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A remarkable regiocontrol in the palladium-catalyzed silylstannylation of fluoroalkylated alkynes – highly regio- and stereoselective synthesis of multi-substituted fluorine-containing alkenes†

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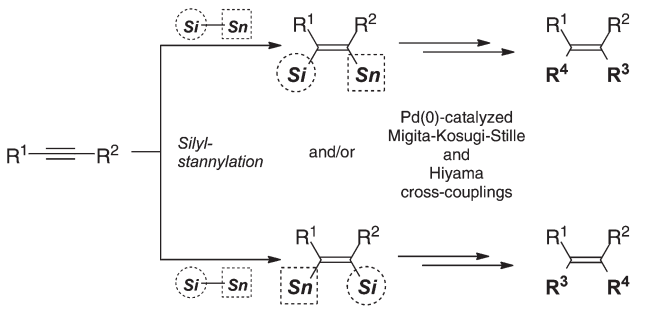
On treating fluorine-containing internal alkynes with 1.2 equiv. of (trimethylsilyl)tributyltin in the presence of 2.5 mol% of $Pd(PPh_3)_2Cl_2$ in THF at the reflux temperature for 6 h, the silylstannylation reaction proceeded smoothly to afford the corresponding silylstannylated adducts in high yields in a highly regio- and *cis*-selective manner. Switching the palladium catalyst from $Pd(PPh_3)_2Cl_2$ to $Pd(t\text{-BuNC})_2Cl_2$ promoted the formation of silylstannylated adducts with opposite regioselectivity. The thus obtained silylstannylated adducts were subjected to Stille cross-coupling reactions to furnish the corresponding fluoroalkylated vinylsilanes whose C–Si bond was converted to a C–C bond by treating with aldehyde in the presence of TBAF and $Zn(OTf)_2$, the corresponding fluoroalkylated tetra-substituted alkenes being afforded in moderate to good yields with a defined stereochemistry.

Introduction

The transition metal-catalyzed silylstannylation has been recognized as a powerful synthetic tool in organic synthesis because two different types of carbon–metal bonds, such as carbon–tin (C–Sn) and carbon–silicon (C–Si) bonds, are simultaneously introduced across a triple bond in a stereoselective manner to afford the corresponding alkenyl metal intermediate which can be easily transformed into various substituted ethenes with retention of configuration through the Migita–Kosugi–Stille and Hiyama cross-coupling reactions (Scheme 1).[1]

Furthermore, the high chemoselectivity and very mild reactivity of organostannanes and organosilanes, as compared with other organometallic reagents, such as lithium, magnesium, chromium reagents, and so on, make the silylstannylation and the following coupling reactions extremely valuable and applicable for preparing a wide range of versatile substances.

It is not surprising, therefore, that the silylstannylation reaction of various *non-fluorinated alkynes* has been extensively studied so far.[2] However, little attention has been paid to such a reaction of *fluoroalkylated alkynes*, though selective preparation of fluoroalkyl-substituted alkenes has been of great importance since they can be considered versatile building blocks[3] as well as monomers for high performance fluorinated materials.[4]



Scheme 1 Construction of multi-substituted alkenes *via* silylstannylation of alkynes.

Recently, we focused our efforts on the bismetallation reaction of fluorine-containing internal alkynes revealed that stereoselective bisstannylation reactions, followed by Stille cross-coupling reactions, proceeded smoothly to afford fluoroalkylated tetra-substituted alkenes in good yields with a defined stereochemistry.[5] During the course of our continuous bismetallation studies, we found that the fluoroalkylated alkynes underwent palladium-catalyzed silylstannylation

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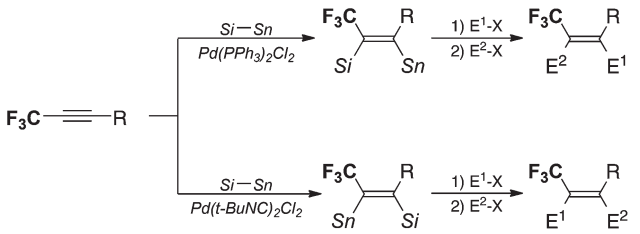


Scheme 2 Preparation of fluoroalkylated tetra-substituted alkenes *via* Pd(0)-catalyzed silylstannylation/coupling reactions with electrophiles.

reactions in a regio- and stereoselective manner, whose regioselectivity was fully inverted by switching a palladium catalyst. In this paper are presented the details of such regio- and stereoselective silylstannylation reactions (Scheme 2).

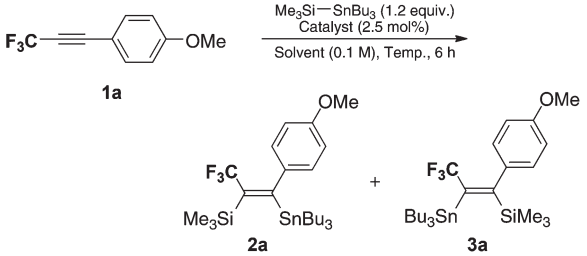
Results and discussion

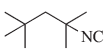
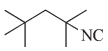
Our initial studies were begun with an optimization of the reaction conditions for the palladium-catalyzed silylstannylation reaction of fluorine-containing internal alkyne **1a**. The results are listed in Table 1.

Thus, on treating **1a** with 1.2 equiv. of (trimethylsilyl)tributyltin ($Me_3SiSnBu_3$) in the presence of 2.5 mol% of $Pd(PPh_3)_4$ in THF at the reflux temperature for 6 h, the reaction successfully proceeded, the corresponding silylstannylated products **2a** and **3a** being provided in 97% combined yield without any trace of the starting alkyne **1a** (entry 1).

In this case, we were very pleased that an excellent regioselectivity (**2a** : **3a** = 96 : 4) was observed. The employment of $Pd(PPh_3)_2Cl_2$ instead of $Pd(PPh_3)_4$ was also found to be very effective, leading to the products **2a** + **3a** in 85% yield with an excellent regioselectivity (**2a** : **3a** = 95 : 5) (entry 2). On the other hand, other palladium catalysts, such as $PdCl_2$, $Pd(OAc)_2$, and $Pd_2(dba)_3$, did not work well (entries 3–5). Palladium catalysts coordinated with tricyclohexylphosphine or tri(*o*-tolyl)phosphine were not suitable for the present reaction as well (entries 6 and 7). Very surprisingly, the catalyst, generated by treating $Pd(OAc)_2$ with 1,1,3,3-tetramethylbutyl isocyanide,[2d] led to quantitative formation of **2a** and **3a** (entry 8). Additionally, the regioselectivity opposite to that in the $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$-catalyzed reaction was observed (**2a** : **3a** = 27 : 73). The silylstannylation reaction at ambient temperature resulted in a slight improvement of the regioselectivity (**2a** : **3a** = 18 : 82) (entry 9). Furthermore, $Pd(t\text{-BuNC})_2Cl_2$ [5,6] also catalysed

Table 1 Optimization of the silylstannylation reaction of fluorine-containing internal alkyne **1a**



Entry	Catalyst	Solvent	Temp./°C	Yield[a]/% of **2a** + **3a**	Ratio[a] **2a** : **3a**	Recovery[a]/% of **1a**
1	$Pd(PPh_3)_4$	THF	Reflux	97	**96** : 4	0
2	$Pd(PPh_3)_2Cl_2$	THF	Reflux	85	**95** : 5	0
3	$PdCl_2$	THF	Reflux	12	—	76
4	$Pd(OAc)_2$	THF	Reflux	09	—	73
5	$Pd_2(dba)_3$	THF	Reflux	5	—	80
6	$Pd_2(dba)_3$ + PCy_3	THF	Reflux	17	—	71
7	$Pd_2(dba)_3$ + P(*o*-Tol)$_3$	THF	Reflux	29	55 : 45	50
8	$Pd(OAc)_2$ + 	THF	Reflux	Quant	27 : **73**	0
9	$Pd(OAc)_2$ + 	THF	rt	Quant	18 : **82**	0
10	$Pd(t\text{-BuCN})_2Cl_2$	THF	rt	Quant	18 : **82**	0
11	$Pd(t\text{-BuCN})_2Cl_2$	THF	0	Quant	21 : **79**	0
12	$Pd(t\text{-BuCN})_2Cl_2$	Et_2O	rt	96	23 : **77**	0
13	$Pd(t\text{-BuCN})_2Cl_2$	Toluene	rt	Quant	25 : **75**	0
14	$Pd(t\text{-BuCN})_2Cl_2$	CH_2Cl_2	rt	97	22 : **78**	0
15	$Pd(t\text{-BuCN})_2Cl_2$	1,4-Dioxane	rt	96	26 : **74**	0
16[b]	$Pd(t\text{-BuCN})_2Cl_2$	THF	rt	Quant	19 : **81**	0
17[c]	$Pd(t\text{-BuCN})_2Cl_2$	THF	rt	95	22 : **78**	0

[a] Determined by ^{19}F NMR. [b] Carried out under high dilution conditions (*ca.* 0.01 M). [c] The amount of $Pd(t\text{-BuNC})_2Cl_2$ employed was 5.0 mol%.

effectively the silylstannylation reaction to afford **2a** and **3a** in quantitative yield with a high regioselectivity retained (**2a** : **3a** = 18 : 82) (entry 10). As shown in entry 11, the reaction at 0 °C did not bring about any significant improvement in regioselectivity. In addition, switching the solvent from THF to Et_2O, toluene, CH_2Cl_2, and 1,4-dioxane did not cause a substantial change in the regioselectivity (entries 12–15). Furthermore, the reaction in high dilution conditions or under the influence of 5 mol% of the catalyst did not also lead to a satisfactory result (entries 16 and 17).

To extend the scope of the synthetic method, a broad range of fluorine-containing alkynes **1** were tested for the present silylstannylation by using $Pd(PPh_3)_2Cl_2$ (**Condition A**) or Pd(*t*-BuNC)$_2Cl_2$ (**Condition B**) as a catalyst.‡ The results are summarized in Table 2.

Reaction of fluorine-containing alkynes having an electron-donating group on the benzene ring, **1a–c** with 1.2 equiv. of $Me_3SiSnBu_3$ under **Condition A** took place sufficiently to provide the corresponding silylstannylated products in 56–75% yield with an excellent regioselectivity (**2** : **3** to 90 : 10) (entries 1–3). The alkynes having an aromatic group substituted by an electron-withdrawing group, such as *p*-ClC_6H_4 (**1d**) and *p*-$EtO_2CC_6H_4$ (**1e**), also underwent regioselective silylstannylation to afford the adducts (63%; **2d** : **3d** = 83 : 17 for **1d**, 65%; **2e** : **3e** = 77 : 23 for **1e**) in a highly regioselective fashion (entries 4 and 5). The fluorine-containing alkynyl ester **1f** reacted effectively to form the silylstannylated products **2f** and **3f** in moderate yield with an erosion of the regioselectivity (entry 6), while alkynyl phosphonate **1g** did not bring about any products (entry 7). As shown in entries 8–12, it was revealed that 1-substituted 4,4,4-trifluoropropargyl alcohol derivatives as a substrate were not good substrates for the silylstannylation, resulting in a large amount recovery of starting alkynes **1h–l**.

Subsequently, the silylstannylation reaction under **Condition B** was examined. Thus, reaction of alkyne **1** with 1.2 equiv. of $Me_3SiSnBu_3$ in the presence of 2.5 mol% of Pd(*t*-BuNC)$_2Cl_2$ in THF at room temperature for 6 h was performed, and the results are shown in entries 13–24. Alkynes carrying various types of aromatic groups with a substituent like *p*-MeO, *m*-MeO, *o*-MeO as well as *p*-Cl, *p*-EtO_2C **1a–e** were subjected well to the silylstannylation reaction to give the corresponding products in 82–90% yield with a high regioselectivity (**2** : **3** up to 16 : 84) (entries 13–17). In the case of alkynes having an ester or a phosphonate as R, the reaction under **Condition B** was found to be sluggish, a large amount of starting alkyne **1f–g** being recovered (entries 18 and 19). In sharp contrast to the reactions under **Condition A**, 4,4,4-trifluoropropargyl alcohol derivatives **1h–j** having an aromatic or aliphatic substituent at the 1-position could participate nicely in silylstannylation to give rise to the corresponding silylstannylated products in high to excellent yields (65–94%), though the regioselectivity was somewhat eroded (entries 20–22). Moreover, the 4,4,4-trifluoropropargyl ether derivative was also found to be a relevant substrate to the present reaction with $Me_3SiSnBu_3$ as well as $Me_2PhSiSnBu_3$,[2c] leading to the corresponding adducts in 85% (**2k** : **3k** = 58 : 42) and 62% yields (**2k** : **3k** = 45 : 55), respectively, with no regioselectivity (entries 23 and 24).

A determination of the stereochemistry of the silylstannylated products **2** and **3** was carried out on the basis of the NMR analysis after appropriate stereospecific chemical transformations.

Thus, the mixture of **2a** and **3a** (**2a** : **3a** = 21 : 79) was treated with 4.4 equiv. of tetrabutylammonium fluoride (TBAF) in THF–DMF (1/1) at room temperature for 48 h to form the corresponding protodesilylstannylated product **4a** in 93% yield as a sole product (Scheme 3). The **4a**, bearing a *p*-methoxyphenyl group, is a known compound,[7] the characterization data of which were completely in agreement with the reported one, *i.e.* the stereochemistry of **4a** was determined as *Z* configuration. This strongly suggested that the silylstannylation reaction to alkyne **1a** took place in a *cis*-selective manner.

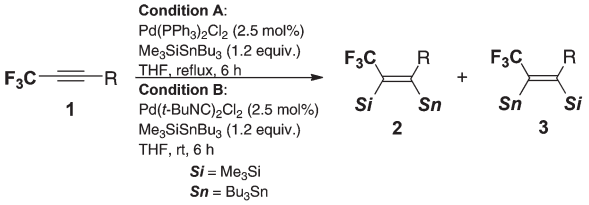
Additionally, selective destannylation[8] of the **2a** and **3a** (**2a** : **3a** = 22 : 78) by treating with 30 equiv. of pyridinium *p*-toluenesulfonate (PPTS) in MeOH at reflux temperature for 52 h led to the corresponding vinylsilanes **5a** and **6a** in 19% and 81% yield, respectively (Scheme 4).

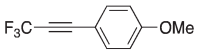
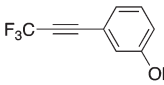
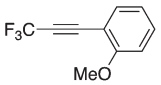
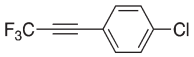
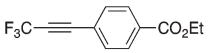
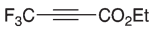
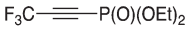
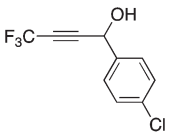
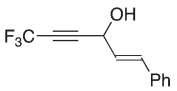
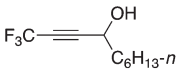
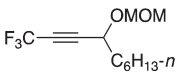
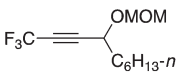
The comparison with a spin–spin splitting pattern between **5a** and **6a** in ^{19}F as well as ^1H NMR enabled us to assign their stereochemistry. Thus, both spin–spin splitting patterns of CF_3 in ^{19}F NMR and C(sp^2)-*H* in ^1H NMR of **5a** were singlet, while those of **6a** were doublet for CF_3 and quartet for C(sp^2)-*H*.

‡**Typical procedure for the silylstannylation of 1-(4-chlorophenyl)3,3,3-trifluoropropyne (1d) under Condition A:** To a solution of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (**1d**, 0.051 g, 0.25 mmol) and $Pd(PPh_3)_2Cl_2$ (0.007 g, 0.00625 mmol, 2.5 mol%) in THF (2.5 mL) was added a THF solution of trimethyl(tributylstannyl)silane (0.109 g, 0.30 mmol) at room temperature. The reaction was stirred for 6 h at 80 °C. The resulting mixture was then quenched with H_2O. The reaction mixture was extracted with Et_2O three times. The combined organic layers were dried over anhydride Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane–AcOEt = 30 : 1) to afford the corresponding silylstannylated product (**2d** + **3d**, 0.089 g, 0.16 mmol, 63%). **2d** (Major isomer); ^1H NMR ($CDCl_3$) δ 0.31 (s, 9H), 0.80–1.45 (m, 18H), 0.85 (t, J = 7.39 Hz, 9H), 6.71 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 1.3, 13.8, 13.9, 27.6, 29.2, 125.0 (q, J = 283.5 Hz), 125.8 to 126.1 (m, 1C), 128.0, 131.0, 143.9 (q, J = 24.0 Hz), 146.1, 172.5 (q, J = 5.7 Hz); ^{19}F NMR ($CDCl_3$) δ −49.70 (s, 3F); IR (neat) ν 2957, 2923, 2873, 1721, 1483, 1252, 1233, 1184, 1142, 1097, 1015, 962 cm^{-1}.

Typical procedure for the silylstannylation of 1d under Condition B: To a solution of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (**1d**, 0.051 g, 0.25 mmol) and Pd(*t*-BuNC)$_2Cl_2$ (0.002 g, 0.00625 mmol, 2.5 mol%) in THF (2.5 mL) was added a THF solution of trimethyl(tributylstannyl)silane (0.109 g, 0.30 mmol) at room temperature. The reaction was stirred for 6 h at room temperature. The resulting mixture was then quenched with H_2O. The reaction mixture was extracted with Et_2O three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane–AcOEt = 30 : 1) to afford the corresponding silylstannylated product (**2d** + **3d**, 0.128 g, 0.23 mmol, 90%). **3d** (Major isomer); ^1H NMR ($CDCl_3$) δ 0.06 (s, 9H), 0.80–1.60 (m, 18H), 0.93 (t, J = 7.39 Hz, 9H), 6.78 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 1.1, 14.0 (q, J = 1.7 Hz), 14.3, 28.0, 29.5, 125.01 (q, J = 283.5 Hz), 126.4 (q, J = 2.5 Hz), 128.3, 132.1, 143.9, 147.5 (q, J = 28.6 Hz), 167.8 (q, J = 7.2 Hz); ^{19}F NMR ($CDCl_3$) δ −49.54 (s, 3F); IR (neat) ν 2957, 2855, 1547, 1484, 1465, 1420, 1377, 1232, 1184, 1139, 1095, 1015, 962 cm^{-1}; HRMS (FAB) calcd for (M + Na) $C_{24}H_{40}ClF_3NaSiSn$: 591.1460, found 591.1459.

Table 2 Regioselective silylstannylation reaction of various fluorine-containing internal alkynes **1**

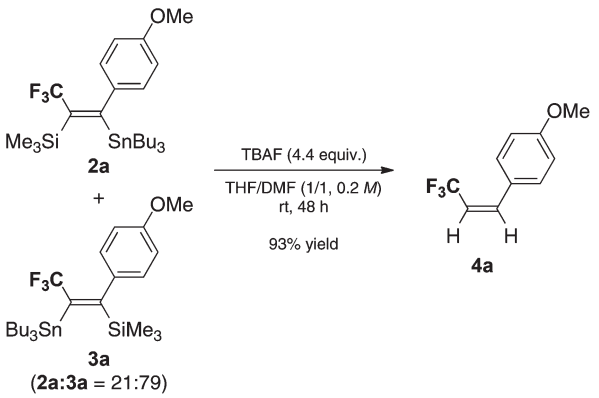


			Conditions A			Conditions B	
Entry	Substrate		Yield[a]/%	Ratio[b] **2 : 3**	Entry	Yield[a]/%	Ratio[b] **2 : 3**
1		(**a**)	75	**95** : 5	13	82	18 : **82**
2		(**b**)	56	**90** : 10	14	87	21 : **79**
3		(**c**)	61	**95** : 5	15	86	17 : **83**
4		(**d**)	63	**83** : 17	16	90	16 : **84**
5		(**e**)	65	**77** : 23	17	90	19 : **81**
6		(**f**)	52	39 : 61	18	26[b]	43 : 57
7		(**g**)	0	—	19	0	—
8		(**h**)	0	—	20	94	27 : **73**
9		(**i**)	21[b]	66 : 34	21	75	30 : **70**
10		(**j**)	0	—	22	65	46 : 54
11		(**k**)	0	—	23	85	58 : 42
12[c]		(**l**)	0	—	24[c]	62	45 : 55

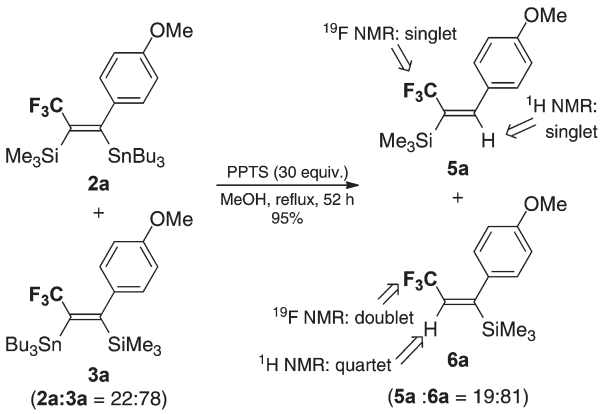
[a] Isolated yields are shown. [b] Determined by ^{19}F NMR. [c] Silylstannylation was conducted by using $PhMe_2SiSnBu_3$ instead of $Me_3SiSnBu_3$.

These observations clearly demonstrate that the Bu_3Sn group in **2a** is bonded with a vinylic carbon distal to the CF_3 group, and the Bu_3Sn group in **3a**, on the other hand, is attached with a vinylic carbon having the CF_3 group.

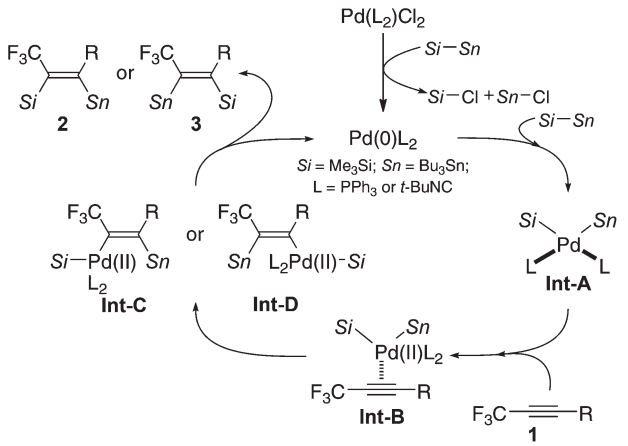
Based on these findings, a proposed reaction mechanism for Pd(0)-catalyzed silylstannylation reaction of fluoroalkylated alkyne **1** is illustrated in Scheme 5. Thus, the present silylstannylation reaction presumably proceeds *via* (i) generation of $Pd(0)L_2$ through the reduction of $Pd(II)L_2Cl_2$ by $Me_3SiSnBu_3$, (ii) oxidative addition of $Me_3SiSnBu_3$ to $Pd(0)L_2$ to form the silylstannylpalladium intermediate **Int-A**, (iii) coordination of the alkyne **1** to the Pd center of **Int-A**, as shown by **Int-B**, followed by insertion into the Sn–Pd bond, not into the Si–Pd bond, due to the difference in electrophilicity between Si and Sn as well as in the stability between highly coordinated Si and Sn, furnishing the vinylpalladium intermediate **Int-C** and/or **Int-D**,[9] and finally (iv) reductive elimination to afford the silylstannylated adducts **2** and/or **3** in a *cis*-selective fashion, and regeneration of $Pd(0)L_2$.



Scheme 3 Determination of stereochemistry by protodesilylstannylation of **2a** and **3a**.

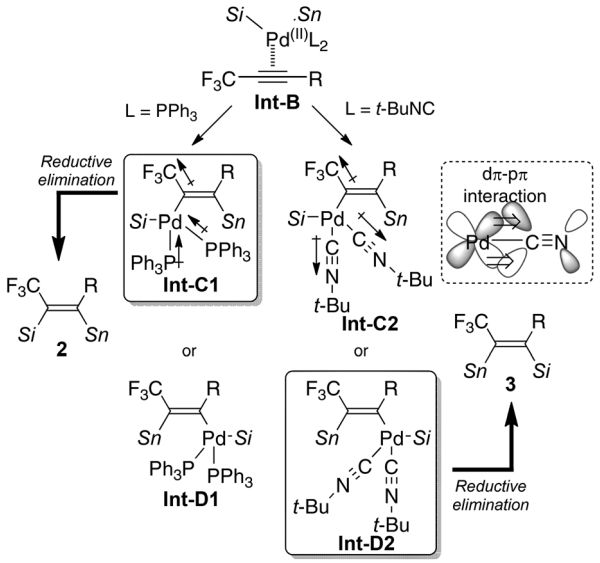


Scheme 4 Assignment of regioisomers.



Scheme 5 A proposed reaction mechanism for Pd(0)-catalyzed silylstannylation reaction of fluoroalkylated alkyne **1**.

The mechanism for the regioselection has not been fully clarified at present; however, for some substrates, it may be understood by taking into consideration an electronic density distribution on the Pd center of their intermediates (Scheme 6).

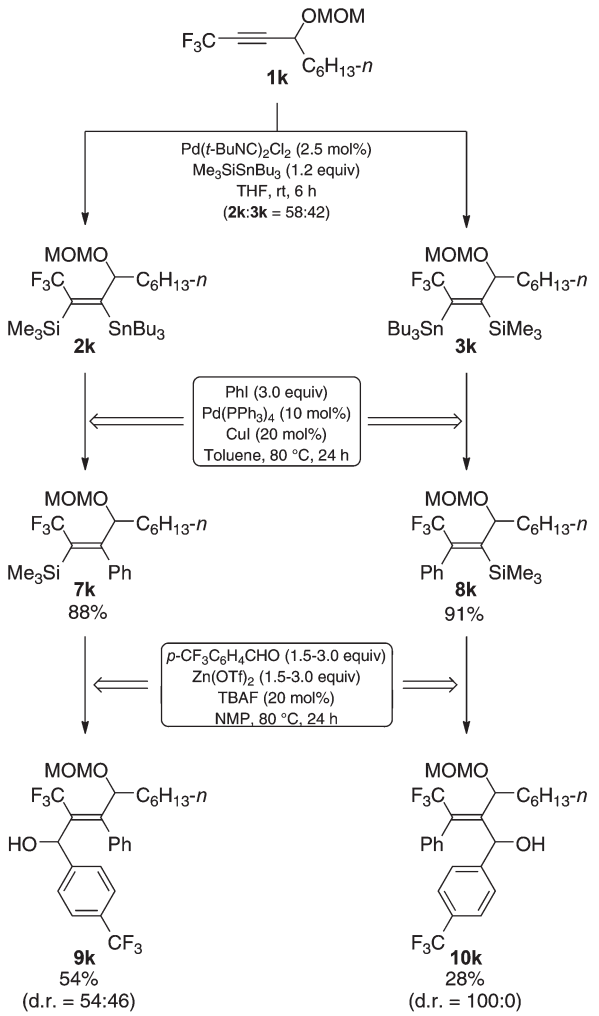


Scheme 6 A plausible mechanism for the regioselection.

Thus, when $Pd(PPh_3)_2Cl_2$ or $Pd(t\text{-BuNC})_2Cl_2$ is employed as a catalyst, **Int-C1**/**Int-D1** or **Int-C2**/**Int-D2** may be possible as the intermediates in the insersion of alkyne into the Sn–Pd bond, respectively. When PPh_3 is coordinated with Pd as a ligand, the vinylpalladium complex **Int-C1** is more stable than the other regioisomeric **Int-D1** due to both the electron-donating nature of PPh_3 and the electron-withdrawing nature of CF_3, which smoothly leads to a reductive elimination to form the silylstannylated product **2** in a stereoselective manner. In the case of *t*-BuNC as a ligand, on the other hand, **Int-C2** might be unstable rather than **Int-D2** since an electron density on the Pd center significantly decreases by a strongly electron-withdrawing effect of the CF_3 group as well as a dπ–pπ interaction between the Pd center and the isonitrile moiety. Therefore, the insertion of alkyne into Sn–Pd may proceed preferentially *via* **Int-D2**, followed by immediate reductive elimination, giving rise to the product **3** as a major isomer.

Finally, we challenged the syntheses of stereo-defined fluoroalkylated tetra-substituted alkenes *via* the coupling reactions by using the above obtained silylstannylated products (Scheme 7).

Thus, silylstannylated compounds **2k** and **3k**, which were prepared from **1k** as shown in entry 23 in Table 2, were smoothly subjected to the Stille cross-coupling reaction, leading to the corresponding coupling products **7k** and **8k** in 88% and 91% yield, respectively. Subsequently, on treatment with the vinylsilanes **7k** and **8k** with 1.5–3.0 equiv. each of (*p*-trifluoromethyl)benzaldehyde and zinc triflate in the presence of 20 mol% of TBAF in *N*-methyl-2-pyrrolidone (NMP) at 80 °C for 24 h,[10] the coupling reaction proceeded to provide the corresponding allylic alcohol derivatives **9k** (this was obtained as a diastereomeric mixture; diastereomeric ratio = 54 : 46) and **10k** (this was obtained as a single isomer; diastereomeric ratio = 100 : 0) in 54% and 28%[11] yields, respectively.



Yields, regioselectivities, and diastereoselectivities are determined by ^{19}F NMR.

Scheme 7 Synthetic application to stereo-defined fluoroalkylated tetra-substituted alkenes.

Conclusions

In conclusion, we have demonstrated that the palladium-catalyzed silylstannylation reaction of fluorine-containing internal alkynes with (trimethylsilyl)tributyltin took place smoothly to give the corresponding adducts in good to high yields in a *cis*-selective manner. In this reaction, two regioisomers could be prepared selectively by using different catalysts, such as Pd$(PPh_3)_2Cl_2$ and Pd(*t*-BuNC)$_2Cl_2$, for each reaction. Thus obtained silylstannylated products underwent a Stille cross-coupling reaction, followed by a fluoride-ion promoted coupling reaction with aldehyde, converting to the stereo-defined fluoroalkylated tetra-substituted alkenes in moderate to good yields.

Notes and references

1 For a recent review on element–element addition to unsaturated carbon–carbon bonds catalyzed by transition metal complexes, see: (*a*) I. Beletsukaya and C. Moberg, *Chem. Rev.*, 2006, **106**, 2320–2354; (*b*) M. Suginome and Y. Ito, *Chem. Rev.*, 2000, **100**, 3221–3256.

2 For selected reports on silylstannylation to alkynes, see: (*a*) S. Apte, B. Radetich, S. Shin and T. V. RajanBabu, *Org. Lett.*, 2004, **6**, 4053–4056; (*b*) T. E. Nielsen, S. Le Quement and D. Tanner, *Synthesis*, 2004, 1381–1390; (*c*) S. Warren, A. Chow, G. Fraenkel and V. T. RajanBabu, *J. Am. Chem. Soc.*, 2003, **125**, 15402–15410; (*d*) M. Murakami, H. Amii, N. Takizawa and Y. Ito, *Organometallics*, 1993, **13**, 4223–4227; (*e*) T. N. Mitchell, R. Wickenkamp, A. Amamria, R. Dicke and U. Schneider, *J. Org. Chem.*, 1987, **52**, 4868–4874; (*f*) B. L. Chenard and C. M. Van Zyl, *J. Org. Chem.*, 1986, **51**, 3561–3566; (*g*) For selected reports on silylstannylation to alkenes, see: (*h*) M. Jeganmohan, M. Shanmugasundaram, K.-J. Chang and C.-H. Cheng, *Chem. Commun.*, 2002, 2552–2553; (*i*) T. N. Mitchell and U. Schneider, *J. Organomet. Chem.*, 1990, **407**, 319–327; (*j*) T. N. Mitchell, H. Killing, R. Dicke and R. Wickenkamp, *J. Chem. Soc., Chem. Commun.*, 1985, 354–355; for selected reports on silylstannylation to 1,3-dienes, see: (*k*) N. Saito, M. Mori and Y. Sato, *J. Organomet. Chem.*, 2007, **692**, 460–471; (*l*) Y. Tsuji and Y. Obora, *J. Am. Chem. Soc.*, 1991, **113**, 9368–9369.

3 For selected reports on the reaction of fluoroalkylated alkenes, see: (*a*) A. Morigaki, M. Kawamura, S. Arimitsu, T. Ishihara and T. Konno, *Asian J. Org. Chem.*, 2013, **2**, 239–243; (*b*) A. Morigaki, T. Miyabe, K. Tsugade, S. Arimitsu, T. Ishihara and T. Konno, *Synthesis*, 2013, 101–105; (*c*) A. Morigaki, T. Tanaka, T. Miyabe, T. Ishihara and T. Konno, *Org. Biomol. Chem.*, 2013, **11**, 586–595; (*d*) A. Morigaki, K. Tsukade, S. Arimitsu, T. Konno and T. Kubota, *Tetrahedron*, 2013, **69**, 1521–1525; (*e*) S. Bigotti, L. Malpezzi, M. Molteni, A. Mele, W. Panzeri and M. Zanda, *Tetrahedron Lett.*, 2009, **50**, 2540–2542.

4 For selected reviews and books, see: (*a*) T. Kubota, *J. Synth. Org. Chem., Jpn.*, 2013, **71**, 196–206; (*b*) *Current Fluoroorganic Chemistry: New Synthetic Directions, Technologies, Materials, and Biological Applications (ACS Symposium Series)*, ed. V. A. Soloshonok, K. Mikami, T. Yamazaki, J. T. Welch, J. F. Honek, American Chemical Society, 2007; (*c*) S. Krishnan, Y.-J. Kwark and C. K. Ober, *Chem. Rec.*, 2004, **4**, 315–330; (*d*) *Organofluorine Compounds. Chemistry and Applications*, ed. T. Hiyama, Springer, New York, 2000; (*e*) *Organofluorine Chemistry: Fluorinated Alkenes and Reactive Intermediates (Topics in Curent Chemistry)*, ed. R. D. Chambers, Springer, New York, 1997.

5 T. Konno, R. Kinugawa, A. Morigaki and T. Ishihara, *J. Org. Chem.*, 2009, **74**, 8456–8459.

6 The catalyst realized a bisstannylation of alkynes, see: J. Mansuso and M. Lauten, *Org. Lett.*, 2003, **5**, 1653–1655.

7 X.-G. Zhang, M.-W. Chen, P. Zhong and M.-L. Hu, *J. Fluorine Chem.*, 2008, **129**, 335–342.

8 K. G. Packard and D. S. Rychnovsky, *Org. Lett.*, 2001, **3**, 3393–3396.

9 M. Hada, Y. Tanaka, M. Ito, M. Murakami, H. Amii, Y. Ito and H. Nakatsuji, *J. Am. Chem. Soc.*, 1994, **116**, 8754–8765.
10 For the cross-coupling reaction of vinylsilane with aldehydes, see: (*a*) T. Konno, K. Taku, S. Yamada, K. Moriyasu and T. Ishihara, *Org. Biomol. Chem.*, 2009, **7**, 1167–1170; (*b*) D. Tomita, R. Wada, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2005, **127**, 4138–4139; (*c*) T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu and T. Hiyama, *Tetrahedron*, 2002, **58**, 6381–6395.
11 The corresponding desilylated product was also obtained in 41% yield.