard), ^{13}C NMR ($CDCl_3$: δ: 77.00 ppm as an internal standard) and ^{19}F NMR ($PhCF_3$: δ: -64.0 ppm as an external standard) spectra were recorded on JEOL ECZ-400S spectrometer (400 MHz, 100 MHz and 376 MHz) in $CDCl_3$. IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer and reported in terms of frequency of absorption (cm^{-1}). Only selected IR bands are reported. Mass spectra were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 mA). Column chromatography was performed on Silica Gel 60 N (Kanto Chemical Co., Inc.). Each reagent was purchased from Wako Pure Chemical Industries, Ltd. Japan, Tokyo Kasei Kogyo Co., LTD and SIGMA-ALDRICH Japan K.K. and used without further purification.

4.2. Preparation of t-butyl-12-aryl-5,6,7,12-tetrahydrodibenzo[c,f][1,5]azastibocines

Azastibocines were prepared according to the literature and the spectroscopic data of known compounds are in accordance with the literature [13]. **1a**; m.p. 130–133 °C (Lit. 134–135 °C), **1b**; m.p. 136–138 °C (Lit. 142–143 °C), **1c**; m.p. 179–180.5 °C (Lit. 183–184 °C), **1d**; m.p. 140–142 °C (Lit. 148–149 °C)

4.2.1. t-Butyl-12-p-trifluoromethylphenyl-5,6,7,12-tetrahydrodibenzo[c,f][1,5]azastibocine (**1e**)

Colorless prism, m.p. 174–176 °C (from CH_2Cl_2/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, 2H, J = 7.8 Hz, Ar-H), 7.64 (d, 2H, J = 7.8 Hz, Ar-H), 7.19 (td, 2H, J = 7.3, 1.4 Hz, Ar-H), 7.10–7.03 (m, 6H, Ar-H), 4.20 (d, 2H, J = 15.6 Hz, CH_2), 4.18 (d, 2H, J = 15.6 Hz, CH_2) 1.25 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4 (C), 146.7 (C),139.1 (CH), 136.02 (CH), 135.92 (C), 130.0 (C, q, $^2J_{C,F}$ = 31 Hz), 128.1 (CH), 127.3 (CH), 126.3 (CH), 124.61 (CH, q, $^3J_{C,F}$ = 3.9 Hz), 124.59 (C, q, $^1J_{C,F}$ = 272 Hz), 57.8 (C), 54.8 (CH_2), 26.9 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.7. LRMS (EI): m/z 517.1 ([M]$^+$, 5), 446.0 (5), 372.0 ([M-($C_6H_4CF_3$)]$^+$, 100), 316.0 (45). HRMS: m/z [M]$^+$ calcd for $C_{25}H_{25}F_3NSb$: 517.0977. Found: 517.0974.

4.3. General procedure for the Heck reaction with azastibocines

A mixture of azastibocine (1.0 mmol), alkene (3.0 mmol, 3 eq.) and $PdCl_2$ (18 mg, 0.1 mmol, 10 mol%) in DMA (3.0 mL) was stirred at 80 °C under air. The completion of the reaction was monitored using TLC. After being completed, the reaction mixture was cooled to room temperature and purified by chromatography (**17**: *n*-Hexane, **3, 14**: *n*-Hexane:CH_2Cl_2 = 5:1, **10–13, 15, 18–22, 25**: *n*-Hexane:EtOAc = 5:1, **24**: *n*-Hexane:EtOAc = 2:3) to give the Heak reaction product.

4.3.1. Benzylideneacetone (**3**) [32]

Colorless oil (136 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.54 (m, 2H, Ar-H), 7.50 (d, 1H, J = 16.0 Hz, CH=C*H*CO), 7.41–7.39 (m, 3H, Ar-H), 6.73 (d, 1H, J = 16.5 Hz, ArC*H*=CH), 2.38 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4 (C), 143.4 (CH), 134.4 (C), 130.5 (CH), 128.9 (CH), 128.2 (CH), 127.1 (CH), 27.5 (CH_3). FTIR (neat): 3003, 1681, 1654, 1452, 1361, 1257, 1176, 985, 669 cm^{-1}. LRMS (EI): m/z 145.1 ([M-H]$^+$, 75), 131.1 (100), 103.1 (95), 77.1 (50). HRMS: m/z [M]$^+$ calcd for $C_{10}H_{10}O$: 146.0732. Found: 146.0734.

4.3.2. (E)-4-(4′-Methoxylphenyl)-3-buten-2-one (**10**) [33]

Colorless plate (167 mg, 95%), m.p. 70–72 °C (from Hexane, Lit. 72–74 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.46 (m, 3H, Ar-H+CH=C*H*CO), 6.92 (dt, 2H, J = 9.6, 2.8 Hz, Ar-H), 6.61 (d, 1H, J = 16.8 Hz, ArC*H*=CH), 3.85 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5 (C), 161.7 (C), 143.4 (CH), 130.1 (CH), 127.1 (C), 125.1 (CH), 114.5 (CH), 55.5 (CH_3), 27.5 (CH_3). FTIR (KBr): 2941, 1681, 1626, 1465, 1392, 1290, 1172, 989, 667 cm^{-1}. LRMS (EI): m/z 177.1 ([M+H]$^+$, 75), 161.1 (100), 133.1 (40), 115.1 (16). HRMS: m/z [M]$^+$ calcd for $C_{11}H_{12}O_2$: 176.0837. Found: 176.0840.

4.3.3. (E)-4-(4′-Methylphenyl)-3-buten-2-one (**11**) [32]

Pale yellow oil (141 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 1H, J = 16.0 Hz, CH=C*H*CO), 7.43 (d, 2H, J = 8.4 Hz, Ar-H), 7.19 (d, 2H, J = 8.4 Hz, Ar-H), 6.67 (d, 1H, J = 16.0 Hz, ArC*H*=CH), 2.37 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7 (C), 143.6 (CH), 141.1 (C), 131.7 (C), 129.8 (CH), 128.4 (CH), 126.3 (CH), 27.5 (CH_3), 21.6 (CH_3). FTIR (neat): 2941, 1681, 1626, 1423, 1359, 1249, 1172, 989, 667 cm^{-1}. LRMS (EI): m/z 160.1 ([M]$^+$, 13), 145.1 (100), 115.1 (49), 91.1 (20). HRMS: m/z [M]$^+$ calcd for $C_{11}H_{12}O$: 160.0888. Found: 160.0890.

4.3.4. (E)-4-(4′-Chlorophenyl)-3-buten-2-one (**12**) [33]

Colorless needle (148 mg, 82%), m.p. 57–59 °C (from Hexane, Lit. 59–60 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.44 (m, 3H, Ar-H+CH=C*H*CO), 7.37 (dt, 2H, J = 8.8, 2.4 Hz, Ar-H), 6.68 (d, 1H, J = 16.4 Hz, ArC*H*=CH), 2.38 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3 (C), 142.1 (CH), 136.6 (C), 133.1 (C), 129.6 (CH), 129.4 (CH), 127.6 (CH), 27.9 (CH_3). FTIR (KBr): 2970, 1660, 1626, 1419, 1361, 1298, 1180, 977, 684 cm^{-1}. LRMS (EI): m/z 180.0 ([M]$^+$, 27), 165.0 (100), 137.0 (48), 102.1 (58). HRMS: m/z [M]$^+$ calcd for $C_{10}H_9ClO$: 180.0342. Found: 180.0339.

4.3.5. (E)-4-(4′-Trifluoromethylphenyl)-3-buten-2-one (**13**) [33]

Colorless plate (152 mg, 71%), m.p. 60–62 °C (from MeOH, Lit. 60–61 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 4H, Ar-H), 7.52 (d, 1H, J = 16.4 Hz, CH=C*H*CO), 6.78 (d, 1H, J = 16.4 Hz, ArC*H*=CH), 2.41 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1 (C), 141.5 (CH), 138.0 (C), 132.1 (C, q, $^2J_{C,F}$ = 33 Hz), 129.3 (CH), 128.5 (CH), 126.1 (C, q, $^3J_{C,F}$ = 3.8 Hz), 123.9 (C, q, $^1J_{C,F}$ = 271 Hz), 27.9 (CH_3). FTIR (KBr): 2934, 1664, 1614, 1415, 1329, 1259, 1168, 979, 758 cm^{-1}. LRMS (EI): m/z 215.1 ([M+H]$^+$, 21), 199.0 (100), 171.0 (53), 151.0 (73). HRMS: m/z [M]$^+$ calcd for $C_{11}H_9F_3O$: 214.0605. Found: 214.0608.

4.3.6. (E)-1-Phenyl-1-penten-3-one (**14**) [34]

Pale yellow oil (144 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.54 (m, 3H, Ar-H+CH=C*H*CO), 7.41–7.39 (m, 3H, Ar-H), 6.75 (d, 1H, J = 16.4 Hz, ArC*H*=CH), 2.71 (q, 2H, J = 7.2 Hz, CH_2), 1.17 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2 (C), 142.4 (CH), 134.8 (C), 130.5 (CH), 129.1 (CH), 128.4 (CH), 126.2 (CH), 34.2 (CH_2), 8.41 (CH_3). FTIR (neat): 2976, 1666, 1610, 1458, 1375, 1188, 977, 690 cm^{-1}. LRMS (EI): m/z 160.1 ([M]$^+$, 26), 131.1 (100), 103.1 (57), 77.1 (29). HRMS: m/z [M]$^+$ calcd for $C_{11}H_{12}O$: 160.0888. Found: 160.0887.

4.3.7. (E)-1-Phenyl-1-octen-3-one (**15**) [34]

Pale yellow oil (138 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.53 (m, 3H, Ar-H+CH=C*H*CO), 7.40–7.39 (m, 3H, Ar-H,), 6.75 (d, 1H, J = 16.4 Hz, ArC*H*=CH), 2.66 (t, 2H, J = 7.2 Hz, CH_2), 1.72–1.67 (m, 2H, CH_2), 1.36–1.33 (m, 4H, CH_2), 0.91 (t, 3H, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9 (C), 142.5 (CH), 134.8 (C), 130.6 (CH), 129.1 (CH), 128.4 (CH), 126.4 (CH), 41.1 (CH_2), 31.7 (CH_2), 24.3 (CH_2), 22.7 (CH_2), 14.2 (CH_3). FTIR (neat): 2928, 1664, 1647, 1450, 1371, 1178, 981, 688 cm^{-1}. LRMS (EI): m/z 202.1 ([M]$^+$,

4), 146.1 (49), 133.1 (100), 103.1 (40). HRMS: *m/z* $[M]^+$ calcd for $C_{14}H_{18}O$: 202.1358. Found: 202.1355.

*4.3.8. (E)-Stilbene (**17**) [35]*

Colorless flake (97 mg, 54%), m.p. 124–125 °C (from MeOH, Lit. 121–123 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 4H, J = 7.6 Hz, Ar-H), 7.35 (t, 4H, J = 7.6 Hz, Ar-H), 7.25 (tt, 2H, J = 7.3, 1.3 Hz, Ar-H), 7.11 (s, 2H, C*H*=CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3 (C), 128.6 (CH), 127.6 (CH), 126.5 (CH). LRMS (EI): *m/z* 179.1 ([M-H]$^+$, 100), 165.0 (60), 89.0 (30). HRMS: *m/z* $[M]^+$ calcd for $C_{14}H_{12}$: 180.0939. Found: 180.0935.

*4.3.9. (E)-Dec-1-enylbenzene (**18**) [35]*

Colorless oil (162 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.27 (m, 4H, Ar-H), 7.18–7.15 (m, 1H, Ar-H), 6.36 (d, 1H, J = 16.0 Hz, ArC*H*=CH), 6.22 (dt, 1H, J = 16.0, 6.8 Hz, ArC*H*=C*H*), 2.22–2.15 (m, 2H, CH_2), 1.34–1.27 (m, 12H, CH_2), 0.87 (t, 3H, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9 (C), 131.3 (CH), 129.6 (CH), 128.5 (CH), 126.7 (CH), 125.9 (CH), 33.1 (CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3). LRMS (EI): *m/z* 216.2 ([M]$^+$, 18), 117.1 (83), 104.1 (100), 91.1 (25). HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{24}$: 216.1878. Found: 216.1881.

*4.3.10. Ethyl cinnamate (**19**) [36]*

Colorless oil (141 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, 1H, J = 16.0 Hz, CH=C*H*CO), 7.53–7.50 (m, 2H, Ar-H), 7.39–7.36 (m, 3H, Ar-H), 6.44 (d, 1H, J = 16.0 Hz, ArC*H*=CH), 4.27 (q, 2H, J = 6.8 Hz, CH_2), 1.34 (t, 3H, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0 (C), 144.5 (CH), 134.4 (C), 130.2 (CH), 128.8 (CH), 128.0 (CH), 118.2 (CH), 60.5 (CH_2), 14.3 (CH_3). FTIR (neat): 2982, 1712, 1637, 1450, 1392, 1280, 1176, 979, 684 cm^{-1}. LRMS (EI): *m/z* 176.1 ([M]$^+$, 40), 147.1 (25), 103.1 (100), 77.1 (40). HRMS: *m/z* $[M]^+$ calcd for $C_{11}H_{12}O_2$: 176.0837. Found: 176.0839.

*4.3.11. tert-Butyl cinnamate (**20**) [36]*

Colorless oil (193 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, 1H, J = 16.0 Hz, CH=C*H*CO), 7.50 (dd, 2H, J = 9.4, 1.8 Hz, Ar-H), 7.38–7.34 (m, 3H, Ar-H), 6.37 (d, 1H, J = 16.0 Hz, ArC*H*=CH), 1.54 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (C), 143.5 (CH), 134.6 (C), 129.9 (CH), 128.8 (CH), 127.9 (CH), 120.1 (CH), 80.5 (C), 28.1 (CH_3). FTIR (neat): 2931, 1708, 1637, 1450, 1367, 1296, 1151, 979, 684 cm^{-1}. LRMS (EI): *m/z* 204.1 ([M]$^+$, 5), 147.1 ([M-Bu]$^+$, 100), 131.1 (75), 103.1 (40), 57.1 (50). HRMS: *m/z* $[M]^+$ calcd for $C_{13}H_{16}O_2$: 204.1150. Found: 204.1147.

*4.3.12. (E)-Phenyl cinnamate (**21**) [36]*

Colorless plate (187 mg, 83%), m.p. 74–76 °C (from Hexane, Lit. 76–78 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 1H, J = 16.0 Hz, CH=C*H*CO), 7.59–7.58 (m, 2H, Ar-H), 7.44–7.39 (m, 5H, Ar-H), 7.27–7.22 (m, 1H, Ar-H), 7.18–7.15 (m, 2H, Ar-H,), 6.63 (d, 1H, J = 16.0 Hz, ArC*H*=CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (C), 150.9 (C), 146.7 (CH), 134.3 (C), 130.8 (CH), 129.5 (CH), 129.1 (CH), 128.4 (CH), 125.9 (CH), 121.7 (CH), 117.4 (CH). FTIR (KBr): 3028, 1735, 1635, 1492, 1450, 1199, 1143, 993, 680 cm^{-1}. LRMS (EI): *m/z* 224.1 ([M]$^+$, 4), 179.1 (3), 131.1 (100), 103.1 (31). HRMS: *m/z* $[M]^+$ calcd for $C_{15}H_{12}O_2$: 224.0837. Found: 224.0834.

*4.3.13. (E)-Methyl 2-methyl-3-phenylacrylate (**22**) [37]*

Colorless oil (132 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (q, 1H, J = 1.2 Hz, ArC*H*=CCH_3), 7.39–7.38 (m, 4H Ar-H), 7.33–7.30 (m, 1H, Ar-H), 3.81 (s, 3H, CH_3), 2.12 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3 (C), 139.1 (CH), 135.9 (C), 129.7 (CH), 128.5 (CH), 128.4 (CH), 52.2 (CH_3), 14.2 (CH_3). FTIR (neat): 2951, 1633, 1435, 1386, 1255, 1116, 981, 692 cm^{-1}. LRMS (EI): *m/z* 176.1 ([M]$^+$, 50), 145.1 (30), 115.1 (100), 91.1 (31). HRMS: *m/z* $[M]^+$ calcd for $C_{11}H_{12}O_2$: 176.0837. Found: 176.0841.

*4.3.14. (E)-Cinnamamide (**24**) [36]*

Colorless needle (106 mg, 72%), m.p. 141–143 °C (from Hexane-AcOEt, Lit. 145–146 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 1H, J = 16.0 Hz, CH=C*H*CO), 7.52–7.48 (m, 2H, Ar-H), 7.39–7.34 (m, 3H, Ar-H), 6.46 (d, 1H, J = 16.0 Hz, ArC*H*=CH), 5.76 (brs, 1H, NH_2), 5.68 (brs, 1H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9 (C), 142.6 (CH), 134.6 (C), 130.1 (CH), 128.9 (CH), 128.0 (CH), 119.5 (CH). FTIR (KBr): 3365, 1656, 1604, 1396, 1244, 1114, 968, 756 cm^{-1}. LRMS (EI): *m/z* 146.1 ([M-H]$^+$, 100), 130.1 (42), 103.1 (159), 77.1 (40). HRMS: *m/z* $[M]^+$ calcd for C_9H_9NO: 147.0684. Found: 147.0680.

*4.3.15. (E)-Cinnamonitrile (**25**) [38]*

Colorless oil (71 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.37 (m, 6H, CH=C*H*CO+Ar-H), 5.87 (d, 1H, J = 16.4 Hz, ArC*H*=CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7 (CH), 133.6 (C), 131.3 (CH), 129.2 (CH), 127.5 (CH), 118.3 (C), 96.4 (CH). FTIR (neat): 3059, 2218, 1618, 1599, 1271, 1207, 1074, 966, 748 cm^{-1}. LRMS (EI): *m/z* 129.1 ([M]$^+$, 100), 102.1 (40), 76.1 (13), 51.1 (13). HRMS: *m/z* $[M]^+$ calcd for C_9H_7N: 129.0578. Found: 129.0578.

*4.4. X-ray crystallography of **1a***

The colorless prismatic crystal (0.300 × 0.200 × 0.200 mm^3), obtained from dichloromethane/methanol, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. The diffraction experiment was performed in a Bruker APEX II system (APEX II CCD detector, MoKα: λ = 0.71073 Å). Absorption correction was performed by an empirical method implemented in SADABS [39]. Structure solution and refinement were performed by using SHELXS-2014/7 and SHELXL-2014/7 [40].

$C_{24}H_{26}NSb$, Mr = 450.21; monoclinic, space group $P2_1/c$, Z = 4, D_{calc} = 1.512 g·cm^{-3}, a = 11.2369(10), b = 8.9414(8), c = 20.1700(18) Å, β = 102.6850(10)°, V = 1977.1(3) Å^3, 17,484 measured and 3457 independent [$I > 2\sigma(I)$] reflections, 238 parameters, final R_1 = 0.0179, wR_2 = 0.0471, S = 1.025 [$I > 2\sigma(I)$].

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 137, 23, and 43) with Uisovalues constrained to 1.2/1.5 Ueq of their parent atoms. Selected bond distance and angles are given in Table 4.

Crystallographic data for the structural analysis of **1a** have been deposited with Cambridge Crystallographic Data Center, CCDC No. 2005015. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44–1233–336,033; E-mail: deposit@ccdc.cam.au.uk or http://ccdc.cam.ac.uk).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2020.121545.

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