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Synthetic Methods |*Hot Paper*|

Practical Stannylation of Allyl Acetates Catalyzed by Nickel with Bu_3SnOMe

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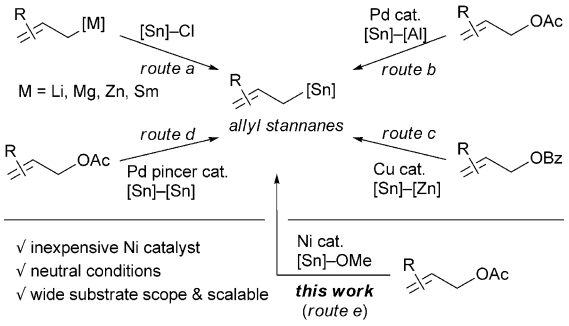
Abstract: A practical and scalable nickel-catalyzed allylic stannylation of allyl acetates with Bu_3SnOMe is described. A variety of acyclic and cyclic allyl acetates, even with base-sensitive moieties, undergoes the stannylation by using $NiBr_2$/4,4′-di-*tert*-butylbipyridine (dtbpy)/Mn catalyst system to afford highly functionalized allyl stannanes with excellent regioselectivity and yields. Furthermore, the scope of protocol is also extended by the reaction of propargyl acetates, giving rise to propargyl or allenyl stannanes. Additionally, a unique diastereoselectivity using the nickel catalyst different from the palladium was demonstrated for the stannylation of cyclic allyl acetates. In the reaction, inexpensive and stable nickel complexes, abundant reductant (Mn), and atom-economical stannyl source were used.



Scheme 1. Synthetic routes to allyl stannanes.

Organostannyl compounds are among the most important building blocks owing to their widespread applications in modern sophisticated organic synthesis.[1] In particular, allyl stannanes are versatile synthetic intermediates that act as nucleophiles,[2] cross-coupling partners,[3] free-radical acceptors,[4] and allyllithium sources[5] that undergo a variety of transformations.[6] Although the toxicity of stannyl residue remaining after transformation using stannyl compounds is frequently viewed with suspicion, the problem is probably exaggerated from a strictly chemical point of view. In fact, the toxicity of the commonly used tri-*n*-butylstannyl derivatives is much lower than that of triethyl- and trimethylstannyls.[1d,7] Consequently, much effort has been made toward developing efficient and convenient methods for the synthesis of various allyl stannanes. Among these, electrophilic stannylation using stoichiometric amounts of allyl metal species, such as allyl lithium, -magnesium, and -zinc reagents, as well as in situ generated allyl samarium species, with stannyl halides has been well documented (Scheme 1, route a).[8] However, the catalytic protocol is quite limited. Trost and co-workers and Oshima and co-workers independently reported the palladium-catalyzed nucleophilic stannylation of allyl alcohol derivatives by using stannylaluminium reagents by the formation of π-allyl palladium electrophiles (route b).[9] Oestrich and co-workers demonstrated the copper-catalyzed allylic substitution of allyl benzoates with stannylzinc reagents via stannylcupration (route c).[10] Although these methods were effective and powerful tools for the preparation of allyl stannanes bearing useful transformable functional groups, they required excess amount of commercially unavailable stannyl anion equivalents. As an alternative method, Wallner and Szabó disclosed the allylic stannylation of allyl acetates with hexaalkyldistannanes catalyzed by a Pd pincer complex (route d).[11] However, the stannylation needs a pincer ligand. The absence of the ligand causes the Stille coupling of allyl acetates with in situ-generated allyl stannanes.[3d] These limitations drastically reduce the usability of allyl stannanes in modern organic transformations. A more practical and conventional method for preparing allyl stannanes has been highly desired.

In contrast to π-allyl palladiums, the nucleophilic reactivity of π-allyl nickel species has been known in reactions with quinones[12] and carbonyl compounds.[13] In recent years, their catalytic reactions have been developed in the allylation of organic electrophiles, such as aldehydes[14] and carbon dioxide.[15] In contrast, we recently demonstrated that aryl nickel complexes proved to be an effective intermediate in a reaction with Bu_3SnOMe, resulting in the direct stannylation of aryl halides to afford functionalized aryl stannanes.[16] Herein, we report the nickel-catalyzed stannylation of allyl acetates (route e), which enables scalable approach to highly functionalized allyl stan-

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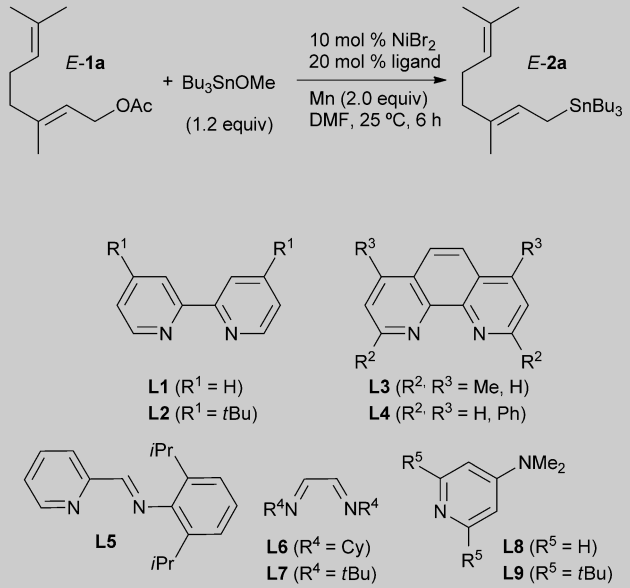
nanes from commercially available and easily prepared allyl acetates.

Initially, we investigated suitable reaction conditions for the stannylation of geranyl acetate (*E*-**1a**) with Bu_3SnOMe as a model substrate. The results are summarized in Table 1. Treatment of *E*-**1a** with Bu_3SnOMe (1.2 equiv) in the presence of $NiBr_2$ (10 mol%), 2,2′-bipyridyl (**L1**, 20 mol%), and Mn powder (2.0 equiv) gave the corresponding stannylation product *E*-**2a** in 84% yield along with 3% yield of the stereoisomer *Z*-**2a** (Table 1, entry 1). Sterically less bulky bidentate nitrogen ligands, such as **L1**–**L4**, were essential for stannylation (entries 1–4). In particular, we found that 4,4′-di-*tert*-butylbipyridine (dtbpy; **L2**) was the most effective ligand (entry 2). In contrast, the bulky iminopyridine **L5**, the diimines (**L6** and **L7**) and the monodentate pyridine ligands (**L8** and **L9**), as well as the absence of a ligand, strongly suppressed the transformation, leading to negligible conversion of the allyl acetate *E*-**1a** (entries 5–10).[17] Additionally, the Stille coupling product was not formed in all cases.[18] The present stannylation strongly depended on the solvent used; thus, DMA was also effective (93% yield (*E*/*Z* 95:5), but DMSO, THF, and Et_2O solvents did not provide the desired stannylation product.[13a,19] The replacement of Mn by Zn decreased the product yield under the same reaction conditions (entry 11).

Table 1. Screening of reaction conditions for the nickel-catalyzed stannylation of geranyl acetate (*E*-**1a**) with Bu_3SnOMe.



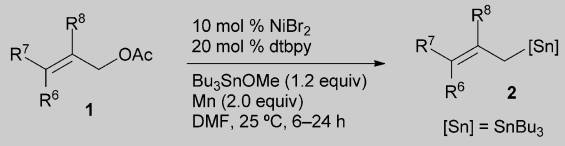
Entry	Ligand	Yield [%][a]	*E*/*Z* ratio[b]
1	**L1**	87	96:4
2	**L2**	94 (90)	97:3
3	**L3**	79	95:5
4	**L4**	74	98:2
5	**L5**	trace	–
6	**L6**	trace	–
7	**L7**	trace	–
8	**L8**	trace	–
9	**L9**	trace	–
10	none	trace	–
11[c]	**L2**	38	89:11

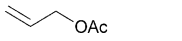
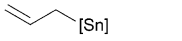
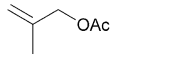
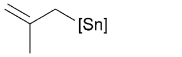
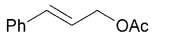
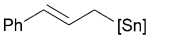
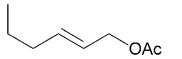
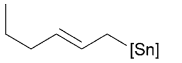
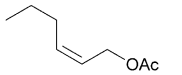
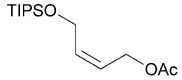
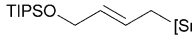
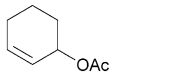
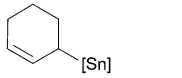
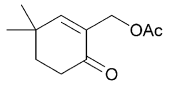
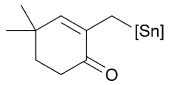
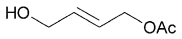
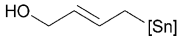
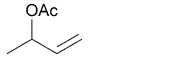
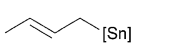
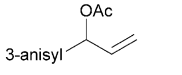
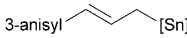
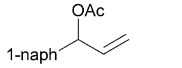
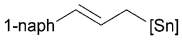
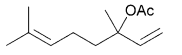
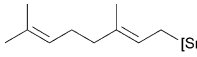
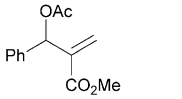
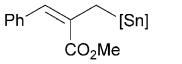
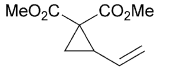
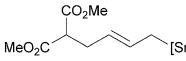
[a] Yield was determined by NMR spectroscopy. Parenthesis value indicates isolated yield. [b] Yield and *E*/*Z* ratio were determined by ^1H NMR spectroscopy of the crude product. [c] Zn was used instead of Mn.

Having determined the optimized conditions (Table 1, entry 2), we next examined the scope of substrates in the stannylation by employing various allyl acetates (Table 2). Unsubstituted (**1b**), branched (**1c**), and linear (**1d** and **e**) allyl acetates were well tolerated in the reaction, giving rise to the corresponding stannylation products in high yields (entries 1–5). Loss of stereochemical purity in vicinal-disubstituted *Z*-allyl acetates was observed in the cases of *Z*-**1e** and **f** (entries 5 and 6). The cyclic allyl acetate **1g** also participated in the reaction, leading to the stannylation product **2g** in good yield (entry 7). Previously reported stannylation reactions by using stannyl anion equivalents are generally sensitive to protonation.[9,10] Importantly, the present Ni-catalyzed stannylation well tolerated the acidic α-proton of the carbonyl group of **1h**[20] and the hydroxyl group of **1i** to provide the corresponding stannylation products **2h** and **i** in 55% and 60% yields, respectively (entries 8 and 9). In the stannylation, the C–Sn bond was selectively formed at the sterically less hindered allylic carbon. Thus, when the branched allyl acetates **1j**–**n** were utilized in the stannylation, only the linear products **2j**–**n** and **a** were produced without the formation of another regioisomer (entries 10–14). The regioselective reaction would indicate that the formation of π-allyl nickel species is involved in the stannylation. In addition, a vinylcyclopropane was also allowed participating in the stannylation instead of allyl acetates. Thus, the stannylative ring-opening reaction of the vinylcyclopropane derivative **1o** (entry 15) could be achieved with the addition of trimethylsilyl chloride (TMSCl, 1.2 equiv), providing the allyl stannane **2o** in 60% yield (*E*/*Z* 72:28).[21]

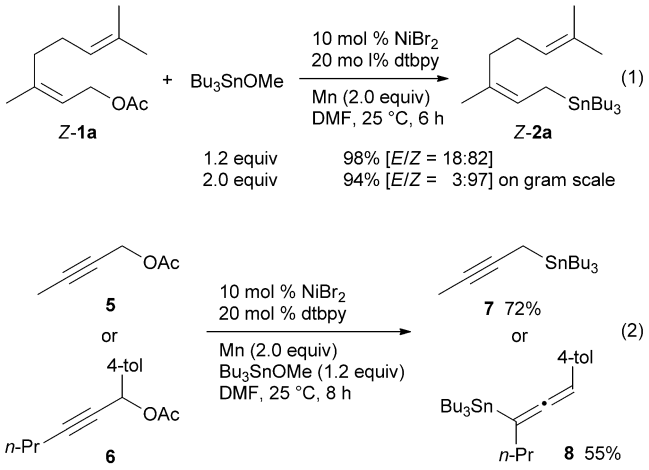
Presumably owing to isomerization of the generated π-allyl nickel, the formation of *E*-allyl stannanes was favored even when *Z*-allyl acetates were employed (Table 2, entries 5 and 6).[22] However, the 1,1,2-trisubstituted allyl acetate neryl acetate (*Z*-**1a**) mainly gave neryl stannane (*Z*-**2a**) with moderate stereospecificity (*E*/*Z* 18:82) (Scheme 2, Eq. (1)). Further studies revealed that the use of an excess amount of Bu_3SnOMe (2.0 equiv) could result in high *Z*-specificity (97%). In addition, we found that stereospecific stannylation successfully proceeded on a gram scale (1.84 g *Z*-**2a**). Stannylation could also be applied to the reaction of the propargyl acetates **5** and **6** with similar regioselectivity, similar to the case of allyl acetates [Eq. (2) in Scheme 2].[23] In other words, the primary propargyl acetate **5** selectively gave the propargyl stannane **7** in 72% yield, whereas the secondary propargyl acetate **6** was exclu-

Table 2. Screening of allyl acetates **1** in nickel-catalyzed stannylation with Bu_3SnOMe.

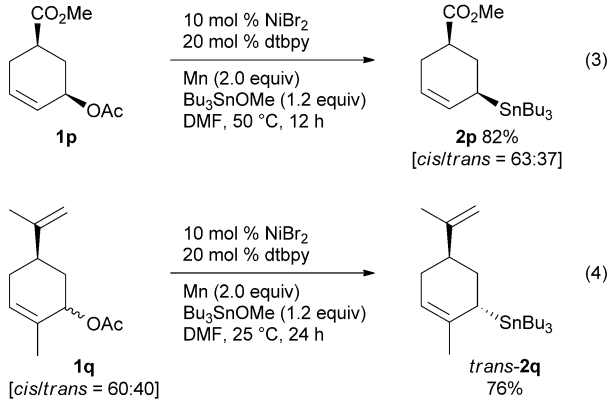


Entry	Substrate	Product	Yield [%][a]
1		**1b** 	**2b** 80
2		**1c** 	**2c** 85
3		**1d** 	**2d** 94[b]
4		*E*-**1e** 	**2e** 72[c]
5		*Z*-**1e**	**2e** 91[d]
6		**1f** 	**2f** 48[e]
7		**1g** 	**2g** 82
8		**1h** 	**2h** 55
9		**1i** 	**2i** 60[f]
10		**1j** 	**2j** 61[g]
11		**1k** 	**2k** 95[h]
12		**1l** 	**2l** 53[i]
13		**1m** 	**2a** 93[j]
14		**1n** 	**2n** 88
15		**1o** 	**2o** 60[k]

[a] Isolated yield. [b] *E*/*Z* 98:2. [c] *E*/*Z* 72:28. [d] *E*/*Z* 60:40. [e] *E*/*Z* 86:14. [f] *E*/*Z* 82:18. [g] *E*/*Z* 64:36. [h] *E*/*Z* 98:2. [i] *E*/*Z* 98:2. [j] *E*/*Z* 74:26. [k] *E*/*Z* 72:28. TMSCl (1.2 equiv) was used as an additive.



Scheme 2. Stereospecific stannylation of neryl acetate (*Z*-**1a**) [Eq. (1)] and stannylation of propargyl acetates (**5** and **6**) [Eq. (2)].

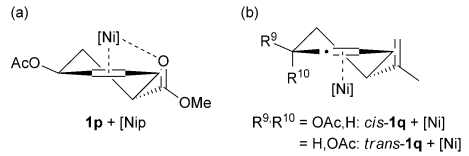


Scheme 3. Diastereoselective stannylation of cyclic allyl acetates (**1r** and **s**).

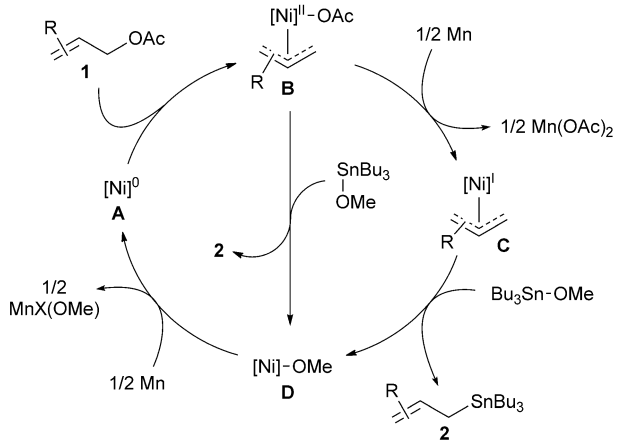
sively converted to the allenyl stannane **8** in 55% yield without the formation of another regioisomer.

The Pd-catalyzed stannylation of *cis*-**1p** (Scheme 3) with Et_2Al-S*n*Bu_3 proceeded by an inversion/retention mechanism to give *trans*-**2p** as the major product.[9a] In contrast, the present Ni-catalyzed stannylation provides the opposite diastereoselectivity to mainly afford *cis*-**2p** [Eq. (3)].[24] Furthermore, the reaction of a *trans*/*cis* mixture (60% *cis*) of carvyl acetate (**1q**) provided only *trans*-**2q** (*trans*/*cis* > 99%) in 76% yield [Eq. (4)].[8d,24] We confirmed that the nickel complex did not react with Bu_3SnOMe in the absence of allyl acetate, even when a stoichiometric amount of the nickel complex was employed. In addition, the generation of allyl manganese reagents during the reaction would be ruled out because of the compatibility of the present stannylation with acidic functional groups (Table 2, entries 8 and 9). The result would conclusively indicate that the allylic C–Sn bond was formed by the electrophilic stannylation of allyl nickels with Bu_3SnOMe and that the unique diastereoselectivity would be attributed to the structure of the allyl nickels. Although further studies, especially of how to form π-allyl nickels and retention or inversion processes, are needed to understand the unique stereoselectivity, [Eqs. (3) and (4) in Scheme 3] could imply that a π-allyl nickel is generated from **1p** through a retention process preferably induced by coordination of the neighboring carbonyl oxygen to the nickel (Scheme 4a),[25] whereas a π-allyl nickel was formed from **1q** via a mixed pathway (retention and inversion) to avoid steric repulsion between the nickel and the propen-2-yl group (Scheme 4b).[26]

A plausible reaction mechanism for the present Ni-catalyzed stannylation of allyl acetates with Bu_3SnOMe is illustrated in



Scheme 4. Plausible processes for the generation of π-allyl nickels by (a) a retention pathway directed by a neighboring polar substituent for **1r** and (b) a mixed pathway (retention and inversion) avoiding a steric interaction for **1s**.



Scheme 5. Plausible reaction mechanism for the Ni-catalyzed allylic stannylation with Bu_3SnOMe.

Scheme 5. The reaction could be started by the reduction of divalent Ni-catalyst precursor with Mn powder to generate the zero-valent nickel catalyst **A**. The oxidative addition of allyl acetates **1** gave π-allyl nickel intermediate **B**, followed by re-reduction to form monovalent π-allyl nickel **C**. A stoichiometric reaction of geranyl acetate (*E*-**1a**) with $Ni(COD)_2$/2 dtbpy (COD = 1,5-cyclooctadiene) and Bu_3SnOMe (1.2 equiv for Ni) in the presence (2.0 equiv for Ni) and absence of Mn reductant revealed that both intermediates **B** and **C** were active for the trapping with the stannyl methoxide to form allylic stannanes **2a**, in which **C** was superior to **B**.[27] Therefore, the two stannylation pathways (**B** to **D** and/or **C** to **D**) might involve in the stannylation process. However, the reducing ability of Mn is higher than that of Zn.[28] These results (the above-mentioned stoichiometric reaction and entries 2 vs. 11 in Table 1) might indicate that the intermediate **C** is favored in the stannylation step. Finally, the catalytic cycle would be closed by reduction of **D** to regenerate **A**.

In conclusion, we have developed an efficient and convenient route to allyl stannanes by using the nickel-catalyzed stannylation of ubiquitous allyl acetates with Bu_3SnOMe in the presence of a Mn reductant. This stannylation enables the selective formation of C–Sn bonds at sterically less demanding allylic positions and can be tolerated by a diverse set of functional groups; in particular, compatibility with base-sensitive functional groups is highly valuable for the further development of organostannane chemistry. Furthermore, we disclose that the stannylation process is effective for the stannylation not only of allyl acetates but also of propargyl acetates, providing propargyl or allenyl stannanes. Although more mechanistic investigations, particularly of the generation of π-allyl nickel intermediates, are needed to understand the details of the present Ni-catalyzed stannylation, further mechanistic studies and new synthetic applications for allylation using the unique diastereoselectivity of the π-allyl nickel intermediates are currently underway in our laboratory.

Experimental Section

Representative procedure for the nickel-catalyzed stannylation of allyl acetates with Bu_3SnOMe (entry 2, Table 1)

Into an oven-dried Schlenk tube, Mn powder (55 mg, 1.0 mmol) was added and heated at 400 °C for 15 min under vacuum. The Schlenk tube was charged with $NiBr_2$ (11 mg, 0.05 mmol, 10 mol%), 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy, 27 mg, 0.1 mmol, 20 mol%), DMF (1 mL), and TMSCl (11 μL, 0.1 mmol 20 mol%), and the mixture was stirred for 10 min. At the time, a color of the reaction mixture changed to black. If the change is not observe, the mixture should be heated at 60–80 °C until the color change is visible. After cooling the mixture, geranyl acetate (*E*-**1a**, 107 μL, 0.5 mmol) and Bu_3SnOMe (172 μL, 0.6 mmol) were added into the mixture, and followed by sequential stirring at 25 °C for 6 h. The obtained mixture was diluted with Et_2O and quenched with water. The conversion of substrates and the yield of **2a** were estimated by GC and ^1H NMR using dimethyl terephthalate as an internal standard. The aqueous phase was extracted with Et_2O. The combined ethereal phases were dried over Na_2SO_4. After filtration and removal of solvent, the residue was purified by gel-permeation chromatography to give a mixture (97:3) of *E*- and *Z*-**2a** in 90% yield.

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Keywords: allyl stannanes · nickel · stannyl alkoxide · stannylation · synthetic method

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