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Synthesis of 5-organostibano-1*H*-1,2,3-triazoles by Cu-catalyzed azide-alkyne cycloaddition and their application in the acyl-induced deantimonation for the preparation of fully substituted 5-acyl-1,2,3-triazoles

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ABSTRACT

The Cu-catalyzed azide-alkyne cycloaddition by the reaction of various ethynylstibanes with benzylazide in the presence of CuBr (5 mol%) under aerobic conditions led to the formation of trisubstituted 5-organostibano-1*H*-1,2,3-triazoles. Further, the acyl-induced deantimonation of 5-stibanotriazoles with acyl chlorides in the presence of *N*,*N*-dimethyl-4-aminopyridine and triethylamine afforded the corresponding trisubstituted 5-acyltriazoles in moderate-to-good yields.

1. Introduction

The chemistry of organoantimony compounds has been developed and the potential of such compounds in organic synthesis is always increasing.[1] With regard to the application of trivalent organoantimony compounds (stibanes), a wide variety of reactions like self-coupling reactions,[2] cross-coupling reactions,[3] photoreactions,[4] oxidations,[5] and asymmetric reactions with optically active organoantimony compounds[6] have been reported during the last three decades. Recently, we reported that trivalent organoantimony compounds bearing alkynyl groups are useful transmetallating agents for Pd-catalyzed cross-coupling reactions with organic halides.[7] In particular, they could be coupled to acyl chlorides, aryl and vinyl halides to afford the corresponding ethynylketones, diarylacetylenes, and 1,3-enynes. Moreover, they could be used for the synthesis of chiral organoantimony compounds by nucleophilic displacement reactions with Grignard or organolithium reagents; the ethynyl groups on the antimony atom serve as moderate leaving groups.[8] Stibane reagents, such as triphenylstibane, have low toxicity,[9] and therefore are promising organic synthetic reagents.

The copper-catalyzed azide-alkyne [3+2] cycloaddition reaction (CuAAC) is widely used for the synthesis of 1,2,3-triazoles because of its excellent regioselectivity and rapid reaction rate[10]; the reaction has also been applied in the fields of biology,[11] and material science.[12] The regioselectivite CuAAC synthesis of fully substituted 5-hetero-1,2,3-triazoles having group 15 and 16 elements such as phosphorus (P),[13] bismuth (Bi),[14] sulfur (S),[15] selenium (Se),[15,16] and tellurium (Te)[17] has been reported. Among these, further derivatization of the 5-position, based on the reactivity of the group 15 and 16 heteroatoms, was carried out only for 5-bismuthano-[14] and 5-tellanyltriazole[17,18] derivatives. Fokin et al. reported the synthesis of 5-bismuthano-1,2,3-triazoles by reacting ethynylbismuthanes with organic azides using CuOTf (5 mol%).[14] Further

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functionalization with electrophiles like acyl chlorides, diphosgene, sulfuryl chloride, and halogens generated the corresponding fully substituted 1,2,3-triazoles after elimination of the bismuth group at the 5-position. Stefani et al. reported the reaction of alkyl phenylethynyl tellurides with organic azides using CuI (1 eq) and pentamethyldiethylenetriamine (1 eq) to form 5-tellanyl-1,2,3-triazoles.[17] Further derivatization was achieved using Sonogashira- and Suzuki-type cross-coupling reactions and Te-Li exchange reaction at the 5-position of the triazoles.[17,18] However, these reactions have a drawback at the cycloaddition step: while the cycloaddition of bismuth compounds required alkyne derivatives based on the phenothiabismuthane-5,5-dioxide framework for stabilization, the cycloaddition of tellurium compounds required stoichiometric amounts of the Cu reagent and base. Recently, we have reported the synthesis of fully substituted 5-organostibano-1,2,3-triazoles by the Cu-catalyzed AAC of an ethynylstibane, (phenylethynyl)di-*p*-tolylstibane, with organic azides.[19] Herein, we reported the complete results of the Cu-catalyzed AAC of various ethynylstibanes (**2**) with benzylazide (**3**) under mild and simple reaction conditions and their further acylation for the preparation of fully substituted 5-acyl-1,2,3-triazoles (**6**–**17**).

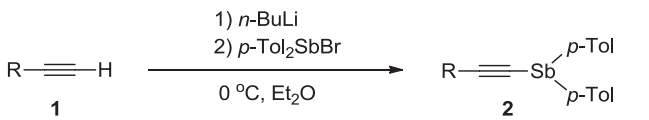
2. Results and discussion

2.1. Preparation of ethynylstibanes (2) and Cu-catalyzed azide-alkyne cycloaddition of 2 with benzyl azide (3)

The key starting compounds, ethynylstibanes (**2a-j**), were prepared by a modified method previously reported by us.[7b] Thus, treatment of terminal alkynes (**1a-j**) with *n*-BuLi, in dry diethyl ether under an argon atmosphere at 0 °C, followed by the addition of bis(4-methylphenyl)antimony bromide affords arylethynyl, vinylethynyl, alkylethynyl, and silylethynyl compounds (**2a-j**) in moderate-to-good yields (Table 1).

We have previously reported that the Cu-catalyzed [3+2] regioselective cycloaddition of ethynylstibane (**2c**) with an organic azides, in the presence of 5 mol% CuBr in THF at 60 °C and under aerobic conditions, generates 5-stibano-1,2,3-triazoles.[19] In order to investigate the efficiency and generality of this reaction, various ethynylstibanes (**2a-j**) were reacted with benzylazide (**3**) under the above optimal experimental conditions. The results are summarized in Table 2. Ethynylstibanes with functional groups such as aryl (**2a-e**), heteroaryl (**2f**, **g**), vinyl (**2h**) and alkyl (**2i**) afforded the corresponding products in good-to-excellent yields. The electronic nature (electron-rich or electron-poor) of the substituents on the phenyl group in the ethynyl moiety (**2a-e**) did not affect the outcome of the reaction. Interestingly, the ethynylstibane (**2j**) having a silyl moiety gave the expected product **4j** with the silyl group intact. This result was inconsistent with Pericàs's report,[20] where the CuAAC reaction of 1-trimethylsilyl-1-alkynes afforded 5*H*-triazoles with desilylation.

Table 1
Preparation of ethynylstibanes **2**.



Entry	R	Yield (%)[a]
1	4-Methoxyphenyl	**2a**: 75
2	4-Methylphenyl	**2b**: 70
3	Phenyl	**2c**: 82
4	4-Bromophenyl	**2d**: 68
5	4-Trifluoromethylphenyl	**2e**: 66
6	2-Thienyl	**2f**: 55
7	2-Pyridyl	**2g**: 58
8	1-Cyclohexenyl	**2h**: 52
9	*n*-Butyl	**2i**: 51
10	Trimethylsilyl	**2j**: 63

[a] Isolated yield.

The regiochemistry of 5-stibanotriazoles (**4a-j**) was elucidated by ^{1}H NMR and confirmed by single-crystal X-ray analysis. A nuclear Overhauser effect (NOE) was observed between the benzyl protons and the aromatic protons of the antimony *p*-tolyl groups. Fig. 1 shows the crystal structure of compound **4g** as a representative example of 5-stibanotriazoles (**4**) and Table 3 shows the selected bond lengths and angles. The single-crystal X-ray analysis of compound **4g** revealed the presence of an intramolecular interaction between the antimony and nitrogen atoms (Fig. 1 red line), with an Sb–N distance of 2.953(4) Å. This was consistent with 82% of the sum of the van der Waals radii (3.60 Å) of the two elements, and equivalent to 143% of the covalent bond length (2.07 Å).[21] The central antimony exhibited a pseudo trigonal bipyramidal (TBP) structure. The C(22) on the tolyl group and the nitrogen on the pyridine ring were approximately *trans* to each other with an N(4)–Sb–C(22) bond angle of 160.27(13)°. These observations indicate that the C1–Sb bond on the triazole and the C15–Sb bond on the tolyl group occupy the equatorial positions together with the lone pair of electrons on the antimony atom, and that the N···Sb intramolecular interaction and the C22–Sb bond on the tolyl group occupy the apical positions (Table 3). Moreover, a π-π interaction was observed between one tolyl group on the antimony atom and the benzyl group. These rings adopt a parallel-displaced structure, with distances of 3.755 Å between the centroids of the two phenyl rings (Fig. 1 blue line).

A possible mechanism of the present Cu-catalyzed cycloaddition is shown in Scheme 1. The catalytic cycle of this reaction would be similar to that of the reaction of 1-iodoalkynes[22] and 1-bismuthanoalkynes[14] with organic azides. As shown in cycle A, the initial step would be the generation of π-complex **A** from the reaction between the Cu(I) catalyst and ethynylstibane **2**. Coordination of complex **A** with organic azides would give complex **B**, which after cyclization *via* a vinylidene-like transition state **C**, would give 5-stibanotriazole **4**. An alternative cycle B *via* copper acetylide **D** and 5-copper triazole **E** is also possible. The reaction of **2c** without benzylazide **3** in the presence of 5 mol% CuBr in THF at 60 °C under aerobic conditions recovered **2c** at isolated yield of 82% (Scheme 2a). In this reaction, formation of ethynylbenzene was slightly observed in gas-liquid chromatography and 1,4-diphenylbuta-1,3-diyne was not detected. Moreover, the cross-over reaction of a 1: 1: 2 mixture of **2c** (0.5 mmol), **1b** (0.5 mmol), and **3** (1 mmol) under the optimized condition gave **4c** and 1-benzyl-4-*p*-tolyl-1,2,3-triazole in 79% and 28%, respectively (Scheme 2b). It seems that *p*-Tol$_2$SbBr **F** was not generated in this crossover reaction. Furthermore, organoantimony compounds such as ethynylstibane **2c** and 5-stibanotriazole **4c** seem to be obstructing generation of 1-benzyl-4-*p*-tolyl-1,2,3-triazole and/or 5-copper triazole in this reaction. Standard CuAAC of 1-ethynyl-4-methylbenzene **1b** with benzylazide **3** without ethynylstibane **2c** afforded 1-benzyl-4-*p*-tolyl-1,2,3-triazole in 88%. These results suggest that cycle A acts on predominance than cycle B. However, the detailed reaction mechanism is unclear at present. An investigation of the reaction mechanisms including regioselectivity is in progress.

2.2. Reaction of 5-stibanotriazoles with acyl chlorides

Insertion of different carbon chain at all positions of the

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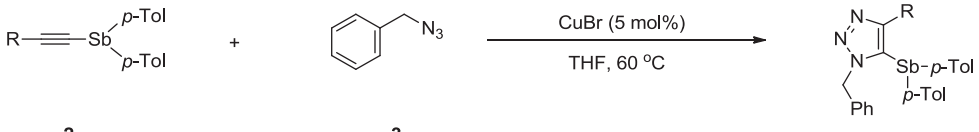
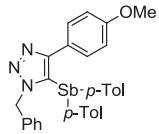
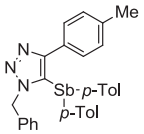
Table 2
Cu-catalyzed [3+2] cycloaddition of **2** with benzyl azide **3**.[a,b]



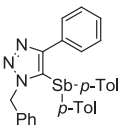
2 3 4



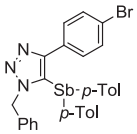
4a: 92% (6 h)



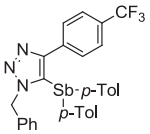
4b: 85% (6 h)



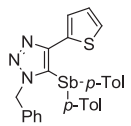
4c: 93% (6 h)



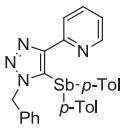
4d: 78% (9 h)



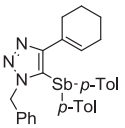
4e: 84% (9 h)



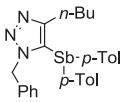
4f: 63% (9 h)



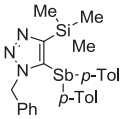
4g: 64% (3 h)



4h: 77% (7 h)



4i: 87% (2 h)



4j: 78% (5 h)

[a] **2** (0.5 mmol), **3** (0.5 mmol), CuBr (0.025 mmol).
[b] Isolated yield.

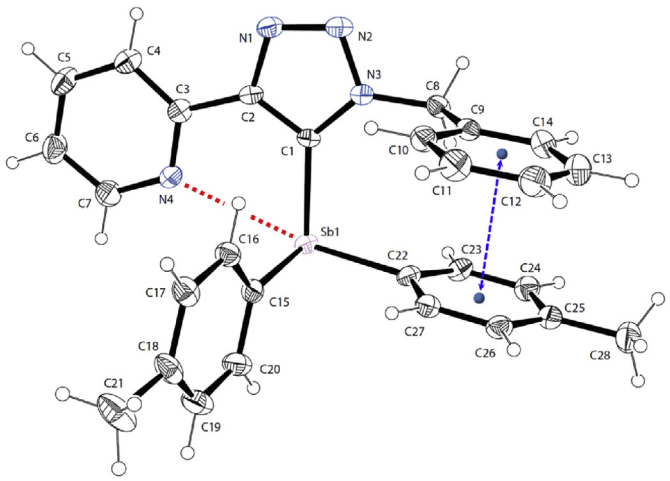


Fig. 1. Molecular structures of **4g** with 50% probability thermal ellipsoids. Red line shows hyper valent interaction and blue line shows intramolecular π-π interaction between the centroids of the two phenyl rings.

Table 3
Selected bond length (Å) and bond angles (°) for **4g**.

Bond lengths	
Sb–C1	2.170(4)
Sb–C15	2.136(4)
Sb–C22	2.165(4)
Sb–N4	2.953(4)
Bond angles	
C1–Sb–C15	96.82(15)
C1–Sb–C22	98.00(15)
C15–Sb–C22	94.32(15)
C1–Sb–N4	66.62(4)
C15–Sb–N4	76.22(13)
C22–Sb–N4	160.27(13)

aromatic heterocycles is a challenging theme. Wang and Hu reported the synthesis of 1,4,5-trisubstituted-1,2,3-triazoles such as 1-benzyl-4-aryl-5-acyl-1,2,3-triazole using the one-pot three component reaction by copper acetylide, benzylazide and acyl chloride in 2013.[23] However, one of the component, copper-acetylide was complicated to synthesize and hard to handle. Recently, we reported the synthesis of $ArBCl_2$ by a boron-induced *ipso*-deantimonation of triarylstibanes with boron halides as electrophiles, which were then transformed to arylboronates.[24] Furthermore, the iron-catalyzed reactions of tris(2-thienyl)stibanes with acyl chlorides give *ipso*-substituted acylthiophenes.[25] Therefore, we investigated whether 5-stibanotriazole (**4**) could be converted into 1,4,5-trisubstituted 5-acyl-1,2,3-triazoles by an acyl-induced deantimonation. Optimization experiments were conducted using **4c** and benzoyl chloride (**5a**) as model substrates, and the results are summarized in Table 4. The reaction of **4c** with **5a** in the presence of Lewis acids (10 mol%) such as $BF_3{\cdot}OEt_2$, $AlCl_3$, $TiCl_4$ or $FeCl_3$ in 1,2-DCE at room temperature gave complex mixtures (Table 4, entries 1–5). Because the benzoylation of 5-bismuthanotriazole with benzoyl chloride (**5a**) using *N,N*-dimethyl-4-aminopyridine (DMAP) and triethylamine (TEA) as additives is known,[14] we applied this reaction in our reaction system. Using the optimal ratio of **5a**, DMAP and TEA of 4: 1: 4 found for the benzoylation of 5-bismuthanotriazole. The 5-stibanotriazole (**4c**) was converted to the corresponding product (**6**) in 63% yield (Table 4, entry 6) after 20 h at 80 °C in DCE. We then determined the optimum amounts of **5a**, DMAP, and TEA (Table 4, entries 6–12) for our system; employing 1.2 equiv. of **5a**, 1 equiv. of DMAP, and 1.2 equiv. of TEA gave the best result (Table 4, entry 8). A possible by-product, 4-methylbenzophenone, obtainable from the acylation at the antimony 4-metylphenyl group of **5a**, was not observed. To investigate the scope of the reaction, 5-stibanotriazoles (**4a-c**, **e**, **i**) were treated with various acyl chlorides (**5**) under the standard conditions (Table 5). The reaction of **4c** with aromatic acyl chlorides (**5a-g**) afforded the corresponding 5-acyl-triazoles (**6**–**12**) in moderate to good yields (Table 5, entries 1–7). Among these, benzoyl chlorides containing electron-donating substituents on the benzene ring, such as methoxy group, exhibited lower reactivities. Unfortunately, the reaction of **4c** with aliphatic acyl chloride such as valeroyl chloride (**5h**) did not afford **13** (Table 5, entry 8). Next, we treated various 5-stibanotriazoles (**4a**, **b**, **e**, **i**) with benzoyl chloride (**5a**) under the same reaction conditions. All these

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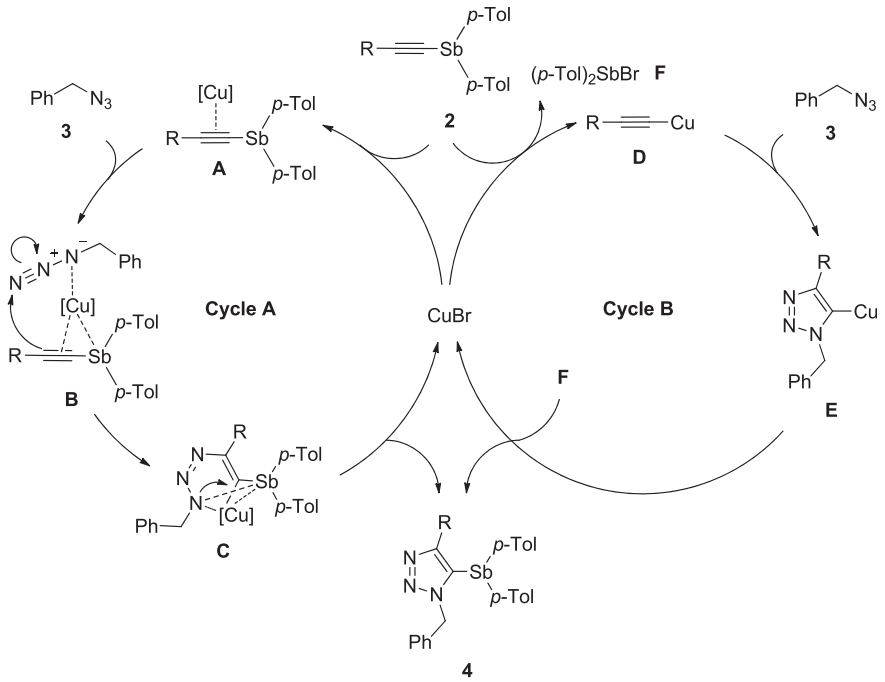
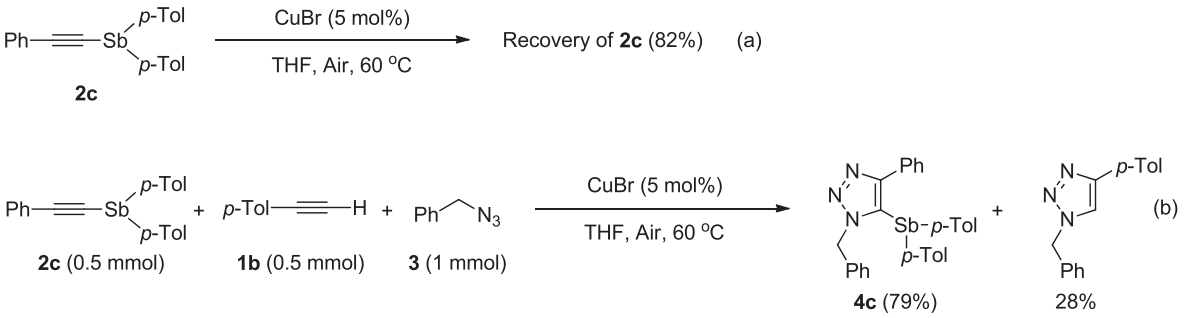
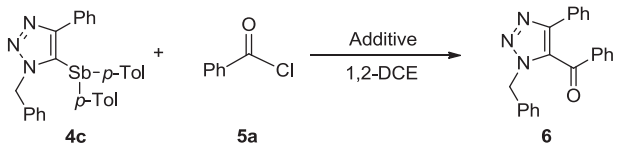


Scheme 1. Possible mechanism.



Scheme 2. Control experiments.

Table 4
Screening of acylation.[a]



Entry	5a (eq)	Additive (eq)	Base (eq)	Yield (%)
1	1.2	$BF_3{\cdot}OEt_2$ (0.1)	–	0
2	1.2	$AlCl_3$ (0.1)	–	0
3	1.2	$TiCl_4$ (0.1)	–	0
4	1.2	$ZnCl_2$ (0.1)	–	0
5	1.2	$FeCl_3$ (0.1)	–	0
6	4.0	DMAP (1)	TEA (4)	63
7	2.0	DMAP (1)	TEA (2)	73
8	1.2	DMAP (1)	TEA (1.2)	76
9	1.2	DMAP (0.3)	TEA (1.2)	38
10	1.2	DMAP (1.2)	–	35
11	1.2	–	TEA (1.2)	15
12	1.2	–	–	0

[a] Isolated yield.

reactions afforded the corresponding 5-acyl-triazoles (**14**–**17**) (Table 5, entries 9–12). 5-Stibanotriazles (**4a**, **b**, **e**, **i**) having electron-donating groups on the phenyl ring such as methoxy (**4a**), or alkyl group at the 4-position (**4i**) gave better results than those with electron-withdrawing groups (**4e**).

The reaction mechanism of the acylation of 5-stibanotriazoles (**4**) with acyl chlorides (**5**) is unclear at present. We consider that the mechanism would be similar to that of the pyridine-catalyzed acylation of alcohols and amines proposed by Zipse,[26] or the transmetallation of triarylstibanes into arylboronates,[24] and the reaction of tris(2-thienyl)stibanes with acyl chlorides, both proposed by us.[25] A possible mechanism for the reaction between 5-stibanotriazoles and acyl chlorides to form of 5-acyltriazoles is depicted in Scheme 3. In the initial step, DMAP reacts with the acyl donor to form *N*-acylpyridine (**A**). Next, the electrophilic attack of **A** onto the 5-position of triazoles would form intermediate **B**. Finally, the chloride ion attacks the antimony to generate 5-acyl-triazoles, *p*-Tol_2SbCl, and DMAP. As diphenylantimony halides are known to react with pyridine to form antimony-pyridine complexes,[27] we speculate that the eliminated DMAP and *p*-Tol_2SbCl form the complex **C**, which would account for the requirement of a full equivalent of DMAP in the reaction.

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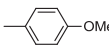
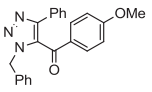
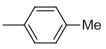
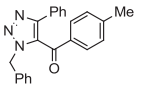
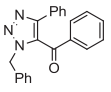
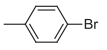
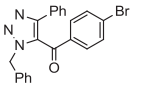
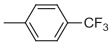
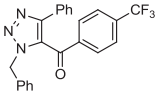
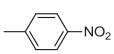
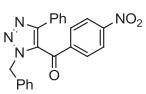
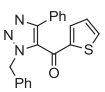
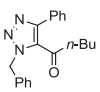
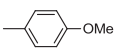
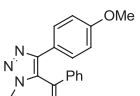
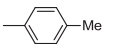
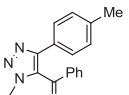
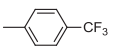
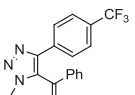
Table 5
Reaction of 5-stibanotriazole **4** with acyl chlorides **5**.[a,b]

Entry	4	R^1	5	R^2	Product	Yield (%)
1	**4c**		**5b**			**7**: 46
2	**4c**		**5c**			**8**: 64
3	**4c**		**5a**			**6**: 76
4	**4c**		**5d**			**9**: 72
5	**4c**		**5e**			**10**: 79
6	**4c**		**5f**			**11**: 77
7	**4c**		**5g**			**12**: 76
8	**4c**		**5h**	—*n*-Bu		**13**: 0
9	**4a**		**5a**			**14**: 75
10	**4b**		**5a**			**15**: 64
11	**4e**		**5a**			**16**: 55
12	**4i**	—*n*-Bu	**5a**			**17**: 76

[a] **4c** (0.5 mmol), **5** (0.6 mmol), DMAP (0.5 mmol), Et_3N (0.6 mmol).
[b] Isolated yield.

3. Conclusion

The Cu-catalyzed azide-alkyne cycloaddition of various ethynylstibanes with benzylazide, under mild reaction conditions, afforded novel trisubstituted 5-organostibano-1*H*-1,2,3-triazoles. Further, a method for the synthesis of fully substituted 5-acyl-1,2,3-triazoles was developed by employing the acyl-induced deantimonation of 5-stibanotriazoles with acyl chlorides in the presence of DMAP and TEA. Detailed mechanistic studies of these reactions and functionalization of 5-stibanotriazoles with other electrophiles are currently in progress and will be reported in the future.

4. Experimental

4.1. General information

Melting points were measured on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and reported as uncorrected values. ^{1}H NMR (TMS: δ: 0.00 or CH_2Cl_2: 5.30 ppm as an internal standard) and ^{13}C NMR ($CDCl_3$: δ: 77.00 ppm as an internal standard) spectra were recorded on JEOL JNM-AL400 (400 MHz and 100 MHz) spectrometers in $CDCl_3$. Mass spectra were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA). 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. Chromatographic separations were carried out using Silica Gel 60N (Kanto Chemical Co., Inc.) under the solvent system stated. Thin-layer chromatography (TLC) was performed using Merck Pre-coated TLC plates (silica gel 60 F254). Each reagents were purchased from Sigma-Aldrich Japan, Wako Pure Chemical Industries and Tokyo Chemical Industry Co., Ltd.

4.2. Preparation of ethynylstibanes (*2*)

An diethyl ether solution of di-*p*-tolylantimony(III) bromide (15 mmol, 15 mL), synthesized from redistribution of tritolylstibane (4.0 g, 10 mmol, 2 eq.) and tribromoantimony (1.8 g, 5 mmol) was added dropwise at 0 °C to an diethyl ether solution (10 mL) of lithium acetylide, prepared from the appropriate acetylene (10 mmol, 2 eq.) and *n*-butyllithium (1.54 M solution in hexane, 6.5 mL, 10 mmol) under argon. After stirring the mixture at the same temperature for 2 h, the reaction mixture was diluted with diethyl ether (50 mL) and quenched with water. The reaction mixture was separated and the aqueous layer was extracted with diethyl ether (50 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexane/CH_2Cl_2) or recrystallization.

4.2.1. 4-Methoxyphenylethynyldi-p-tolylstibane (*2a*)

Colorless needle (3.26 g, 75% yield), mp 79–80 °C (from Et_2O-MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (4H, d, J = 7.8 Hz), 7.43 (2H, d, J = 6.7 Hz), 7.15 (4H, d, J = 7.8 Hz), 6.82 (2H, d, J = 7.8 Hz), 3.81 (3H, s), 2.30 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7 (s), 138.6 (s), 135.4 (d), 134.5 (s), 133.4 (d), 129.7 (d), 115.5 (s), 113.8 (d), 111.0 (s), 84.1 (s), 55.2 (q), 21.3 (q). FTIR (KBr) ν: 2135 cm^{-1}. LRMS (EI) *m/z*: 434 (M^+, 90), 313 (40), 222 (100), 212 (70), 91 (40). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{21}OSb$: 434.0631. Found: 434.0640.

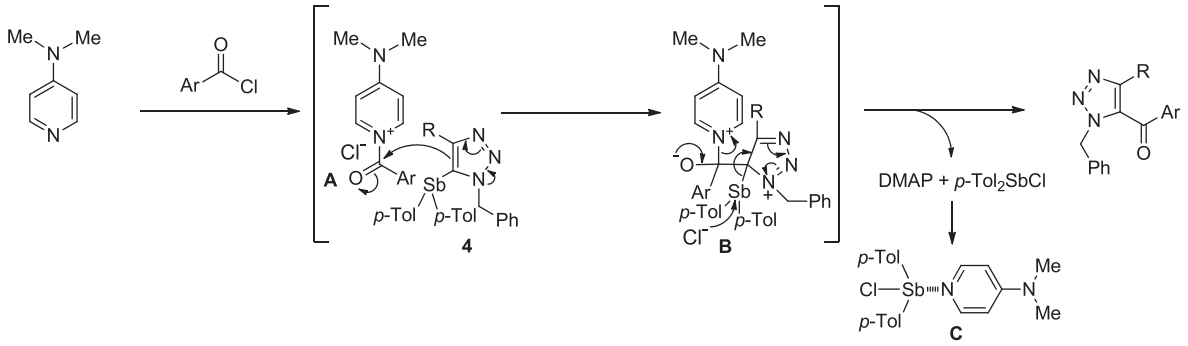
4.2.2. 4-Tolylethynyldi-p-tolylstibane (*2b*)

Colorless needle (2.93 g, 70% yield), mp 85–87 °C (from Et_2O-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (4H, d, J = 7.8 Hz), 7.40 (2H, d, J = 7.8 Hz), 7.16 (4H, d, J = 7.3 Hz), 7.11 (2H, d, J = 7.8 Hz), 2.35 (3H, s), 2.33 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6 (s), 135.5 (d), 134.5 (s), 131.9 (d), 129.7 (d) 128.9 (d), 120.3 (s), 111.2 (s), 85.1 (s), 21.5 (q), 21.3 (q). FTIR (KBr) ν: 2129 cm^{-1}. LRMS (EI) *m/z*: 418 (M^+, 100), 297 (68), 212 (96), 206 (91). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{21}Sb$: 418.0681. Found: 418.0685.

4.2.3. Phenylethynyl-di-p-tolylstibine (*2c*)[7b]

Colorless needle (3.32 g, 82% yield), mp 58–61 °C (Et_2O-MeOH).

Please cite this article in press as: Yamada M, et al., Synthesis of 5-organostibano-1*H*-1,2,3-triazoles by Cu-catalyzed azide-alkyne cycloaddition and their application in the acyl-induced deantimonation for the preparation of fully substituted 5-acyl-1,2,3-triazoles, Tetrahedron (2017), http://dx.doi.org/10.1016/j.tet.2017.03.046



Scheme 3. Possible mechanism.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (4H, d, J = 7.8 Hz), 7.52–7.48 (2H, m), 7.31–7.28 (3H, m), 7.16 (4H, d, J = 7.8 Hz), 2.32 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7 (s), 135.5 (d), 134.4 (s), 132.0 (d), 129.8 (d), 128.4 (d), 128.2 (d), 123.4 (s), 110.9 (s), 86.0 (s), 21.4 (q). FTIR (KBr) ν: 2363 cm^{-1}. LRMS (EI) *m/z*: 405 ([M+H]$^+$, 75), 327 (10), 303 (45), 212 (100), 77 (20). HRMS: *m/z* [M]$^+$ calcd for $C_{22}H_{19}Sb$: 404.0525. Found: 404.0530.

4.2.4. 4-Bromophenylethynyldi-p-tolylstibane (**2d**)

Colorless needle (3.29 g, 68% yield), mp 121–123 °C (from CH_2Cl_2-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (4H, d, J = 8.3 Hz), 7.42 (2H, d, J = 8.8 Hz) 7.34 (2H, d, J = 8.3 Hz), 7.16 (4H, d, J = 7.3 Hz), 2.33 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8 (s), 135.5 (d), 134.2 (s), 133.4 (d), 131.5 (d), 129.8 (d), 122.7 (s), 122.3 (s), 109.6 (s), 87.6 (s), 21.4 (q). FTIR (KBr) ν: 2135 cm^{-1}. LRMS (EI) *m/z*: 484 ([M+H+2]$^+$, 80), 282 (68), 212 (100), 182 (72). HRMS: *m/z* [M]$^+$ calcd for $C_{22}H_{18}BrSb$: 481.9630. Found: 481.9627.

4.2.5. (4-Trifluoromethylphenylethynyl)(di-p-tolyl)stibane (**2e**)

Colorless needle (3.12 g, 66% yield), mp 72–74 °C (from Et_2O-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60–7.55 (8H, m), 7.18 (4H, d, J = 7.8 Hz), 2.34 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.9 (s), 135.5 (d), 134.0 (s), 132.2 (d), 130.1 (s, $^2J_{C,F}$ = 33 Hz), 129.9 (d), 127.1 (s), 125.2 (d, $^3J_{C,F}$ = 4 Hz), 123.9 (s, $^1J_{C,F}$ = 271 Hz), 109.1 (s), 89.5 (s), 21.4 (q). FTIR (KBr) ν: 2134 cm^{-1}. LRMS (EI) *m/z*: 472 (M$^+$, 36), 241 (100), 212 (60), 182 (38). HRMS: *m/z* [M]$^+$ calcd for $C_{23}H_{18}F_3Sb$: 472.0399. Found: 472.0403.

4.2.6. 2-Thienylethynyldi-p-tolylstibane (**2f**)

Colorless needle (2.26 g, 55% yield), mp 75–77 °C (from Et_2O-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (4H, d, J = 8.3 Hz), 7.25 (1H, dd, J = 3.4, 1.5 Hz), 7.23 (1H, dd, J = 5.4, 1.5 Hz), 7.17 (4H, d, J = 7.3 Hz), 6.96 (1H, dd, J = 5.4, 3.4 Hz), 2.33 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8 (s), 135.5 (d), 134.2 (s), 132.5 (d), 129.8 (d) 127.2 (d), 126.8 (d), 123.5 (s), 103.3 (s), 90.8 (s), 21.4 (q). FTIR (KBr) ν: 2125 cm^{-1}. LRMS (EI) *m/z*: 410 (M$^+$, 50), 257 (62), 212 (100), 198 (85). HRMS: *m/z* [M]$^+$ calcd for $C_{20}H_{17}SSb$: 410.0089. Found: 410.0092.

4.2.7. 2-Pyridylethynyldi-p-tolylstibane (**2g**)

Colorless needle (2.36 g, 58% yield), mp 93–95 °C (from Et_2O-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (1H, d, J = 4.4 Hz), 7.61–7.58 (5H, m), 7.45 (1H, d, J = 7.3 Hz), 7.20–7.15 (5H, m), 2.32 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9 (d), 143.1 (s), 138.8 (s), 136.0 (d), 135.6 (d) 133.8 (s), 129.8 (d), 127.4 (d), 122.9 (d), 109.6 (s), 87.2 (s), 21.3 (q). FTIR (KBr) ν: 2312 cm^{-1}. LRMS (EI) *m/z*: 405 (M$^+$, 100), 284 (85), 212 (89), 182 (88). HRMS: *m/z* [M]$^+$ calcd for $C_{21}H_{18}NSb$: 405.0477. Found: 405.0471.

4.2.8. 1-Cyclohexenylethynyldi-p-tolylstibane (**2h**)

Colorless needle (2.13 g, 52% yield), mp 55–57 °C (from Et_2O-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (4H, d, J = 7.8 Hz), 7.14 (4H, d, J = 7.8 Hz), 6.21 (1H, s), 2.32 (6H, s), 2.19–2.17 (2H, m), 2.14–2.11 (2H, m), 1.67–1.53 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4 (s), 135.9 (d), 135.4 (d), 134.7 (s), 129.7 (d) 121.1 (s), 113.3 (s), 82.4 (s), 29.3 (t), 25.6 (t), 22.2 (t), 21.4 (t), 21.3 (q). FTIR (KBr) ν: 2129 cm^{-1}. MS (EI) *m/z*: 408 (M$^+$, 32), 287 (76), 212 (77), 83 (100). HRMS: *m/z* [M]$^+$ calcd for $C_{22}H_{23}Sb$: 408.0838. Found: 408.0841.

4.2.9. n-Butylethynyldi-p-tolylstibane (**2i**)

Colorless oil (1.96 g, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (4H, d, J = 7.8 Hz), 7.14 (4H, d, J = 7.8 Hz), 2.40 (2H, t, J = 6.8 Hz), 2.33 (6H, s), 1.58–1.52 (2H, m), 1.50–1.39 (2H, m), 0.94 (3H, t, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4 (s), 135.3 (d), 134.8 (d), 130.1 (s), 129.2 (s) 113.2 (s), 31.0 (t), 21.9 (t), 21.3 (q), 20.1 (t), 13.6 (q). FTIR (neat) ν: 2150 cm^{-1}. LRMS (EI) *m/z*: 384 (M$^+$, 76), 212 (100), 182 (78), 91 (65). HRMS: *m/z* [M]$^+$ calcd for $C_{20}H_{23}Sb$: 384.0838. Found: 384.0834.

4.2.10. (Trimethylsilylethynyl)(di-p-tolyl)stibane (**2j**)

Colorless needle (2.53 g, 63% yield), mp 87–89 °C (from Et_2O-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (4H, d, J = 7.8 Hz), 7.15 (4H, d, J = 7.8 Hz), 2.33 (6H, s), 0.22 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6 (s), 135.4 (d), 134.3 (s), 129.7 (d), 119.8 (s) 104.6 (s), 21.3 (q), 0.02 (q). FTIR (KBr) ν: 2079 cm^{-1}. LRMS (EI) *m/z*: 400 (M$^+$, 95), 249 (62), 212 (100), 173 (96). HRMS: *m/z* [M]$^+$ calcd for $C_{19}H_{23}SbSi$: 400.0607. Found: 400.0611.

4.3. Preparation of 5-stibanotriazoles (**4**)

CuBr (3.6 mg, 0.025 mmol, 5 mol%), ethynylstibane (**2**: 0.5 mmol), and benzyl azide (**3**: 66.6 mg, 0.5 mmol) were dissolved in THF (4 mL). The reaction mixture was stirred for at 60 °C. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (10 mL). The phases were separated and aqueous layer was extracted with CH_2Cl_2 (30 mL x 2). The combined organic layer was washed 5% aqueous ammonia and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexane/AcOEt).

4.3.1. 1-Benzyl-4-(4-methoxy)-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4a**)

Colorless oil (261 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (2H, d, J = 8.7 Hz), 7.23–7.12 (7H, m), 6.98 (4H, d, J = 8.7 Hz), 6.75 (2H, d, J = 6.8 Hz), 6.71 (2H, d, J = 8.2 Hz), 5.31 (2H, s), 3.73 (3H, s), 2.28 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4 (s), 156.4 (s), 139.2 (s), 135.8 (d), 135.7 (s), 130.8 (s), 130.3 (d), 129.9 (d), 128.3 (d), 127.6 (d), 127.1 (d), 126.3 (s), 124.5 (s), 113.5 (s), 55.2 (q), 54.0 (t),

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21.3 (q). LRMS (FAB) *m/z*: 568 ([M+H]$^+$, 5), 309 (15), 307 (10), 195 (10), 135 (80), 119 (100), 85 (85), 79 (20), 47 (15). HRMS: *m/z* [M]$^+$ calcd for $C_{30}H_{28}N_3OSb$: 567.1271. Found: 567.1269.

4.3.2. 1-Benzyl-4-(4-tolyl)-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4b**)

Colorless plate (235 mg, 85% yield), mp 86–88 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (2H, d, J = 7.8 Hz), 7.19–7.13 (7H, m), 7.04–6.99 (6H, m), 6.74 (2H, d, J = 7.3 Hz), 5.30 (2H, s), 2.30 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.7 (s), 139.2 (s), 137.6 (s), 135.8 (d), 135.7 (s), 130.8 (s), 129.9 (d), 129.1 (s), 128.9 (d), 128.7 (d), 128.3 (d), 127.6 (d), 127.1 (d), 126.5 (s), 53.9 (t), 21.3 (q), 21.2 (q). LRMS (FAB) *m/z*: 552 ([M+H]$^+$, 100), 220 (22), 91 (24). HRMS: *m/z* [M]$^+$ calcd for $C_{30}H_{28}N_3Sb$: 551.1321. Found: 551.1325.

4.3.3. 1-Benzyl-4-phenyl-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4c**)[19]

Colorless plate (250 mg, 93% yield), mp 128–129 °C (from *n*-hexane-Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (2H, m), 7.23–7.10 (10H, m), 7.01 (4H, d, J = 8.3 Hz), 6.75 (2H, d, J = 7.3 Hz), 5.32 (2H, s), 2.29 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5 (s), 139.1 (s), 135.7 (d), 135.6 (s), 131.9 (s), 130.7 (s), 129.9 (d), 129.0 (d), 128.3 (d), 127.9 (d), 127.7 (d), 127.6 (d), 127.0 (d), 126.8 (s), 53.9 (t), 21.3 (q). LRMS (FAB) *m/z*: 538 ([M+H]$^+$, 40), 303 (12), 235 (25), 206 (100), 182 (82), 149 (50), 116 (70), 91 (40), 89 (25), 65 (20). HRMS: *m/z* [M]$^+$ calcd for $C_{29}H_{26}N_3Sb$: 537.1165. Found: 537.1157.

4.3.4. 1-Benzyl-4-(4-bromophenyl)-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4d**)

Colorless plate (241 mg, 78% yield), mp 122–124 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.17 (7H, m), 7.09 (4H, d, J = 7.8 Hz), 6.99 (4H, d, J = 8.3 Hz), 6.83 (2H, d, J = 7.8 Hz), 5.40 (2H, s), 2.31 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2 (s), 139.4 (s), 135.7 (d), 135.3 (s), 130.83 (d), 130.80 (s), 130.5 (d), 130.4 (s), 130.0 (d), 128.5 (d), 127.9 (d), 127.3 (d), 126.9 (s), 121.9 (s), 54.2 (t), 21.3 (q). LRMS (FAB) *m/z*: 618 ([M+H+2]$^+$, 100), 303 (22), 181 (15), 91 (57). HRMS: *m/z* [M]$^+$ calcd for $C_{29}H_{25}BrN_3Sb$: 615.0270. Found: 615.0264.

4.3.5. 1-Benzyl-4-(4-trifluoromethylphenyl)-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4e**)

Colorless needle (255 mg, 84% yield), mp 132–134 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (2H, d, J = 8.3 Hz), 7.30 (2H, d, J = 8.3 Hz), 7.24–7.20 (3H, m), 7.09 (4H, d, J = 7.8 Hz), 6.98 (4H, d, J = 7.3 Hz), 6.92 (2H, d, J = 7.3 Hz), 5.45 (2H, s), 2.28 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.9 (s), 139.5 (s), 135.7 (d), 135.4 (s), 135.3 (s), 130.4 (s), 130.0 (d), 129.4 (s, $^2J_{C,F}$ = 28 Hz), 129.2 (d), 128.6 (d), 128.1 (d), 127.6 (s), 127.5 (d), 124.5, (d, $^3J_{C,F}$ = 4.1 Hz), 124.1 (s, $^1J_{C,F}$ = 272 Hz), 54.4 (t), 21.2 (q). LRMS (FAB) *m/z*: 606 ([M+H]$^+$, 55), 303 (18), 181 (19), 91 (100). HRMS: *m/z* [M]$^+$ calcd for $C_{30}H_{25}F_3N_3Sb$: 605.1039. Found: 605.1042.

4.3.6. 1-Benzyl-4-(2-thienyl)-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4f**)

Colorless plate (172 mg, 63% yield), mp 128–130 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (1H, dd, J = 5.4, 1.4 Hz), 7.17–7.11 (7H, m), 7.06–7.02 (5H, m), 6.86 (1H, dd, J = 5.4, 3.4 Hz), 6.69 (2H, dd, J = 7.4, 1.4 Hz), 5.29 (2H, s), 2.30 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5 (s), 139.3 (s), 135.8 (d), 135.7 (s), 133.8 (s), 130.7 (s), 130.1 (d), 128.3 (d), 127.6 (d), 127.1 (d), 126.94 (d), 126.87 (d), 126.86 (s), 125.8 (d), 53.9 (t), 21.3 (q). LRMS (FAB) *m/z*: 544 ([M+H]$^+$, 100), 303 (25), 212 (44), 91 (96). HRMS: *m/z* [M]$^+$ calcd for $C_{27}H_{24}N_3SSb$: 543.0729. Found: 543.0735.

4.3.7. 1-Benzyl-4-(2-pyridyl) -5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4g**)

Colorless plate (173 mg, 64% yield), mp 166–169 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25–8.23 (2H, m), 7.69 (1H, td, J = 7.3, 2.0 Hz), 7.24–7.11 (7H, m), 7.05–7.02 (1H, ddd, J = 7.6, 4.9, 1.0 Hz), 6.98 (4H, d, J = 7.8 Hz), 6.54 (2H, d, J = 6.3 Hz), 5.13 (2H, s), 2.28 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2 (s), 150.6 (s), 147.4 (d), 138.4 (s), 136.7 (d), 136.4 (s), 136.2 (s), 136.0 (d), 131.1 (s), 129.6 (d), 128.2 (d), 127.3 (d), 126.3 (d), 122.2 (d), 119.9 (d), 53.1 (t), 21.3 (q). LRMS (FAB) *m/z*: 539 ([M+H]$^+$, 20), 449 (76), 447 (100), 207 (32), 91 (77). HRMS: *m/z* [M]$^+$ calcd for $C_{28}H_{25}N_4Sb$: 538.1117. Found: 538.1121.

4.3.8. 1-Benzyl-4-(1-cyclohexenyl)-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4h**)

Colorless plate (209 mg, 77% yield), mp 126–128 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.16 (7H, m), 7.07 (4H, d, J = 7.3 Hz), 6.72 (2H, d, J = 6.8 Hz), 5.63–5.59 (1H, m), 5.23 (2H, s), 2.36–2.34 (2H, m), 2.32 (6H, s), 1.84–1.80 (2H, m), 1.55–1.50 (2H, m), 1.37–1.31 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5 (s), 139.1 (s), 135.8 (d), 135.7 (s), 131.8 (s), 129.81 (d), 129.80 (s), 129.78 (d), 128.3 (d), 127.6 (d), 127.1 (d), 126.0 (s), 53.8 (t), 28.5 (t), 25.2 (t), 22.4 (t), 21.5 (t), 21.3 (q). LRMS (FAB) *m/z*: 542 ([M+H]$^+$, 95), 91 (100), 85 (65). HRMS: *m/z* [M]$^+$ calcd for $C_{29}H_{30}N_3Sb$: 541.1478. Found: 541.1471.

4.3.9. 1-Benzyl-4-butyl-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4i**)

Colorless needle (226 mg, 87% yield), mp 73–74 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19–7.15 (7H, m), 7.10 (4H, d, J = 7.3 Hz), 6.93–6.91 (2H, m), 5.50 (2H, s), 2.33 (6H, s), 2.25 (2H, t, J = 6.8 Hz), 1.29 (2H, sext, J = 7.8 Hz), 1.01 (2H, quin, J = 7.8 Hz), 0.70 (3H, t, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5 (s), 139.2 (s), 135.8 (d), 135.7(s), 130.2 (s), 129.9 (d), 128.5 (d), 127.8 (d), 127.2 (d), 126.3 (s), 54.2 (t), 32.3 (t), 26.3 (t), 22.5 (t), 21.3 (q), 13.6 (q). LRMS (FAB) *m/z*: 518 ([M+H]$^+$, 100), 119 (25), 91 (41), 85 (29). HRMS: *m/z* [M]$^+$ calcd for $C_{27}H_{30}N_3Sb$: 517.1478. Found: 517.1469.

4.3.10. 1-Benzyl-4-trimethylsilyl-5-(di-p-tolylstibano)-1H-1,2,3-triazole (**4j**)

Colorless plate (208 mg, 78% yield), mp 92–95 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (4H, d, J = 7.8 Hz), 7.14–7.04 (7H, m), 6.50 (2H, d, J = 8.3 Hz), 5.18 (2H, s), 2.33 (6H, s), 0.40 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.9 (s), 139.3 (s), 135.8 (s), 135.6 (d), 134.9 (s), 130.5 (s), 130.1 (d), 127.9 (d), 127.1 (d), 126.7 (d), 53.0 (t), 21.3 (q), 0.24 (q). LRMS (FAB) *m/z*: 536 (98), 534 ([M+H]$^+$, 100), 91 (90), 73 (25). HRMS: *m/z* [M]$^+$ calcd for $C_{26}H_{30}N_3SbSi$: 533.1247. Found: 533.1252.

4.4. Preparation of triazolyl ketone (**6**–**12**, **14**–**17**)

5-Stibanotriazole (**4**) (0.5 mmol), 4-dimethylaminopyridine (61.1 mg, 0.5 mmol, 1 eq.), acyl chloride (**5**) (0.6 mmol, 1.2 eq.), triethylamine (83.2 μL, 0.6 mmol, 1.2 eq.) were dissolved in 1,2-DCE (5 mL) and stirred at 80 °C under argon. After 20 h, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and saturated $NaHCO_3$ aqueous solution (5 mL). The phases were separated and aqueous layer was extracted with CH_2Cl_2 (30 mL x 2). The combined organic layers were washed saturated $NaHCO_3$ aqueous solution (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

4.4.1. (1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(phenyl) methanone (**6**)[23]

Colorless needle (129 mg, 76% yield), mp 96–97 °C (from *n*-

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hexane-AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50–7.48 (2H, m), 7.43–7.38 (3H, m), 7.25–7.15 (10H, m), 5.75 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.7 (s), 148.7 (s), 135.7 (s), 134.6 (s), 134.1 × 2 (d), 130.2 (s), 129.6 × 2 (s, d), 128.7 (d), 128.5 (d), 128.4 (d), 128.33 (d), 128.30 (d), 128.1 (d), 53.4 (t). FTIR (KBr) ν: 1655 cm^{-1}. LRMS (EI) *m/z*:339 (M^+, 98), 310 (18), 220 (31), 206 (28), 178 (12), 165 (15), 105 (75), 91 (100), 77 (66), 65 (47). HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{17}N_3O$: 339.1372. Found: 339.1380.

4.4.2. (1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(4-methoxyphenyl) methanone (**7**)

Colorless prism (85 mg, 46% yield), mp 84–86 °C (from *n*-hexane-AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.45 (4H, m), 7.24–7.15 (8H, m), 6.66 (2H, d, J = 8.8 Hz), 5.70 (2H, s), 3.76 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.1 (s), 164.4 (s), 147.7 (s), 134.6 (s), 132.2 (d), 130.6 (s), 129.7 (s), 128.7 × 2 (d, s), 128.41 (d), 128.38 (d), 128.36 (d), 128.2 (d), 128.1 (d), 113.8 (d), 55.5 (q), 53.2 (t). FTIR (KBr) ν: 1641 cm^{-1}. LRMS (EI) *m/z*: 369 (M^+, 25), 343 (70), 152 (50), 135 (86), 91 (100), 83 (46), 61 (47). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{19}N_3O_2$: 369.1477. Found: 369.1468.

4.4.3. (1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(p-tolyl) methanone (**8**)[23]

Colorless plate (113 mg, 64% yield), mp 57–58 °C (from *n*-hexane-EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.42 (2H, m), 7.41 (2H, d, J = 7.8 Hz), 7.23–7.14 (8H, m), 6.98 (2H, d, J = 7.8 Hz), 5.71 (2H, s), 2.27 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.4 (s), 148.1 (s), 145.4 (s), 134.6 (s), 133.2 (s), 130.5 (s), 129.8 (d), 129.7 (s), 129.2 (d), 128.7 (d), 128.38 (d), 128.37 (d), 128.3 (d), 128.2 (d), 128.1 (d), 53.3 (t), 21.7 (q). FTIR (KBr) ν: 1657 cm^{-1}. LRMS (EI) *m/z*: 353 (M^+, 42), 149 (25), 119 (65), 91 (100), 83 (95), 65 (17). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{19}N_3O$: 353.1528. Found: 353.1530.

4.4.4. (1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(4-bromophenyl) methanone (**9**)[23]

Colorless prism (151 mg, 72% yield), mp 152–153 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.38 (2H, m), 7.34–7.29 (4H, m), 7.23–7.17 (8H, m), 5.75 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.6 (s), 148.7 (s), 134.5 (s), 134.4 (s), 131.8 (d), 130.9 (d), 129.8 (s), 129.5 (s), 129.4 (s), 128.8 (d), 128.52 (d), 128.47 (d), 128.3 (d), 128.1 (d),53.4 (t). FTIR (KBr) ν: 1661 cm^{-1}. LRMS (EI) *m/z*: 419($[M+2]^+$, 28), 417 (M^+, 28), 183 (30), 91 (100), 65 (12). HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{16}BrN_3O$: 417.0477. Found: 417.0460.

4.4.5. (1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)[4-(trifluoromethyl)phenyl]methanone (**10**)

Colorless prism (161 mg, 79% yield), mp 79–80 °C (from *n*-hexane-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (2H, d, J = 8.3 Hz), 7.40 (2H, d, J = 8.3 Hz), 7.34 (2H, dd, J = 7.8 Hz, 2.0 Hz), 7.26–7.13 (8H, m), 5.80 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.5 (s), 149.4 (s), 138.4 (s), 135.1 (s), 134.7 (s), 134.5 (s), 129.7 (d), 129.5 (s, $^2J_{C,F}$ = 37.2 Hz), 128.9 (d), 128.8 (d), 128.6 (d), 128.5 (d), 128.4 (d), 128.1 (d), 125.3 (d, $^3J_{C,F}$ = 3.3 Hz), 123.1 (s, $^1J_{C,F}$ = 272.3 Hz), 53.6 (t). FTIR (KBr) ν: 1668 cm^{-1}. LRMS (EI) *m/z*: 407 (M^+, 64), 378 (16), 288 (25), 173 (62), 145 (50), 91 (100), 65 (21). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{16}F_3N_3O$: 407.1245. Found: 407.1238.

4.4.6. (1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(4-nitrophenyl) methanone (**11**)[23]

Yellow plate (148 mg, 77% yield), mp 121–122 °C (from MeOH-AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (1H, d, J = 8.8 Hz), 8.24 (1H, d, J = 8.8 Hz), 7.96 (2H, d, J = 8.1 Hz), 7.33 (2H, d, J = 7.6 Hz), 7.26–7.10 (6H, m), 7.57 (2H, d, J = 8.1 Hz), 5.75 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.7 (s), 150.3 (s), 149.8 (s) 140.2 (s), 134.5 (s), 130.3 (d), 129.3 (s), 129.1 (d), 129.0 (s), 128.9 (d), 128.7 (d), 128.6 (d), 128.5 (d), 128.1 (d), 123.4 (d), 53.7 (t). FTIR (KBr) ν: 1666 cm^{-1}. LRMS (EI) *m/z*: 384 (M^+, 90), 355 (30), 265 (40), 150 (45), 120 (45), 91 (100), 65 (36). HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{16}N_4O_3$: 384.1222. Found: 384.1230.

4.4.7. (1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(2-thienyl) methanone (**12**)

Colorless plate (131 mg, 76% yield), mp 121–122 °C (from *n*-hexane-AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (1H, dd, J = 4.9 Hz, 1.0 Hz), 7.57–7.53 (2H, m), 7.30–7.16 (8H, m), 7.01 (1H, dd, J = 3.9 Hz, 1.0 Hz), 6.75 (1H, dd, J = 4.9 Hz, 3.9 Hz), 5.71 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.2 (s), 147.6 (s), 142.3 (s), 136.4 (d), 136.1 (d), 134.4 (s), 130.3 (s), 129.6 (s), 128.7 (d), 128.6 (d), 128.5 (d), 128.4 (d), 128.3 (d), 128.2 (d), 128.1 (d), 53.2 (t). FTIR (KBr) ν: 1630 cm^{-1}. LRMS (EI) *m/z*: 345 (M^+, 20), 149 (10), 111 (20), 91 (100). HRMS: *m/z* $[M]^+$ calcd for $C_{20}H_{15}N_3OS$: 345.0936. Found: 345.0942.

4.4.8. [1-Benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazol-5-yl](phenyl)methanone (**14**)[23]

Yellow plate (139 mg, 75% yield), mp 81–82 °C (from *n*-hexane-AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (2H, dd, J = 1.2, 8.8 Hz), 7.41 (1H, t, J = 7.6 Hz), 7.34 (2H, d, J = 8.8 Hz), 7.25–7.15 (7H, m), 6.69 (2H, d, J = 8.8 Hz), 5.74 (2H, s), 3.72 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.8 (s), 159.7 (s), 148.5 (s), 135.8 (s), 134.8 (s), 134.0 (d), 129.7 (d), 129.64 (s), 129.58 (d), 128.7 (d), 128.5 (d), 128.4 (d), 128.1 (d), 122.1 (s), 113.8 (d), 55.2 (q), 53.4 (t). FTIR (KBr) ν: 1647 cm^{-1}. LRMS (EI) *m/z*: 369 (M^+, 95), 105 (100), 91 (75), 65 (40). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{19}N_3O_2$: 369.1477. Found: 369.1469.

4.4.9. [1-Benzyl-4-(p-tolyl)-1H-1,2,3-triazol-5-yl](phenyl) methanone (**15**)[23]

Yellow oil (113 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (2H, d, J = 7.8 Hz), 7.41 (1H, t, J = 7.8 Hz), 7.30 (2H, d, J = 8.3 Hz), 7.24–7.14 (7H, m), 6.97 (2H, d, J = 8.3 Hz), 5.73 (2H, s), 2.24 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.9 (s), 148.6 (s), 138.4 (s), 135.7 (s), 134.7 (s), 134.0 (d), 130.0 (s), 129.6 (d), 129.0 (d), 128.7 (d), 128.43 (d), 128.38 (d), 128.2 (d), 128.1 (d), 126.7 (s), 53.3 (t), 21.2 (q). FTIR (neat) ν: 1645 cm^{-1}. LRMS (EI) *m/z*: 353 (M^+, 95), 324 (20), 279 (70), 234 (45), 167 (75), 149 (90), 105 (85), 91 (100), 77 (65), 57 (50). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{19}N_3O$: 353.1528. Found: 353.1533.

4.4.10. {1-Benzyl-4-[4-(trifluoromethyl)phenyl]-1H-1,2,3-triazol-5-yl}(phenyl)methanone (**16**)

Yellow oil (112 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (2H, d, J = 8.2 Hz), 7.50–7.41 (5H, m), 7.25–7.16 (7H, m), 5.74 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.4 (s), 146.9 (s), 135.5 (s), 134.5 (d), 134.3 (s), 133.1 (s), 131.0 (s), 130.3 (s, $^2J_{C,F}$ = 33.1 Hz), 129.5 (d), 128.8 (d), 128.7 (d), 128.6 (d), 128.3 (d), 128.2 (d), 125.3 (d, $^3J_{C,F}$ = 3.7 Hz), 123.8 (s, $^1J_{C,F}$ = 272.3 Hz), 53.5 (t). FTIR (neat) ν: 1655 cm^{-1}. LRMS (EI) *m/z*: 407 (M^+, 25), 379 (70), 378 (15), 274 (20), 105 (70), 91 (100), 77 (40), 65 (20). HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{16}F_3N_3O$: 407.1245. Found: 407.1250.

4.4.11. (1-Benzyl-4-butyl-1H-1,2,3-triazol-5-yl)(phenyl)methanone (**17**)[23]

Colorless oil (121 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64–7.54 (3H, m), 7.44 (2H, t, J = 7.3 Hz), 7.26–7.16 (5H, m), 5.74 (2H, s), 2.42 (2H, t, J = 7.8 Hz), 1.50 (2H, quin, J = 7.8 Hz), 1.13 (2H, sext, J = 7.3 Hz), 0.73 (3H, t, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.4 (s), 150.3 (s), 137.2 (s), 135.1 (s), 133.9 (d), 130.9 (s), 129.1 (d), 128.8 (d), 128.7 (d), 128.3 (d), 128.0 (d), 53.3 (t), 31.4 (t), 25.8 (t), 22.2 (t), 13.5 (q). FTIR (neat) ν: 1655 cm^{-1}. LRMS (EI) *m/z*: 319 (M^+, 75), 105 (80), 91 (100), 65 (30). HRMS: *m/z* $[M]^+$ calcd for $C_{20}H_{21}N_3O$: 319.1685. Found: 319.1679.

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4.5. Single crystal X-ray diffraction experiment data of **4g**

The colourless prismatic crystal (0.060 × 0.060 × 0.020 mm^3), which was obtained from dichloromethane/*n*-hexane, 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 D8VENTURE system (PHOTON-100 CMOS detector, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[28] Structure solution and refinement were performed by using SHELXT-2014/5[29] and SHELXL-2016/4[30].

$C_{28}H_{25}N_4Sb$, *Mr* = 539.27; triclinic, space group *P*-1, *Z* = 2, D_{calc} = 1.463 g cm^{-3}, *a* = 9.1666(7), *b* = 10.1360(8), *c* = 14.1366(11) Å, α = 108.389(3), β = 98.152(3), γ = 94.042(3)°, *V* = 1224.49(17) $Å^3$, 15731 observed and 4422 independent [$I > 2\sigma(I)$] reflections, 300 parameters, final R_1 = 0.0408, wR_2 = 0.0940, *S* = 1.071 [$I > 2\sigma(I)$]. CCDC 1527951.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 137, 23 and 43) with U_{iso} values constrained to 1.2 or 1.5 U_{eq} of their parent atoms.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2017.03.046.

References

1. (a) Matano Y. Antimony and bismuth in organic synthesis. In: Yamamoto H, Oshima K, eds. *Main Group Metals in Organic Synthesis*. vol. 2. Weinheim: Wiley-VCH, Verlag GmbH & Co. KGaA; 2004:753–811;
   (b) Burton JW. Antimony compounds. In: Fleming I, ed. *Science of Synthesis, Category 1*. vol. 4. Stuttgart: Georg Thieme Verlag; 2002:53–116.
2. (a) Barton DHR, Ozbalik N, Ramesh M. *Tetrahedron*. 1988;44:5661–5668;
   (b) Barton DHR, Khamsi J, Ozbalik N, Reibenspies J. *Tetrahedron*. 1990;46:3111–3122.
3. (a) Cho CS, Tanabe K, Uemura S. *Tetrahedron Lett*. 1994;35:1275–1278;
   (b) Cho CS, Tanabe K, Itoh O, Uemura S. *J Org Chem*. 1995;60:274–275;
   (c) Cho CS, Motofusa S, Ohe K, Uemura S. *Bull Chem Soc Jpn*. 1996;69:2341–2348;
   (d) Matoba K, Motofusa S, Cho CS, Ohe K, Uemura S. *J Organomet Chem*. 1999;574:3–10;
   (e) Moiseev DV, Morugova VA, Gushchin AV, Dodonov VA. *Tetrahedron Lett*. 2003;44:3155–3157.
4. Kakusawa N, Tsuchiya T, Kurita J. *Tetrahedron Lett*. 1998;39:9743–9746.
5. (a) Yasuike S, Kishi Y, Kawara S, Kurita J. *Chem Pharm Bull*. 2005;53:425–427;
   (b) Matsumura M, Takada R, Ukai Y, et al. *Heterocycles*. 2016;93:75–83.
6. (a) Yasuike S, Okajima S, Yamaguchi K, Kurita J. *Tetrahedron Lett*. 2003;44:6217–6220;
   (b) Yasuike S, Okajima S, Yamaguchi K, Seki H, Kurita J. *Tetrahedron*. 2003;59:4959–4966;
   (c) Yasuike S, Kawara S, Okajima S, Seki H, Yamaguchi K, Kurita J. *Tetrahedron Lett*. 2004;45:9135–9138.
7. (a) Kakusawa N, Yamaguchi K, Kurita J, Tsuchita T. *Tetrahedron Lett*. 2000;41:4143–4146;
   (b) Kakusawa N, Yamaguchi K, Kurita J. *J Organomet Chem*. 2005;690:2956–2966;
   (c) Kakusawa N, Kurita J. *Chem Pharm Bull*. 2005;53:1369–1371;
   (d) Kakusawa N, Kurita J. *Chem Pharm Bull*. 2006;54:699–702;
   (e) Kakusawa N, Tobiyasu Y, Yasuike S, Yamaguchi K, Seki H, Kurita J. *Tetrahedron Lett*. 2003;44:8589–8592;
   (f) Kakusawa N, Tobiyasu Y, Yasuike S, Yamaguchi K, Seki H, Kurita J. *J Organomet Chem*. 2006;691:2953–2968;
   (g) Kakusawa N, Kurita J. *Hetelocycles*. 2006;68:1335–1348.
8. (a) Kakusawa N, Ikeda T, Osada A, Kurita J, Tsuchiya T. *Synlett*. 2000:1503–1505;
   (b) Okajima S, Yasuike S, Kakusawa N, et al. *J Organomet Chem*. 2002;656:234–242;
   (c) Yasuike S, Kishi Y, Kawara S, Yamaguchi K, Kurita J. *J Organomet Chem*. 2006;691:2213–2220.
9. (a) Fujiwara Y, Mitani M, Yasuike S, Kurita J, Kaji T. *J Health Sci*. 2005;51:333–340;
   (b) Kohri K, Yoshida E, Yasuike S, Fujie T, Yamamoto C, Kaji T. *J Toxicol Sci*. 2015;40:321–327;
   (c) Murakami M, Fujie T, Matsumura M, et al. *Fundam Toxicol Sci*. 2015;2:61–66.
10. (a) Wu P, Fokin VV. *Aldrichim Acta*. 2007;40:7–17;
    (b) Moses JE, Moorhouse AD. *Chem Soc Rev*. 2007;36:1249–1262;
    (c) Meldal M, Tornøe CW. *Chem Rev*. 2008;108:2952–3015;
    (d) Hein JE, Fokin VV. *Chem Soc Rev*. 2010;39:1302–1315;
    (e) Aragão-Leoneti V, Campo VL, Gomes AS, Field RA, Carvalho I. *Tetrahedron*. 2010;66:9475–9492;
    (f) Ackermann L, Potukuchi HK. *Org Biomol Chem*. 2010;8:4503–4513;
    (g) Majumdar KC, Ray K. *Synthesis*. 2011:3767–3783;
    (h) Berg R, Straub BF. *Beilstein J Org Chem*. 2013;9:2715–2750;
    (i) Sokolova NV, Nenajdenko VG. *RSC Adv*. 2013;3:16212–16242;
    (j) Haldón E, Nicasio MC, Pérez PJ. *Org Biomol Chem*. 2015;13:9528–9550;
    (k) Singh MS, Chowdhury S, Koley S. *Tetrahedron*. 2016;72:5257–5283.
11. (a) Thirumurugan P, Matosiuk D, Jozwiak K. *Chem Rev*. 2013;113:4905–4979;
    (b) Debets MF, Berkel SSV, Dommerholt J, Dirks AJ, Rutjes FPJT, Delft FLV. *Acc Chem Res*. 2011;44:805–815;
    (c) Agalave SG, Maujan SR, Pore VS. *Chem Asian J*. 2011;6:2696–2718;
    (d) Mamidyala SK, Finn MG. *Chem Soc Rev*. 2010;39:1252–1261;
    (e) Jewett JC, Bertozzi CR. *Chem Soc Rev*. 2010;39:1272–1279.
12. (a) Golas PL, Matyjaszewski K. *Chem Soc Rev*. 2010;39:1338–1354;
    (b) Qin A, Lam JWY, Tang BZ. *Chem Soc Rev*. 2010;39:2522–2544;
    (c) Bryant JJ, Bunz UH. *Chem Asian J*. 2013;8:1354–1367.
13. Li L, Hao G, Zhu A, Fan X, Zhang G, Zhang L. *Chem Eur J*. 2013;19:14403–14406.
14. Worrell BT, Ellery SP, Fokin VV. *Angew Chem Int Ed*. 2013;52:13037–13041.
15. Wang W, Peng X, Wei F, Tung C-H, Xu Z. *Angew Chem Int Ed*. 2016;55:649–653.
16. Malnuit V, Duca M, Manout A, Bougrin K, Benhida R. *Synlett*. 2009:2123–2128.
17. Stefani HA, Vasconcelos SNS, Manarin F, et al. *Eur J Org Chem*. 2013:3780–3785.
18. Stefani HA, Silva NCS, Vasconcelos SNS, Manarin F, Souza FB. *Tetrahedron Lett*. 2013;54:2809–2812.
19. Yamada M, Matsumura M, Uchida Y, et al. *Beilstein J Org Chem*. 2016;12:1309–1313.
20. Cuevas F, Oliva AI, Pericàs MA. *Synlett*. 2010:1873–1877.
21. Emsley J. *The Elements*. Oxford: Clarendon Press; 1998.
22. Hein JE, Tripp JC, Krasnova LB, Sharpless KB, Fokin VV. *Angew Chem Int Ed*. 2009;48:8018–8021.
23. Wang B, Liu N, Shao C, Zhang Q, Wang X, Hu Y. *Adv Synth Catal*. 2013;355:2564–2568.
24. Yasuike S, Nakata K, Qin W, Kaji T, Kurita J. *Chem Lett*. 2006;35:1402–1403.
25. Kakusawa N, Nakagawa Y, Toshima Y, Yasuike S, Kurita J. *Heterocycles*. 2015;91:1170–1175.
26. Tandon R, Nigst TA, Zipse H. *Eur J Org Chem*. 2013:5423–5430.
27. Nunn M, Begley MJ, Sowerby DB. *Polyhedron*. 1996;15:3167–3174.
28. Sheldrick GM. *SADABS*. Germany: University of Göttingen; 1996.
29. Sheldrick GM. *Acta Cryst*. 2015;A71:3–8.
30. Sheldrick GM. *Acta Cryst*. 2015;C71:3–8.

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