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A highly regio- and stereo-selective hydrostannation reaction of various fluorine-containing internal acetylene derivatives

Jungha Chae, Tsutomu Konno*, Masashi Kanda, Takashi Ishihara, Hiroki Yamanaka

Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

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Abstract

The hydrostannation reaction of various fluoroalkylated acetylene derivatives with tributyltin hydride was investigated using a variety of catalysts in toluene. Among them, the Et_3B-induced hydrostannation reaction gave the highest regio- and stereo-selectivity. Their selectivity was mostly influenced upon the difference of the substituent X at the aromatic ring of the aryl-substituted internal acetylenes. Thus, the acetylenes having a halogen atom or an electron-donating group as X reacted smoothly with tributyltin hydride, affording the vinylstannane **4*Z*** exclusively, while the acetylenes having an electron-withdrawing group (X = CO_2Et, NO_2) resulted in the preferential formation of **5*E***. The plausible mechanism of the formation of these products was discussed.

Keywords: Fluorine-containing internal acetylene derivative; Fluoroalkylated vinylstannane; Regio- and stereo-selectivity; Radical reaction; Ionic reaction

1. Introduction

Vinylstannanes **1** (Fig. 1) have been receiving much attention as one of the most important building blocks in organic synthesis due to their great versatility [1]. Among precedent synthetic methods for their preparation, hydrostannation reaction of alkynes with tributyltin hydride is the simplest and direct route to **1** [2]. In the non-fluorinated chemistry, there have been extensive studies on the reaction under a variety of reaction conditions, for example, transition metal-catalyzed hydrostannation [3] Lewis acid-catalyzed reaction [4] and Et_3B or AIBN-induced radical reaction [5] to succeed in the highly regio- and stereo-selectivity. In sharp contrast, only a few limited studies on the preparation and the applications of fluoroalkylated vinylstannanes have been reported thus far in spite of their great utility [6].[1] In this paper, we wish to describe a highly regio- and stereo-selective hydrostannation reaction of fluoroalkylated acetylenes.

2. Results and discussion

According to the literature [7],[2] the starting materials **1a-l** were prepared from commercially available 2-bromo-3,3,3-trifluoropropene **2a** or polyfluoroalcohol **2k**, **l** via the palladium-catalyzed coupling reaction of zinc acetylide with various aryl iodides (Scheme 1). Other acetylene, **1m** was prepared by dehydroiodination of vinyl iodide **3m**, obtained from the radical addition of trifluoromethyl iodide to the terminal acetylene [8].

In initial experiments, **1a** (Rf = CF_3, $R = p$-ClC_6H_4) was treated with 1.2 equiv. of Bu_3SnH in the presence of 20 mol% of tetrakis(triphenylphophine)palladium(0) ($Pd(PPh_3)_4$) in toluene at 0 °C for 4 h to afford the desired vinylstannanes **4** and **5** quantitatively, but in low regio- and stereo-selective manner (Table 1, Entry 1). Attempts to improve both regio- and stereo-selectivity by using $Pd(OAc)_2$ resulted in a high regio- and stereo-control, but moderate yield (Entry 2). Interestingly, an opposite regio-selectivity was observed when more sterically hindered $(o\text{-Tol})_3P$ was used as a ligand on palladium (Entry 4). Nickel-catalyzed hydrostannation reaction was more regio- and stereo-selective to

* Corresponding author. Tel.: +81-75-724-7573; fax: +81-75-724-7580.
E-mail address: konno@chem.kit.ac.jp (T. Konno).

[1] Hydrostannation of γ-trifluoromethylated propargyl alcohol has been reported.

[2] Recently, we have reported the easy access to various fluoroalkylated acetylene derivatives. Also other several synthetic methods for the preparation of fluoroalkylated alkynes have also been reported.

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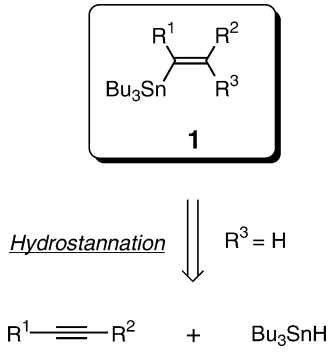
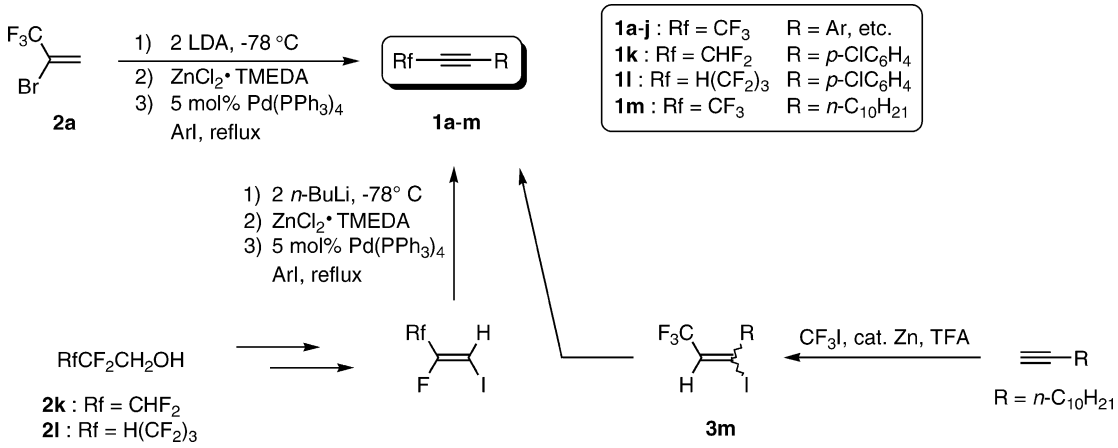


Fig. 1. Vinylstannanes **1**.

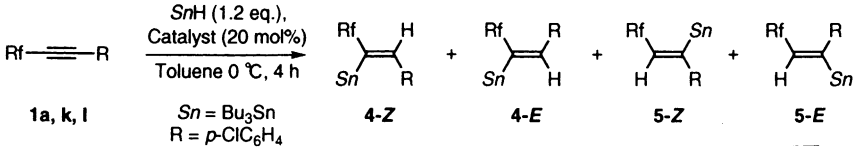
afford the vinylstannane as a single isomer, but in only 25% yield (Entry 5).

As described in Entry 6, Lewis acid-catalyzed hydrostannation proved also to be regio- and stereo-selective and gave the pure vinylstannane **4a-*Z*** in 71% isolated yield, although 11% of starting material still remained unreacted. Furthermore, the Et_3B-induced radical hydrostannation reaction resulted in the exclusive formation of **4a-*Z*** in almost quantitative yield (Entries 8–10) while the use of AIBN (Entry 7) at 80 °C instead of Et_3B gave a slight decrease of stereoselectivity (**4Z**/**4E** = 95/5). The high regio- and stereoselectivity were not influenced by the difference of the fluoroalkyl group such as difluoromethyl or hexafluoropropyl groups, as shown in Entries 9 and 10.



Scheme 1.

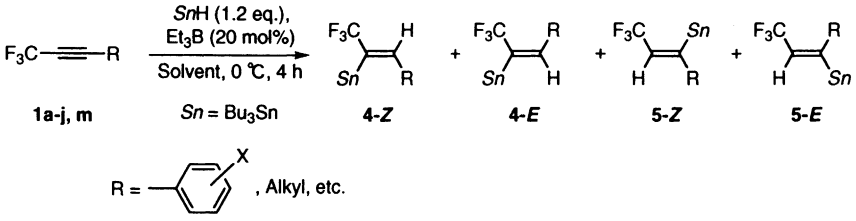
Table 1
Hydrostannation reaction of 1 ($R = p$-ClC_6H_4)



Entry	Catalyst (20 mol%)	Rf	Yield[a] (% of **4** and **5**)	Isomer ratio[b] **4** (*Z*:*E*):**5** (*Z*:*E*)	Recovery[c] (% of **1**)
1	$Pd(PPh_3)_4$	CF_3	quant (83)	71 (11:89):29 (24:76)	0
2	$Pd(OAc)_2$	CF_3	62	97 (89:11):3 (0:100)	22
3[b]	$Pd_2(dba)_3{\cdot}CHCl_3$	CF_3	34	87 (34:66):13 (0:100)	32
4[b]	$Pd_2(dba)_3{\cdot}CHCl_3$ +8(o-Tol)$_3$P	CF_3	96	31 (0:100):69 (0:100)	3
5	$Ni(acac)_2$	CF_3	25	100 (100:0):0	62
6	$ZrCl_4$	CF_3	74 (71)	100 (100:0):0	11
7	AIBN	CF_3	quant (95)	100 (95:5):0	0
8	Et_3B	CF_3	99 (95)	100 (100:0):0	0
9	Et_3B	HCF_2	99 (82)	100 (100:0):0	0
10	Et_3B	$HCF_2CF_2CF_2$	99 (98)	100 (100:0):0	0

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[b] Ten mol% of metal catalyst was used.
[c] The reaction was performed at the reflux temperature of benzene.

Table 2
Hydrostannation of various substituted aryl alkynes



Entry	*R*	Yield[a] (% of **4** and **5**)	Isomer ratio[b] **4** (*Z*:*E*):**5** (*Z*:*E*)	Recovery[b] (% of **1**)
1	*p*-ClC_6H_4 (**a**)	99 (95)	100 (100:0):0	0
2	*p*-MeC_6H_4 (**b**)	99 (91)	100 (98:2):0	0
3	*p*-$MeOC_6H_4$ (**c**)	99 (90)	100 (98:2):0	0
4	*o*-ClC_6H_4 (**d**)	69 (55)	100 (100:0):0	30
5	*o*-$MeOC_6H_4$ (**e**)	89	100 (100:0):0	11
6	*m*-ClC_6H_4 (**f**)	99 (92)	100 (100:0):0	0
7	Me_2PhSi (**g**)	99 (93)	98 (82:18):2 (0:100)	0
8	*n*-$C_{10}H_{21}$ (**m**)	32	100 (62:38):0	67
9	*p*-$EtO_2CC_6H_4$ (**h**)	78	35 (0:100):65 (0:100)	21
10[c]	*p*-$EtO_2CC_6H_4$ (**h**)	77	35 (0:100):65 (0:100)	23
11	*p*-$O_2NC_6H_4$ (**i**)	74	19 (0:100):81 (0:100)	26
12[c]	*p*-$O_2NC_6H_4$ (**i**)	64	17 (0:100):83 (0:100)	36
13	*p*-$F_3CC_6H_4$ (**j**)	46	33 (0:100):67 (0:100)	54

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[b] Determined by ^{19}F NMR.
[c] The reaction was performed at −78 °C.

We then examined the Et_3B-induced radical hydrostannation reaction of various substituted aryl alkynes **1a–j**, **m** as summarized in Table 2 and found the interest results that the regio- and stereo-selectivity were mostly influenced by the difference of the substituent X at the aromatic ring.

Thus, as shown in Entries 1–3, acetylene derivatives bearing a halogen atom or an electron-donating group as X could participate nicely in the present reaction to afford ***4Z*** exclusively. *Ortho*- or *meta*-substituted aryl alkynes were also applied efficiently for the radical hydrostannation, giving rise to the excellent regio- and stereo-selectivity (Entries 4–6), although the yield decreased in *ortho*-substituted aryl alkyne. It was found that **1g** in which the silyl group was directly combined with the acetylenic carbon, caused the decrease of the stereo-selectivity while the regioselectivity still remained excellent (Entry 7). The use of the acetylene bearing an alkyl group also led to unsatisfactory result (Entry 8). Interestingly, switching the substituent X from the electron-donating group to the electron-withdrawing group induced the significant change on the regio- and stereo-selectivity. Thus, by using the acetylenes bearing the ethoxycarbonyl, nitro, or trifluoromethyl groups as X, an opposite regio-selectivity was observed in favor of **5** (Entries 9, 11 and 13). Additionally, no ***Z*** isomer was detected. It should be noted that higher regio-selectivity was observed when the more electronwithdrawing group was employed as X (Entries 9 versus 11). Furthermore, the reaction proceeded relatively smoothly even at −78 °C to afford the same regio- and stereo-selectivity (Entries 10 and 12).

We next attempted the hydrostannation reaction in the absence of Et_3B as illustrated in Table 3.

The absence of Et_3B in the reaction of the acetylenes bearing a halogen atom at the aromatic ring caused a significant decrease of the yield (Entries 1–3). When the ethoxycarbonyl or nitro group was used as substituent X at the aromatic ring, on the other hand, the reaction proceeded smoothly to give the desired vinylstannanes in the almost same yield and selectivity as in the presence of Et_3B (Entries 4 and 5).

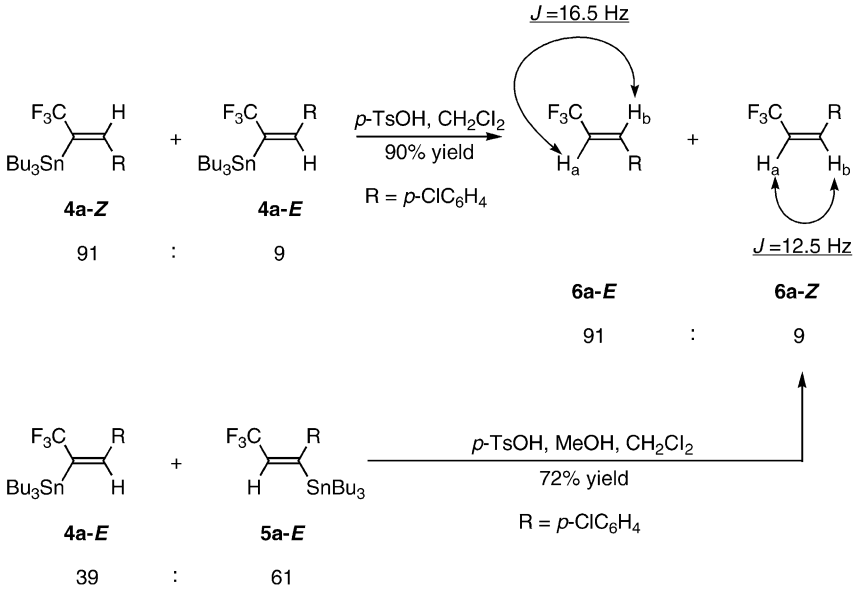
The regio- and stereo-chemical assignment of the products **4** or **5** was carried out as follows (Scheme 2).

Thus, the mixture of stereo-isomers **4a** in a ratio of 91:9 was treated with an excess amount of *p*-TsOH in CH_2Cl_2 at room temperature overnight to give the destannylated disubstituted alkenes **6a** in a ratio of 91:9 in 90% isolated yield.

Table 3
Hydrostannation reaction of 1 in the absence of Et_3B

Entry	*R*	Yield[a] (% of **4** and **5**)	Isomer ratio[a] **4** (*Z*:*E*):**5** (*Z*:*E*)	Recovery[a] (% of **1**)
1	*p*-ClC_6H_4 (**a**)	3	100 (100:0):0	97
2	*o*-ClC_6H_4 (**d**)	2	100 (100:0):0	98
3	*m*-ClC_9H_4 (**f**)	3	100 (100:0):0	97
4	*p*-$EtO_2CC_6H_4$ (**h**)	65	35 (0:100):65 (0:100)	35
5	*p*-$O_2NC_6H_4$ (**i**)	66	21 (0:100):79 (0:100)	34

[a] Determined by ^{19}F NMR.



Scheme 2.

^{1}H NMR analysis revealed that the vicinal coupling constants ($J_{Ha–Hb}$) of the major and minor isomers **6a** were 16.5 and 12.5 Hz, respectively, suggesting that the former and the latter possess ***E*** and ***Z*** configuration, respectively. Accordingly, the stereo-chemistry of major and minor isomers **4a** was determined as ***Z*** and ***E***, respectively. The similar treatment of the mixture of regio-isomers **4a**-***E*** and **5** in a ratio of 39:61 resulted in the exclusive formation of **6a**-***Z*** in 72% isolated yield, indicating that the vinylstannane **5** possesses ***E*** configuration.

Furthermore, the chemical shift of the vinylstannanes in ^{19}F NMR proved to be independent of the nature of the substituent X. In all cases, peaks for four regio- and stereo-isomers appeared approximately at 16 ppm (singlet), 23 ppm (singlet), 26 ppm (doublet), and 18 ppm (doublet). Based on the stereo-chemical assignment of **4a**-***Z*** (^{19}F NMR: 16 ppm), **4a**-***E*** (^{19}F NMR: 23 ppm), and **5a**-***E*** (^{19}F NMR: 18 ppm), the stereo-chemistry of the other vinylstannanes was determined as shown in Fig. 2.

A plausible mechanism for the present radical hydrostannation reaction is described in Scheme 3.

In the case of acetylenes bearing a halogen atom or the electron-donating group as X at the aromatic ring, tributyltin radical reacts with the acetylene **1** to give the corresponding vinyl radicals **Int**-**A**–**D**. Among four possible radicals, **Int**-**C** and **D** are more stable than the others **Int**-**A** and **B** due to the resonance effect of the benzene ring. Furthermore, it is highly possible that the tributyltin hydride comes to the side occupied by fluoroalkyl group, avoiding a bulkier tributylstannyl group due to a large steric repulsion. Therefore, the vinylstannane **4*Z*** was formed preferentially. When the electron-withdrawing group such as CO_2Et, NO_2, CF_3, was employed as a substituent at the aromatic ring, on the contrary, the reaction may proceed via an ionic four-centered transition state (**Int**-**E** or **F**). Presumably, tributyltin hydride may coordinate with the triple bond like **Int**-**F** because the electron density of the acetylenic carbon attached with a CF_3 moiety is lower than that of the other, leading to the preferential formation of **5*E***.

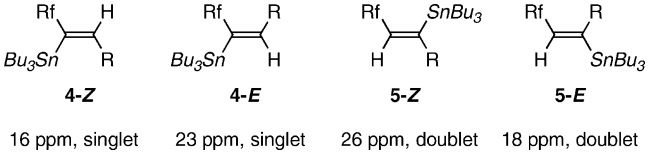


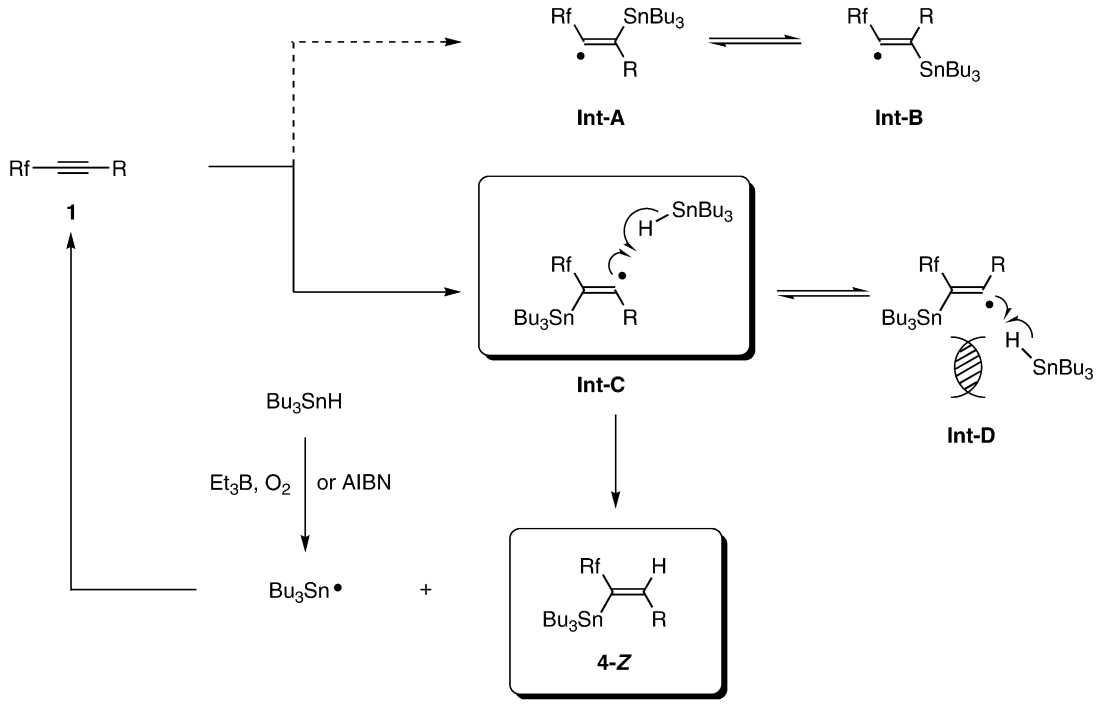
Fig. 2. Determination of stereo-chemistry of other vinylstannanes.

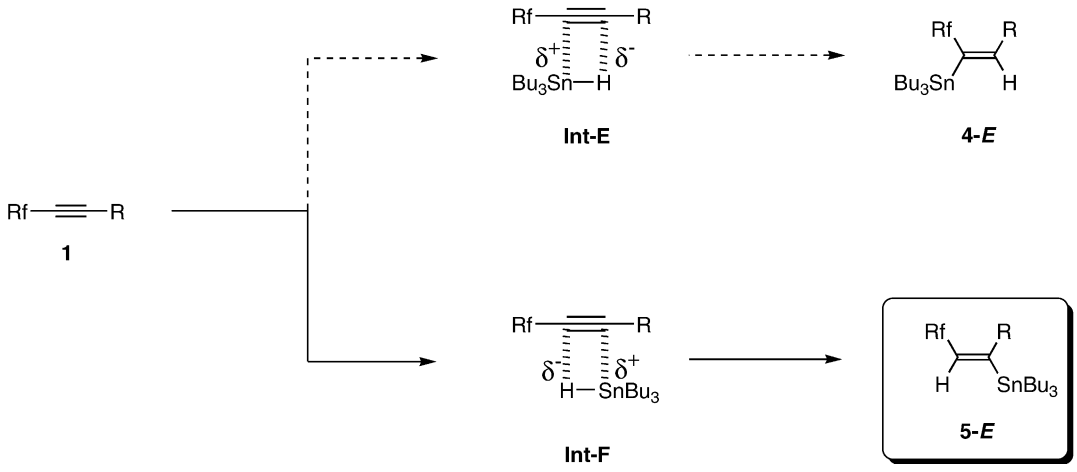
As the synthetic application, we attempted the coupling reaction [9] of the vinylstannane **4a**-***Z*** with various aryl iodides (Scheme 4).

The vinylstannane **4a**-***Z*** was treated with various halides in the presence of 10 mol% each of $Pd(PPh_3)_4$ and CuI in DMF at 70 °C. After stirring for 6 h, the stereo-chemical-defined trisubstituted alkenes **7** were obtained in good to excellent yields with retention of the olefinic configuration.

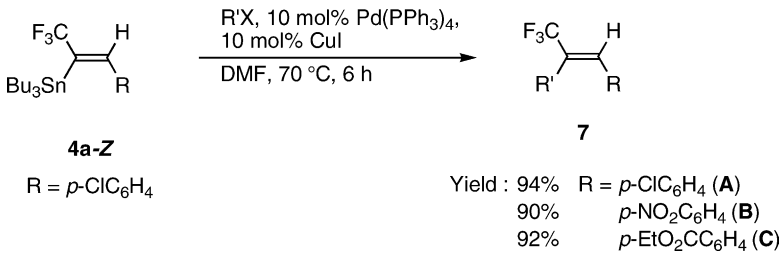
3. Conclusion

In summary, we have examined the hydrostannation reaction of fluoroalkylated acetylene derivatives with tributyltin hydride under the various reaction conditions. The Et_3B-induced radical reaction was especially efficient, and the high level of selectivity was obtained when the reaction was carried out at 0 °C in toluene. Interestingly, the difference of the substituent X at the aromatic ring in the aryl acetylenes could significantly cause the large influence on the regio- and stereo-selectivity. Thus, the reaction proceeded via vinyl radical intermediate to afford the *trans*-adduct **4*Z*** exclusively in the case of a halogen atom or an





Scheme 3.



Scheme 4.

electron-donating group as X. On the other hand, the use of an electron-withdrawing group as X lead to ionic four centered-transition state, giving rise to the preferential formation of *cis*-adduct **5*E***.

The vinylstannanes could also be condensed with various aryl iodides in the presence of a catalytic amount of $Pd(PPh_3)_4$ to afford the stereo-chemical-defined trisubstituted alkenes in high yields.

4. Experimental

4.1. General experimental procedures

^1H NMR spectra were measured with Bruker DRX (500.13 MHz) spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane (Me_4Si) as an internal reference. ^{13}C NMR spectra were recorded on a Bruker DRX (125.77 MHz). A Nippondenshi JNM-EX90F (84.21 MHz, FT) spectrometer was used for determining ^{19}F NMR yield with internal C_6F_6. It was used for determining regio- and stereo-selectivity and was used for taking ^{19}F NMR spectra in a $CDCl_3$ solution with internal $CFCl_3$ too. $CFCl_3$ was used ($\delta_F = 0$) as an internal standard for ^{19}F NMR. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8200A (PC) spectrophotometer. Mass spectra (MS) were taken on a Nippondenshi JMS-700.

4.1.1. Materials

Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone kethyl. Toluene was freshly distilled from calcium hydride (CaH_2). Butyllithium (1.6 M hexane solution) was commercially available from Wako chemicals. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. Thin layer chromatography (TLC) was done with Merck silica gel 60 F_{254} plates, and column chromatography was carried out with Wako gel C-200.

4.2. Representative synthetic procedures

4.2.1. Hydrostannation of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (*1a*) using zirconium chloride ($ZrCl_4$) as catalyst

To a solution of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne **1a** (0.204 g, 1.0 mmol) and tributyltin hydride (0.349 g, 1.2 mmol) in toluene (4.0 ml) was added zirconium(IV) chloride ($ZrCl_4$) (0.046 g, 0.2 mmol) at 0 °C (ice bath) and the whole solution was stirred for 4 h. The reaction mixture was passed through silica gel which was treated with the basic solution (triethylamine:hexane = 1:100) for removal of $ZrCl_4$. The mixture was concentrated in vacuo, and the residue was chromatographed on silica gel under the basic condition as described above to afford tri-*n*-butyl[(*Z*)-2-(4-chlorophenyl)-1-trifluoromethylethenyl]stannane **4a-*Z*** (0.352 g, 0.71 mmol) (71%).

4.2.2. Hydrostannation of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (*1a*) using azobisisobutylonitrile (AIBN) as catalyst

To a solution of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne **1a** (0.204 g, 1.0 mmol) and tributyltin hydride (0.349 g, 1.2 mmol) in benzene (4.0 ml) was added 2,2′-azobisisobutyronitrile and the whole solution was stirred for 4 h at the reflux temperature of benzene. The reaction mixture was quenched with $NaHCO_3$ aq. and extracted with Et_2O three times. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica gel which was treated with the basic solution (triethylamine:hexane = 1:100) to afford tri-*n*-butyl[(*Z*)-2-(4-chlorophenyl)-1-trifluoromethylethenyl]stannane **4a-*Z*** (0.471 g, 0.95 mmol) (95%).

4.2.3. Hydrostannation of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (*1a*) using triethylborane (Et_3B) as catalyst

To a solution of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne **1a** (0.204 g, 1.0 mmol) and tributyltin hydride (0.349 g, 1.2 mmol) in toluene (4.0 ml) was added 0.2 ml (0.2 mmol) of Et_3B (1.0 M hexane solution) at 0 °C (ice bath) and the whole solution was stirred for 4 h. The reaction mixture was quenched with 2,6-di-*tert*-butyl-4-methylphenol (BHT) and extracted with Et_2O three times. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica gel which was treated with the basic solution (triethylamine:hexane = 1:100) to afford tri-*n*-butyl[(*Z*)-2-(4-chlorophenyl)-1-trifluoromethylethenyl]stannane **4a-*Z*** (0.47 g, 0.95 mmol) (95%).

*4.2.3.1. Tri-n-butyl[(Z)-2-(4-chlorophenyl)-1-trifluoromethylethenyl]stannane (**4a-Z**).* Yield 95%; ^1H NMR ($CDCl_3$) δ 0.85 (15H, t, $J = 7.3$ Hz), 1.23 (6H, sex., $J = 7.3$ Hz), 1.36 (6H, quint, $J = 7.8$ Hz), 7.18 (2H, d, $J = 8.5$ Hz), 7.34 (2H, d, $J = 8.5$ Hz), 7.84 (1H, d, $J = 2.0$ Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 11.40, 13.53, 27.10, 28.62, 126.97 (q, $J = 273.3$ Hz), 128.58, 129.10, 134.56, 136.57, 137.43 (q, $J = 32.2$ Hz), 145.58 (q, $J = 10.6$ Hz); ^{19}F NMR ($CDCl_3$) δ −59.39 (3F, s) ppm; IR (neat) ν 2959 (s), 2924 (s), 2874 (m), 2855 (m), 1612 (m), 1489 (m), 1462 (w), 1258 (s), 1211 (w), 1138 (s), 1111 (s), 1015 (w), 899 (w), 818 (w), 671 (w) cm^{-1}.

*4.2.3.2. Tri-n-butyl[(Z)-2-(4-methylphenyl)-1-trifluoromethylethenyl]stannane (**4b-Z**).* Yield 91%; ^1H NMR ($CDCl_3$) δ 0.83 (15H, t, $J = 7.2$ Hz), 1.22 (6H, sex., $J = 7.3$ Hz), 1.36 (6H, quint, $J = 7.8$ Hz), 2.36 (3H, s), 7.14 (4H, dd, $J = 12$ Hz), 7.8 (1H, d, $J = 2.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 11.36, 13.53, 21.23, 27.11, 28.64, 127.25 (q, $J = 272.5$ Hz), 127.69, 129, 135.24, 135.35 (q, $J = 28.1$ Hz), 138.48, 146.92 (q, $J = 10.5$ Hz); ^{19}F NMR ($CDCl_3$) δ −58.97 (3F, s); IR (neat) ν 2958 (s), 2923 (s), 2854 (m), 1620 (w), 1508 (w), 1461 (w), 1257 (s), 1218 (w), 1134 (s), 1107 (s), 810 (w) cm^{-1}.

*4.2.3.3. Tri-n-butyl[(Z)-2-(4-methoxyphenyl)-1-trifluoromethylethenyl]stannane (**4c-Z**).* Yield 90%; ^{1}H NMR ($CDCl_3$) δ 0.82–0.87 (15H, m), 1.23 (6H, sex., $J = 7.3$ Hz), 1.37 (6H, quint, $J = 7.8$ Hz), 3.82 (3H, s), 6.87 (2H, d, $J = 9.0$ Hz), 7.19 (2H, d, $J = 8.5$ Hz), 7.83 (1H, d, $J = 2.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 11.37, 13.55, 27.11, 28.65, 55.32, 113.75, 127.34 (q, $J = 271$ Hz), 129.19, 130.51, 134.19 (q, $J = 31.63$ Hz), 146.5 (q, $J = 10.6$ Hz), 159.99; ^{19}F NMR ($CDCl_3$) δ −58.68 (3F, s); IR (neat) ν 2923 (s), 2854 (m), 1608 (m), 1512 (s), 1461 (w), 1253 (s), 1215 (w), 1176 (w), 1134 (s), 1103 (s), 1037 (w), 825 (w) cm^{-1}.

*4.2.3.4. Tri-n-butyl[(Z)-2-(2-chlorophenyl)-1-trifluoromethylethenyl]stannane (**4d-Z**).* Yield 55%; ^{1}H NMR ($CDCl_3$) δ 0.78 (6H, t, $J = 8.5$ Hz), 0.84 (9H, t, $J = 7.2$ Hz), 1.21 (6H, sex., $J = 7.3$ Hz), 1.35 (6H, quint, $J = 7.8$ Hz), 7.2 (1H, d, $J = 7.0$ Hz), 7.26 (1H, t, $J = 7.2$ Hz), 7.3 (1H, t, $J = 7.6$ Hz), 7.39 (1H, d, $J = 8$ Hz), 7.88 (1H, d, $J = 2.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 11.24, 13.52, 27.12, 28.53, 126.61, 126.78 (q, $J = 272.5$ Hz), 129.34, 129.39, 129.88, 133.76, 136.83, 138.22 (q, $J = 31.8$ Hz), 144.6 (q, $J = 10.6$ Hz); ^{19}F NMR ($CDCl_3$) δ −59.63 (3F, s); IR (neat) ν 2958 (s), 2923 (s), 2854 (s), 1616 (w), 1465 (w), 1442 (w), 1257 (s), 1215 (w), 1137 (s), 1110 (s), 1056 (w), 756 (s) cm^{-1}.

*4.2.3.5. Tri-n-butyl[(Z)-2-(2-methoxylphenyl)-1-trifluoromethylethenyl]stannane (**4e-Z**).* Yield 89%; ^{1}H NMR ($CDCl_3$) δ 0.79 (6H, t, $J = 5.7$ Hz), 0.83 (9H, t, $J = 7.5$ Hz), 1.21 (6H, sex., $J = 7.3$ Hz), 1.35 (6H, quint, $J = 7.8$ Hz), 3.82 (3H, s), 6.85 (1H, d, $J = 6.8$ Hz), 6.9 (1H, t, $J = 7.2$ Hz), 7.1 (1H, d, $J = 7.0$ Hz), 7.3 (1H, t, $J = 10$ Hz), 7.9 (1H, d, $J = 2.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 11.26, 13.55, 27.15, 28.58, 55.27, 110.16, 120.15, 127.36, 127.34 (q, $J = 272.36$ Hz), 128.73, 130.16, 135.38 (q, $J = 32.24$ Hz), 144.07 (q, $J = 10.7$ Hz), 157.37; ^{19}F NMR ($CDCl_3$) δ −58.92 (3F, s); IR (neat) ν 2923 (s), 2854 (m), 1596 (m), 1488 (m), 1461 (m), 1434 (w), 1261 (s), 1134 (s), 1107 (s), 1029 (w), 752 (m) cm^{-1}.

*4.2.3.6. Tri-n-butyl[(Z)-2-(3-chlorophenyl)-1-trifluoromethylethenyl]stannane (**4f-Z**).* Yield 92%; ^{1}H NMR ($CDCl_3$) δ 0.83–0.87 (15H, m), 1.23 (6H, sex., $J = 7.3$ Hz), 1.37 (6H, quint, $J = 7.7$ Hz), 7.12 (1H, d, $J = 7.5$ Hz), 7.25 (1H, s), 7.28–7.33 (2H, m), 7.83 (1H, d, $J = 2.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 11.39, 13.53, 27.10, 28.60, 126.08, 126.88 (q, $J = 273.29$ Hz), 127.66, 128.49, 129.66, 134.41, 138.27 (q, $J = 32.09$ Hz), 139.94, 145.3 (q, $J = 10.75$ Hz) ppm; ^{19}F NMR ($CDCl_3$) δ −59.60 (3F, s); IR (neat) ν 2958 (s), 2923 (s), 2854 (m), 1566 (w), 1465 (m), 1419 (w), 1261 (s), 1215 (w), 1137 (s), 1110 (s), 1076 (w), 941 (w), 875 (w), 783 (w) cm^{-1}; MS (FAB) *m/z* (relative intensity) 435 (35) Calcd for $C_{21}H_{32}{}^{35}ClF_3{}^{116}Sn$ 494.1167.

*4.2.3.7. Tri-n-butyl[2-dimethylphenylsilyl-1-trifluoromethylethenyl]stannane (**4g**).* Yield 93%; ^{1}H NMR ($CDCl_3$) δ 0.44 (6H, s), 0.82–1.02 (15H, m), 1.22–1.52 (12H, m), 7.36–7.39 (4H, m), 7.5 (2H, d, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$) δ −1.19, 11.45, 13.57, 27.17, 28.70, 125.93 (q, $J = 274.31$ Hz), 127.9, 129.43, 133.93, 137.52, 148.56 (q, $J = 7.7$ Hz), 152.54 (q, $J = 32.35$ Hz); IR (neat) ν 2958 (s), 2923 (s), 2854 (m), 1461 (w), 1427 (w), 1377 (w), 1296 (w), 1234 (s), 1207 (w), 1141 (s), 1110 (s), 1076 (w), 875 (m), 837 (m), 817 (m), 783 (w), 729 (w), 698 (w) cm^{-1}; MS (FAB) *m/z* (relative intensity) 459 (36) Calcd for $C_{23}H_{39}F_3Si^{116}Sn$ 518.1795.

Z isomer (major): ^{19}F NMR ($CDCl_3$) δ −62.74 (3F, s), −63.94 (3F, d).

E isomer (minor): ^{19}F NMR ($CDCl_3$) δ −57.16 (3F, s).

*4.2.3.8. Tri-n-butyl[2-(4-ethoxycarbonylphenyl)-1-trifluoromethylethenyl]stannane (**4h-E** and **5h-E**).* Yield 93%; ^{1}H NMR ($CDCl_3$) 0.8–1.1 (18H, m), 1.21–1.61 (12H, m), 4.33–4.4 (2H, m); IR (neat) ν 2927 (s), 2854 (m), 1720 (s), 1604 (m), 1461 (m), 1365 (w), 1272 (s), 1226 (m), 1176 (m), 1107 (s), 1022 (m), 806 (w) cm^{-1}; MS (EI) *m/z* (relative intensity) 532 (7.7), 477 (100), 476 (40.6), 475 (76.1), 474 (31.5), 174 (26.9) Calcd for $C_{24}H_{37}F_3O_2{}^{116}Sn$ 532.1768, Found: 532.1722.

Major (**5h-*E***): ^{1}H NMR ($CDCl_3$) δ 5.88 (1H, q, $J = 9.3$ Hz), 6.99 (2H, d, $J = 8$ Hz), 7.98 (2H, d, $J = 8$ Hz); ^{19}F NMR ($CDCl_3$) δ −58.25 (3F, d, $J = 8.7$ Hz).

Minor (**4h-*E***): ^{1}H NMR ($CDCl_3$) δ 6.99 (1H, s), 7.38 (2H, d, $J = 8$ Hz), 8.01 (2H, d, $J = 8$ Hz); ^{19}F NMR ($CDCl_3$) δ −52.21 (3F, s).

*4.2.3.9. Tri-n-butyl[2-(4-nitrophenyl)-1-trifluoromethylethenyl]stannane (**4i-E** and **5i-E**).* Yield 74%; ^{1}H NMR ($CDCl_3$) δ 0.76–1.05 (15H, m), 1.17–1.59 (12H, m); ^{13}C NMR ($CDCl_3$) δ 10.42, 13.53, 27.16, 28.64, 123.25 (q, $J = 244$ Hz), 123.32, 123.55, 125.38, 126.13 (q, $J = 31.94$ Hz), 150.18, 160.02 (q, $J = 7$ Hz); IR (neat) ν 2927 (s), 2854 (s), 1593 (s), 1519 (s), 1461 (w), 1346 (s), 1269 (s), 1222 (w), 1180 (w), 1137 (s), 906 (w), 856 (w), 690 (w) cm^{-1}; MS (EI+) *m/z* (relative intensity) 450 (100) Calcd for $C_{21}H_{32}F_3NO_2{}^{116}Sn$ 503.1403, Found: 503.1403.

Major (**5i-*E***): ^{1}H NMR ($CDCl_3$) δ 5.85 (1H, q, $J = 7.6$ Hz), 6.99 (2H, d, $J = 9$ Hz), 8.1 (2H, d, $J = 8.5$ Hz); ^{19}F NMR ($CDCl_3$) δ −57.92 (3F, d, $J = 8.8$ Hz).

Minor (**4i-*E***): ^{1}H NMR ($CDCl_3$) δ 6.92 (1H, s), 7.38 (2H, d, $J = 10$ Hz), 8.12 (2H, d, $J = 11$ Hz); ^{19}F NMR ($CDCl_3$) δ −51.8 (3F, s).

*4.2.3.10. Tri-n-butyl[2-(4-trifluoromethylphenyl)-1-trifluoromethylethenyl]stannane (**4j-E** and **5j-E**).* Yield 46%; ^{1}H NMR ($CDCl_3$) δ 0.81–1.1 (15H, m), 1.23–1.57 (12H, m); IR (neat) ν 2927 (s), 2854 (m), 1612 (m), 1461 (m), 1326 (s), 1272 (m), 1222 (w), 1130 (s), 1068 (m), 1018 (m), 906 (w), 840 (w) cm^{-1}; MS (FAB) *m/z* (relative intensity) 469 (57) Calcd for $C_{22}H_{32}F_6{}^{116}Sn$ 528.1430.

Major isomer (**5j-*E***): ^{1}H NMR ($CDCl_3$) δ 5.9 (1H, q, $J = 7.6$ Hz), 7.03 (2H, d, $J = 8$ Hz), 7.53 (2H, d, $J = 8$ Hz); ^{19}F NMR ($CDCl_3$) δ −63.86 (3F, s), −58.65 (3F, d, $J = 8.7$ Hz).

Minor isomer (**4j**-***E***): ^{1}H NMR ($CDCl_3$) δ 6.97 (1H, s), 7.42 (2H, d, $J = 8.5$ Hz), 7.59 (2H, d, $J = 8.5$ Hz); ^{19}F NMR ($CDCl_3$) δ −64.15 (3F, s), −53.06 (3F, s).

*4.2.3.11. Tri-n-butyl[(Z)-2-(4-chlorophenyl)-1-difluoromethylethenyl]stannane (**4k**-**Z**).* Yield 82%; ^{1}H NMR ($CDCl_3$) δ 0.82–0.88 (15H, m), 1.23 (6H, sex., $J = 7.2$ Hz), 1.37 (6H, quint, $J = 7.7$ Hz), 6.15 (1H, t, $J = 59.76$ Hz), 7.18 (2H, d, $J = 8.5$ Hz), 7.32 (2H, d, $J = 8.5$ Hz), 7.5 (1H, t, $J = 5$ Hz); ^{13}C NMR ($CDCl_3$) δ 11.21, 13.56, 27.13, 28.76, 121.44 (t, $J = 233.31$ Hz), 128.48, 129.07, 134.21, 136.99, 142.96 (t, $J = 33.5$ Hz), 145.92 (t, $J = 17.56$ Hz); ^{19}F NMR ($CDCl_3$) δ −93.93 (2F, d); IR (neat) ν 2923 (s), 2854 (m), 1612 (w), 1488 (m), 1461 (w), 1373 (w), 1141 (m), 1064 (m), 1014 (m), 891 (w), 817 (w) cm^{-1}.

*4.2.3.12. Tri-n-butyl[(Z)-2-(4-chlorolphenyl)-1-hexafluorohexylethenyl]stannane (**4l**-**Z**).* Yield 98%; ^{1}H NMR ($CDCl_3$) δ 0.79 (6H, t, $J = 8.5$ Hz), 0.84 (9H, t, $J = 7.2$ Hz), 1.22 (6H, sex., $J = 7.2$ Hz), 1.33 (6H, quint, $J = 7.8$ Hz), 6.05 (1H, tt, $J = 52.2$ Hz), 7.18 (2H, d, $J = 8.0$ Hz), 7.34 (2H, d, $J = 8.0$ Hz), 7.78 (1H, s); ^{13}C NMR ($CDCl_3$) δ 12.14, 13.51, 27.10, 28.60, 102–110.5 (3C, m), 128.53, 129.2, 134.55, 136.94, 137.5 (t, $J = 31.43$ Hz), 148.75 (t, $J = 13.83$ Hz); ^{19}F NMR ($CDCl_3$) δ −101.38 (2F, s), −128.71 (2F, s), −136.86 (2F, d, $J = 52.8$ Hz) ppm; IR (neat) ν 2923 (s), 2854 (m), 1604 (w), 1488 (m), 1461 (w), 1400 (w), 1253 (w), 1134 (s), 1095 (m), 995 (m), 879 (w), 821 (m), 759 (m) cm^{-1}; MS (FAB) *m/z* (relative intensity) 517.05 (23) Calcd for $C_{23}H_{33}{}^{35}ClF_6{}^{116}Sn$ 576.1197.

*4.2.3.13. Tri-n-butyl(2-decanyl-1-trifluoromethylethenyl)-stannane (**4m**).* Yield 32%; The product could not be inseparable with tributyltin hydride, so that the observed unique signal for **4m** is shown as follows:

Major isomer (**4m**-***Z***): ^{1}H NMR ($CDCl_3$) δ 0.89 (12H, t, $J = 7.0$ Hz) 0.96 (8H, t, $J = 8.2$ Hz) 1.30 (8H, sex., $J = 7.5$ Hz) 1.49 (20H, quint, $J = 8.0$ Hz) 5.97 (1H, t, $J = 7.50$ Hz). ^{19}F NMR ($CDCl_3$) δ −62.88 (s).

Minor isomer (**4m**-***E***): ^{19}F NMR ($CDCl_3$) δ −56.05 (s).

*4.2.4. Synthesis of 1-trifluoromethyl-2-(4-chlorophenyl)-ethene (**6**)*

The tri-*n*-butyl[(*Z*)-2-(4-chlorophenyl)-1-trifluoromethylethenyl]stannane **4a** (0.19 g, 0.38 mmol) was added to *p*-TsOH·H_2O (0.1 g, 0.575 mmol) in CH_2Cl_2 (5.0 ml) at room temperature and the whole solution was stirred for overnight. The reaction mixture was quenched with $NaHCO_3$ aq. and extracted with CH_2Cl_2 three times and the organic layer was dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (hexane only) to afford 1-trifluoromethyl-2-(4-chlorophenyl)ethene **6a**-***E*** and **6a**-***Z*** (0.07 g, 0.345 mmol).

*4.2.4.1. 1-Trifluoromethyl-2-(4-chlorophenyl)ethene (**6a**-**E** and **6a**-**Z**).* Yield 90%; ^{13}C NMR ($CDCl_3$) δ 116.13 (q, $J = 33.95$ Hz), 123.4 (q, $J = 268.9$ Hz), 128.7, 129.1, 131.8, 135.9, 136.3 (q, $J = 6.5$ Hz); IR (neat) ν 1666 (s), 1596 (w), 1492 (s), 1407 (w), 1315 (s), 1276 (s), 1203 (w), 1126 (s), 1014 (w), 972 (s), 945 (w), 837 (s), 810 (w), 705 (w) cm^{-1}; MS (EI) *m/z* (relative intensity) 206 (100, M^+), 171 (20.6), 137 (7.6), 102 (5.5) Calcd for $C_9H_6{}^{35}ClF_3$ 206.0110, Found: 206.0108.

E isomer (major isomer, **6a**-***E***): ^{1}H NMR ($CDCl_3$) δ 6.17 (1H, dq, $J = 17.6$ Hz), 7.10 (1H, dq, $J = 16.1$ Hz), 7.37 (4H, dd, $J = 11.5$ Hz); ^{19}F NMR ($CDCl_3$) δ −63.97 (3F, dd, J =6.6 Hz).

Z isomer (minor isomer, **6a**-***Z***): ^{1}H NMR ($CDCl_3$) δ 5.78 (1H, dq, $J = 12.5$ Hz), 6.86 (1H, d, $J = 12.5$ Hz), 7.33 (4H, d, $J = 2$ Hz) ppm; ^{19}F NMR ($CDCl_3$) δ −58.14 (3F, d, $J = 8.8$ Hz).

*4.2.5. Coupling reaction of tri-n-butyl[(Z)-2-(4-chlorophenyl)-1-trifluoromethylethenyl]-stannane (**4a**-**Z**) with various halides*

To a solution of tri-*n*-butyl[(*Z*)-2-(4-chlorophenyl)-1-trifluoromethylethenyl]stannane **4a**-***Z*** (0.149 g, 0.30 mmol), 4-chloroiodobenzene (0.086 g, 0.36 mmol) and copper (I) iodide (0.006 g, 0.03 mmol) in DMF (4.0 ml) was added $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol) and the whole solution was stirred for 4 h at 70 °C. The reaction mixture was quenched with NH_4Cl aq. and extracted with Et_2O three times. After evaporation of the organic layer, the residue was diluted with ether, and the whole solution was treated with KF aqueous solution at room temperature for 30 min. The reaction mixture was filtrated and extracted with Et_2O three times and the organic layer was dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (hexane only) to afford (*E*)-1,2-bis(4-chlorophenyl)-3,3,3-trifluoropropene **7** (0.076 g, 0.24 mmol).

*4.2.5.1. (**E**)-1,2-Bis(4-chlorophenyl)-3,3,3-trifluoropropene (**7A**).* Yield 80%; ^{1}H NMR ($CDCl_3$) δ 6.96 (2H, d, $J = 8.5$ Hz), 7.18 (2H, d, $J = 8.5$ Hz), 7.21 (1H, s), 7.23 (2H, d, $J = 8.5$ Hz), 7.39 (2H, d, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 123.39 (q, $J = 273.4$ Hz), 128.70, 129.43, 129.73 (q, $J = 89.4$ Hz), 130.68, 131.16, 131.18, 131.61, 132.52 (q, $J = 16.2$ Hz), 135.10, 135.22.

*4.2.5.2. (**E**)-1-(4-Chlorophenyl)-2-(4-nitrophenyl)-3,3,3-trifluoropropene (**7B**).* Yield 90%; ^{1}H NMR ($CDCl_3$) δ 6.93 (2H, d, $J = 8.5$ Hz), 7.17 (2H, d, $J = 8.5$ Hz), 7.31 (1H, d, $J = 1.0$ Hz), 7.31 (2H, d, $J = 8.5$ Hz), 8.26 (2H, d, $J = 9.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 123.06 (q, $J = 273.6$ Hz), 124.20, 124.80, 128.90, 130.95, 131.08, 131.11, 133.80 (q, $J = 5.5$ Hz), 135.61, 138.62, 148.15; ^{19}F NMR ($CDCl_3$) δ −65.83 (3F, s).

*4.2.5.3. (**E**)-1-(4-Chlorophenyl)-2-(4-ethoxycarbonylphenyl)-3,3,3-trifluoropropene (**7C**).* Yield 92%; ^{1}H NMR ($CDCl_3$) δ 1.41 (3H, t, 6.96 $J = 7.0$ Hz), 4.41 (2H, q, $J = 7.2$ Hz), 6.92 (2H, d, $J = 8.5$ Hz), 7.14 (2H, d, $J = 8.5$ Hz),

7.23 (1H, s), 7.36 (2H, d, $J = 8.0$ Hz), 8.07 (2H, d, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.29, 61.24, 123.33 (q, $J = 273.0$ Hz), 128.70, 129.90, 130.09 (q, $J = 29.7$ Hz), 130.19, 131.03, 131.17, 131.17, 131.49, 132.68 (q, $J = 5.8$ Hz), 135.16, 136.94, 166.00; ^{19}F NMR ($CDCl_3$) δ −66.14 (3F, s).

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