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Stereodivergent Hydrosilylation, Hydrostannylation, and Hydrogermylation of α-Trifluoromethylated Alkynes and Their Synthetic Applications

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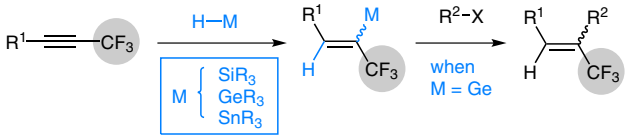
Dedicated to the memory of Jean-François Normant, an outstanding scientist and artist



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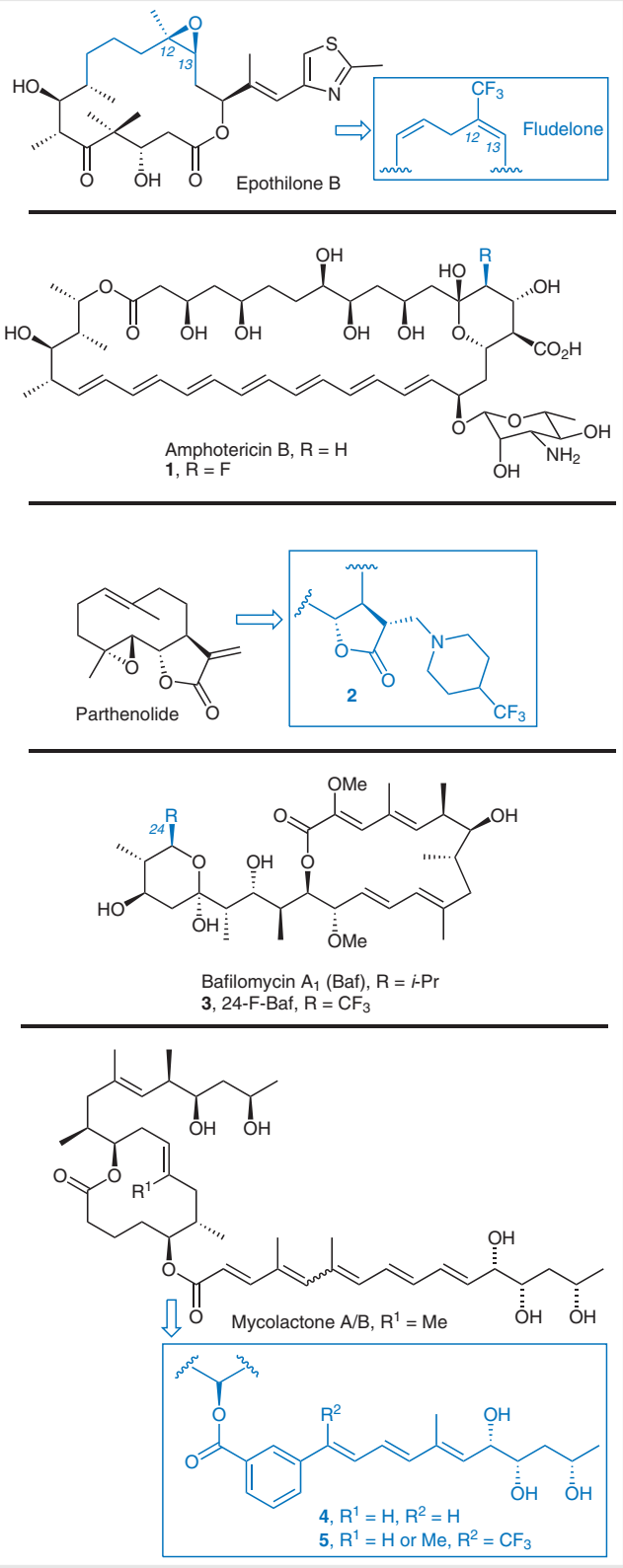
Abstract Stereoselective hydrometalation reactions of aryl- and alkyl-substituted trifluoromethylated alkynes with triethylsilane, tributylstannane, and triphenylgermane have been investigated. (*E*)-α-CF_3-Vinylsilanes, -stannanes, and -germanes were obtained under palladium-catalyzed conditions whereas the corresponding (*Z*)-α-CF_3-vinylgermanes were obtained under radical conditions. These reactions proceed in good to excellent yields and possess a broad functional group tolerance. Applications of the (*Z*)- and (*E*)-α-CF_3-vinylgermanes in palladium-catalyzed cross-coupling reactions with aryl halides having diverse electronic requirements were also investigated. The corresponding (*Z*)- and (*E*)-α-CF_3-styrenes were obtained as single isomers, thus demonstrating the utility of these versatile synthons for the synthesis of stereodefined trifluoromethylated alkenes.

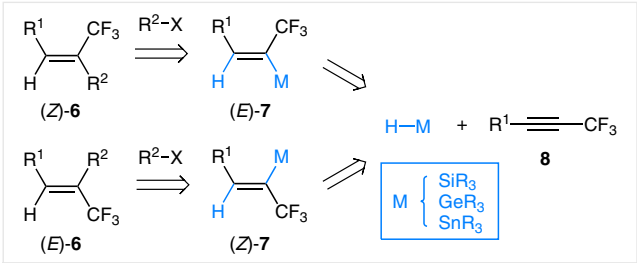
Key words hydrosilylation, hydrostannylation, hydrogermylation, trifluoromethylated alkynes, trifluoromethylated alkenes, fluorinated probes, natural products

The selective introduction of fluorine and fluoroalkyl substituents into organic molecules has been central to the fine modulation of their physicochemical as well as biological activities and has found applications in numerous areas of our daily life, ranging from material to life sciences.[1] In particular, the structural editing of natural products with fluorinated motifs can lead to improved biological activities, as exemplified in the epothilone series wherein the C12–C13 trisubstituted epoxide of the natural product was replaced by a (*E*)-trifluoromethyl-substituted alkene in fludelone, thereby enhancing the therapeutic index of this promising antimitotic compound (Scheme 1).[2] In addition, incorporation of ^{19}F atoms into natural product derivatives is also a unique strategy to investigate the biological mechanisms that the latter induce by multinuclear NMR owing to the magnetic properties of the fluorine atom.[3] Representative examples of such a fascinating endeavor have been reported in fluorinated probes **1**, **2**, and **3** derived from amphotericin,[4] parthenolide,[5] or bafilomycin, respectively (Scheme 1).[6] For the past few years, we have been investigating Buruli ulcer, a neglected human mycobacterial disease caused by mycolactones A/B, the exotoxins of *Mycobacterium ulcerans*.[7] We have reported several synthetic strategies to finely modulate the different sectors of these macrolides.[8] The resulting library of mycolactone analogues contributed not only to the elucidation of the structure–activity relationships of these macrolides,[9] but also to the discovery that certain simplified analogues were able to bind and activate a sub-domain of one of the proteic target of mycolactone, the N-WASP protein.[8b,10] To gain more insight into the physical interactions of mycolactones and their biological targets, the use of fluorinated mycolactones probes should prove very useful in structural biology investigations using NMR spectroscopy. Following the lead of the epothilone series, the stereoselective introduction of (*E*)- and (*Z*)-trisubstituted trifluoromethylated alkenes in the mycolactones scaffolds, as in **5**, which is related to the previously reported analogue **4**, was investigated on model substrates.



Scheme 1 Selection of fluorinated analogues of natural products

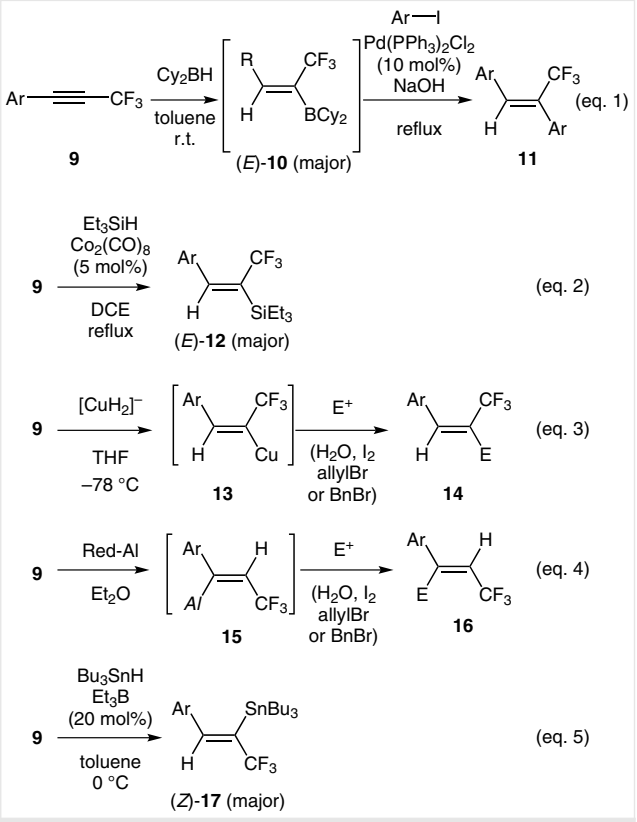
Trifluoromethylated alkenes can be prepared with moderate selectivity by a fluorine-induced Horner–Wadsworth–Emmons olefination reaction,[11] by transition-metal-mediated electrophilic trifluoromethylation of alkenyl halides, vinylboron, vinyl halides (and pseudo-halides) or acrylic acids,[12] by radical processes,[13] and by direct transition-metal-catalyzed sp^2 C–H bond trifluoromethylation.[14] Another strategy for the stereoselective synthesis of the challenging trisubstituted trifluoromethylated alkenes **6** would call for the cross-coupling of a (*Z*)- or (*E*)-α-CF_3-vinylmetal species **7** that, in turn, could be obtained from the stereoselective hydrometalation of α-CF_3-alkynes **8** (Scheme 2).



Scheme 2 Synthetic blueprints for the synthesis of trifluoromethylated alkenes **6** from trifluoromethylated alkynes via regio- and stereoselective hydrometalation and cross-coupling reactions

Indeed, hydrometalation reactions of α-CF_3-alkynes[15] have the potential to craft, in a single step, valuable α-CF_3-vinylmetal building blocks, either partners of metal-catalyzed cross-couplings or precursors of the corresponding α-CF_3-vinyl halides. Provided that the regio- and stereoselectivity of the hydrometalation could be controlled, this strategy would afford a straightforward entry into the selective formation of polysubstituted CF_3-alkenes.[16] Among the reports of hydrometalation of α-CF_3-alkynes, Konno has described that hydroboration of aryl-substituted α-CF_3-alkynes **9** proceeded mainly with (*Z*)-stereoselectivity and that the intermediate vinylborane **10** could be submitted to Suzuki–Miyaura cross-coupling with aryl iodides (Scheme 3, eq. 1).[17] Similarly, hydrosilylation of **9** (aryl-, benzyl- or propargyl-substituted) was efficiently catalyzed by $Co_2(CO)_8$ in refluxing 1,2-dichloroethane, but the regioselectivity was lower than that obtained with the hydroboration reaction (Scheme 3, eq. 2).[18] Hydro- and carbocupration of **9** were also developed by the same group and excellent regio- and stereoselectivities were noticed.[19] However, only potent electrophiles could be used to trap the intermediate vinylcopper species **13** (Scheme 3, eq. 3). The same trend was observed with the hydroalumination of **9** (Scheme 3, eq. 4).[19]

Rare examples of hydrostannylation reactions of α-CF_3-alkynes have been reported since the seminal work of Cullen and Styan in 1966,[20,21] but it is under the impulsion

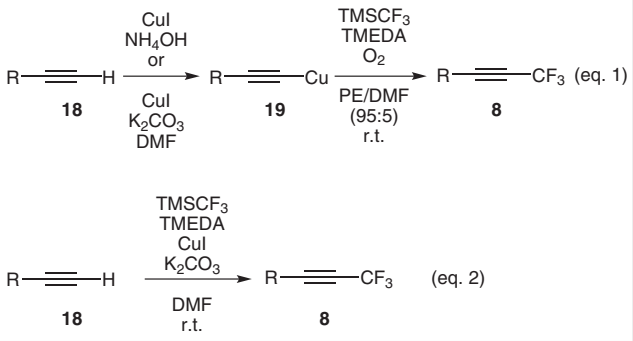


Scheme 3 Reported hydroboration, hydrosilylation, hydrocupration, hydroalumination, and hydrostannylation reactions of α-CF_3-alkynes **9**

of the group of Konno that the scope was more thoroughly explored.[19,22] Indeed, they demonstrated that moderate to excellent yields of α-CF_3-vinyl stannanes **17** could be obtained from the aryl-substituted trifluoromethylated alkynes **9** using tributyltin hydride and a catalytic amount of triethylborane as a radical initiator (Scheme 3, eq. 5). The stereoselectivity of the process was directly linked to the electronics of the aryl substituent. Iodolysis or copper-catalyzed cross-coupling of related vinylstannanes with activated electrophiles were also reported by Abarbri.[23] Strangely, a hydrometalation that has not been yet investigated in the context of α-CF_3-alkynes is hydrogermylation[24] although germanium also belongs to group 14, together with silicon and tin, and has been reported to react with alkynes under transition-metal[25] or Lewis acid catalysis,[26] and also under radical conditions as elegantly reported by Oshima.[25f,27]

Although an arsenal of hydrometalation reactions of aryl-substituted α-CF_3-alkynes **9** have been reported, it should be noticed that stereoselective access to (*Z*)- or (*E*)-alkyl-substituted α-CF_3-vinylmetal is still challenging. In addition, a practical access to valuable (*E*)-α-CF_3-vinylstannanes, not accessible by reported methods, would be stereocomplementary to existing methods. We report herein the full account of our preliminary investigations[28] concerning the hydrometalation of α-CF_3-alkynes using group 14 element hydrides, namely silanes, germanes, and stannanes. In addition, selected synthetic applications of the resulting α-CF_3-vinylgermanes and α-CF_3-vinylstannanes are discussed.

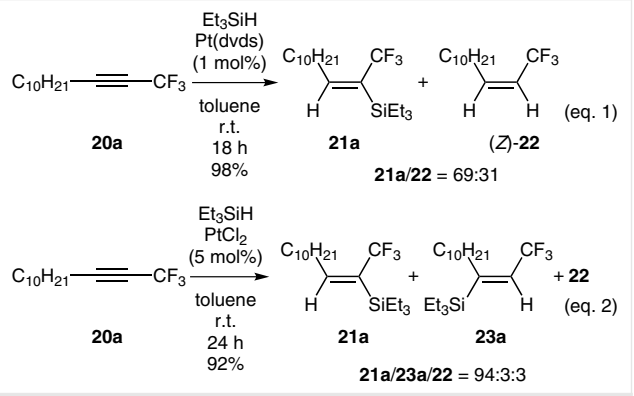
We indeed recently reported that terminal alkynes **18**, whether alkyl- or aryl-substituted, could be easily transformed into the corresponding α-CF_3-alkynes **8** in good to excellent yields using two practical procedures.[29] In the first one (Scheme 4, eq. 1), copper acetylides are synthesized by direct cupration of the terminal alkyne **18** (CuI, NH_4OH or K_2CO_3, DMF) followed by their trifluoromethylation using an excess of the Ruppert–Prakash reagent and TMEDA under an atmosphere of oxygen, in petroleum ether (PE)/DMF (95:5) at room temperature. In the second procedure (Scheme 4, eq. 2), terminal alkynes **18** are treated with CuI, TMEDA, the Ruppert–Prakash reagent, and K_2CO_3 in DMF at room temperature. These two protocols are unique with regards to functional group tolerance and were thus selected for the synthesis of a range of α-CF_3-alkynes **8**, precursors of the hydrometalation reaction with group 14 element hydrides.



Scheme 4 Two practical protocols for the copper-mediated synthesis of α-CF_3-alkynes **8** from terminal alkynes **18**

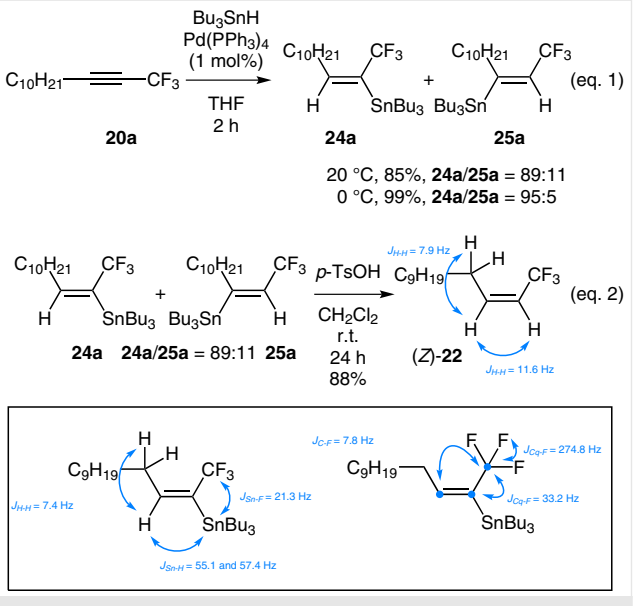
Our investigations of the hydrometalation reactions of α-CF_3-alkynes began with the platinum-catalyzed hydrosilylation reaction (Scheme 5). Based on the pioneering work of Tsipis,[30] in 2012 the group of Ferreira reported a *cis*-hydrosilylation of internal alkynes catalyzed by $PtCl_2$ or Pt(dvds).[31] Inspired by this work, Pt(dvds) (1 mol%) {dvds = $[(H_2C{=}CH)Me_2Si]_2O$} was used in the hydrosilylation of **20a** in toluene at room temperature for 18 h (Scheme 5, eq. 1). A moderate yield of the desired (*E*)-α-CF_3-vinylsilane **21a** was obtained (69%) together with protodesilylation product **22**. On the other hand, the use of $PtCl_2$ (5 mol%) in toluene at room temperature for 24 h afforded cleanly the desired (*E*)-α-CF_3-vinylsilane **21a** with only traces of the other regioisomer **23a** and the protodesilylated alkene **22** (**21a**/**23a**/**22** 94:3:3) as measured by ^{19}F NMR of the crude reaction mixture (see the Supporting Information). The vinylsilane **21a** was then submitted to iodolysis in dichloromethane at

40 °C for 12 h, but no trace of the desired α-CF_3-vinyl iodide was obtained thus demonstrating that this π-system is too electron-deficient to undergo an efficient iododesilylation.



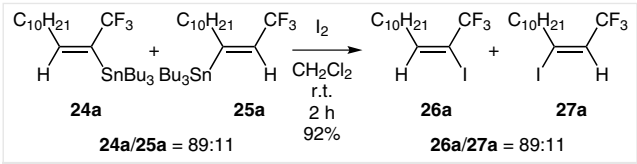
Scheme 5 Platinum-catalyzed hydrosilylation of α-CF_3-alkyne **20a**

We next turned our attention to another element of group 14 and focused on the transition-metal-catalyzed hydrostannylation of α-CF_3-alkynes (Scheme 6). When alkyne **20a** was treated with tributyltin hydride and $Pd(PPh_3)_4$ (1 mol%) in THF at room temperature for 2 h, a good yield of two isomeric (*E*)-α-CF_3-vinylstannanes **24a** and **25a** was obtained (**24a**/**25a** 89:11) (Scheme 6, eq. 1). A better regioisomeric ratio was obtained at 0 °C under the same conditions (**24a**/**25a** 95:5). This high regioselectivity is presumably largely electronically driven although a steric contribution might also be at play. Although the radical hydrostannylation of α-CF_3-alkynes was reported (Scheme 3, eq. 5), the examples in Scheme 6 constitute the first report of a palladium-catalyzed hydrostannylation of α-CF_3-alkynes to the best of our knowledge.



Scheme 6 Palladium-catalyzed hydrostannylation of α-CF_3-alkyne **20a**

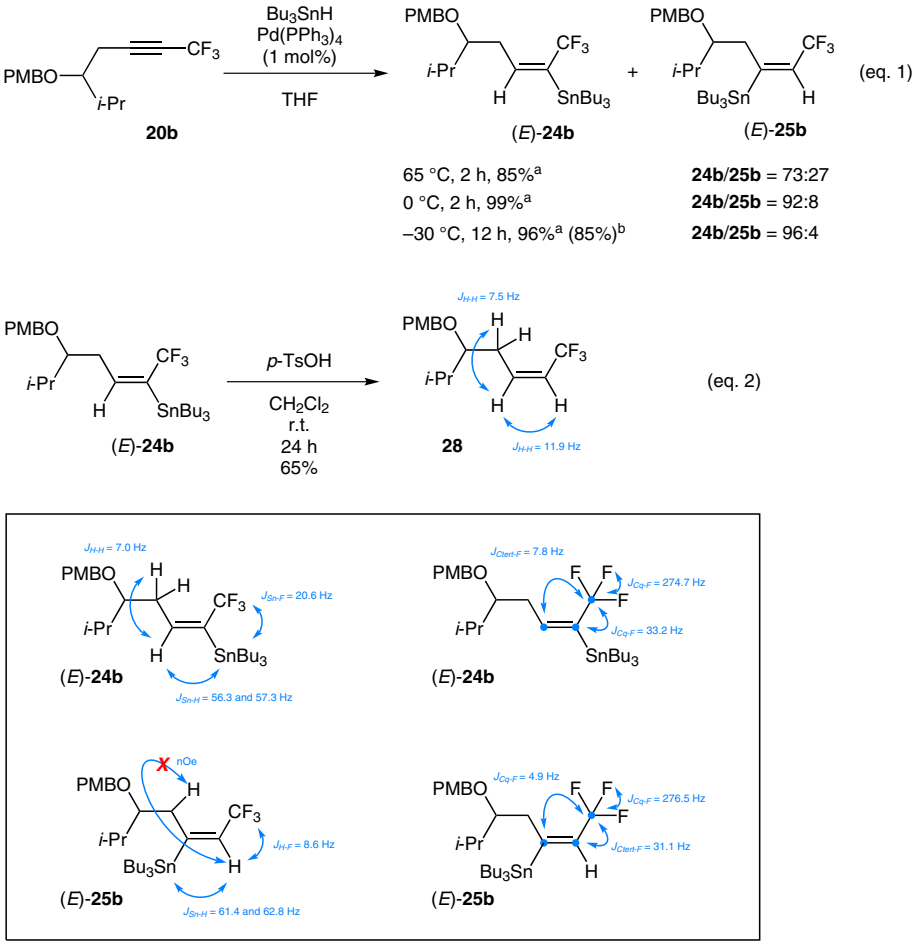
The connectivity of the major compound **24a** was established through the measurement of its coupling constants in ^1H, ^{19}F, and ^{13}C NMR (Scheme 6), while the configuration of the π-system was determined by chemical correlation. Indeed, when the mixture of the two regioisomeric vinylstannanes **24a** and **25a** were treated with *p*-toluenesulfonic acid in dichloromethane,[22b] a single α-CF_3-alkene (*Z*)-**22** was obtained in 88% (Scheme 6, eq. 2; see the Supporting Information). The (*Z*)-configuration of the alkene **22** was unambiguously determined by the measure of its coupling constants. Contrary to the vinylsilane **21a**, vinylstannanes **24a** and **25a** are excellent precursors of the corresponding vinyl iodides **26a** and **27a** upon treatment with I_2 in dichloromethane, a fact that could be attributed to the higher intrinsic nucleophilicity of stannanes compared to silanes (Scheme 7). After the simple treatment of the crude reaction mixture with the Roush KF on Celite® protocol[32] and a short filtration on silica gel, an excellent 92% yield of **26a** and **27a** was obtained (see the Supporting Information).



Scheme 7 Iodolysis of α-CF_3-vinylstannanes **24a** and **25a**

This hydrostannylation of α-CF_3-alkynes can be extended to a more complex substrate as exemplified in Scheme 8. The α-CF_3-alkyne **20b** bearing a *p*-methoxybenzyl ether in the homopropargylic position was also found to undergo a clean hydrostannylation in refluxing THF for 2 h (Scheme 8, eq. 1). Although the ratio of the two regioisomeric and chromatographically separable stannanes was low (**24b**/**25b** 73:27 as determined by ^{19}F NMR of the crude reaction mixture), it could be further increased to 92:8 at 0 °C (slightly eroded compared to the hydrostannylation of **20a** at 0 °C in Scheme 6) and to 96:4 at –30 °C. The yield of the latter transformation was only slightly decreased upon a three-fold increase in the scale of the –30 °C reaction (96% on 0.5 mmol and 85% on a 1.5 mmol) thus showing that this process is not only simple to set up, but also reliable.

As in the case of the hydrostannylation of the α-CF_3-dodecyne **20a**, the determination of the structures of the two regioisomers **24b** and **25b** was based on a combination of NMR studies (^1H, ^{19}F, and ^{13}C) and chemical correlation (Scheme 8). Actually, treatment of a pure sample of **24b** with *p*-toluenesulfonic acid in dichloromethane for 24 hours delivered the (*Z*)-α-CF_3-alkene **28** in 65% yield (Scheme 8, eq. 2).

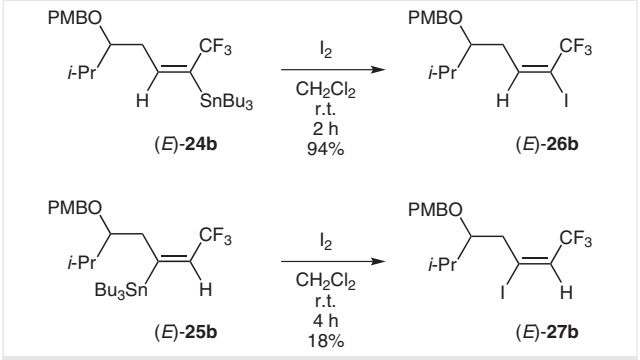


Scheme 8 Palladium-catalyzed hydrostannylation of α-CF_3-alkyne **20b**. [a] 0.5 mmol of **20b**. [b] 1.5 mmol of **20b**.

Having in hand the two regioisomeric α-CF_3-vinylstannanes **24b** and **25b**, their behavior in iododestannylation was investigated (Scheme 9). As anticipated, **24b** led to a clean and high-yielding reaction that offered **26b**, in only 2 h, in 94% yield. On the other hand, iododestannylation of the minor regioisomer **25b** was very slow in dichloromethane at room temperature for 4 h and only 18% yield of the (*E*)-α-CF_3-β-iodoalkene **27b** was obtained. This could be explained by the electronically disfavored formation of an intermediate carbocation adjacent to the CF_3 group.

While the hydrosilylation and hydrostannylation reactions of α-CF_3-alkynes were being investigated in our group, we also became interested in another element of the group 14, the chemistry of which has been underexplored from our own point of view, namely germanium. While organogermanes are slightly more expensive than the corresponding organostannanes,[33] they possess much lower toxicity,[24] greater stability, and can be used in cross-coupling reactions (provided that the electronics of the germanium atom are adequately tuned).[34] The latter properties were of special interest for us as they could represent a unique balance not found in the silane- or stannanes series investigated in Schemes 5 to 9.

Inspired by Konno's radical hydrostannylation of aryl-substituted α-CF_3-alkynes,[19,22] conditions for the efficient generation of germyl radicals were screened. It was quickly



Scheme 9 Iodolysis of α-CF_3-vinylstannanes (*E*)-**24b** and (*E*)-**25b**

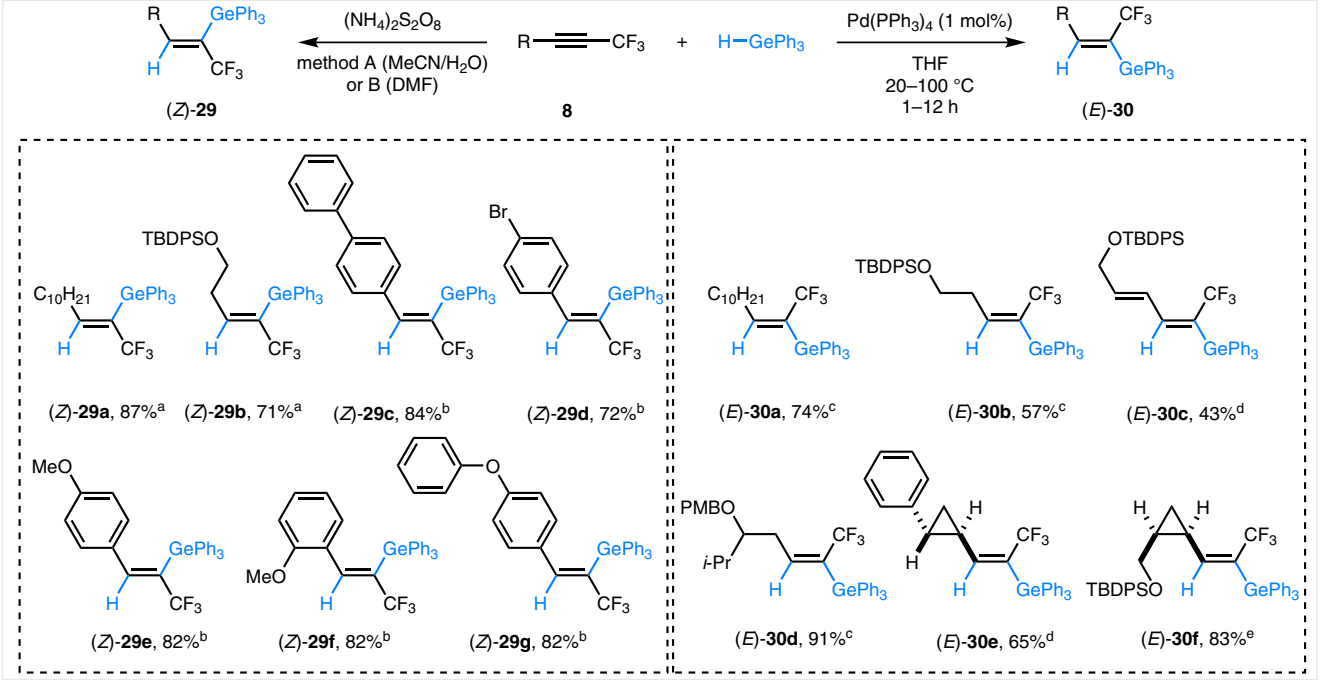
found that commercially available triphenylgermane could be oxidized to the corresponding radical cation using ammonium persulfate[35] in aqueous acetonitrile (Scheme 10). In addition, the germyl radical could be trapped by *N*-*tert*-butyl-α-phenylnitrone leading to the adduct whose structure has been confirmed by EPR spectroscopy (a_N = 14.6 G and a_H = 5.4 G), thus demonstrating the intermediacy of the triphenylgermyl radical.[28]

Much to our pleasure, implementation of these practical conditions to α-CF_3-alkynes **8** delivered (*Z*)-α-CF_3-vinylgermanes **29** as single stereoisomers (Scheme 10). As a model substrate, 1,1,1-trifluorotridec-2-yne (**20a**) was investigated and its hydrogermylation delivered α-CF_3-vinylgermane **29a** in 87% yield as a single regio- and stereoisomer. The structure of the latter was determined by a combination of ^{19}F NMR and nuclear Overhauser effects and was in line with the (*Z*)-selectivity observed for the related radical hydrostannylation (Scheme 3).

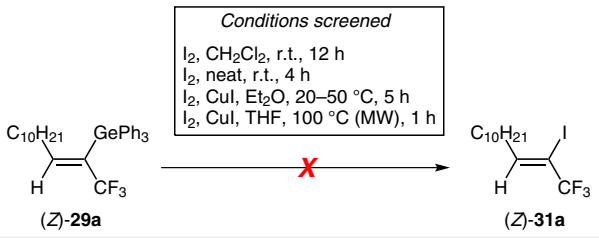
The scope of this (*Z*)-selective radical hydrogermylation was next explored with diverse α-CF_3-alkynes **20b**–**g** in aqueous acetonitrile (Method A) or in DMF (Method B) at 20 °C. Indeed, it was observed that Method B led to higher yields for aromatic substituted CF_3-alkynes. In all the cases investigated, a single regio- and stereoisomer **29b**–**g** was produced, as determined by ^{19}F NMR analysis of the crude reaction mixture, in 71–87% yield. Alkyl-substituted α-CF_3 alkynes were tolerated (**29a** and **29b**) as well as aryl-substituted ones (**29c**–**g**).

Although this (*Z*)-selective hydrogermylation delivered unique fluorinated building blocks, a stereocomplementary access to the corresponding (*E*)-α-CF_3-vinylgermanes **30** would be also essential. Inspired by the palladium-catalyzed hydrosilylation and hydrostannylation reactions reported in Schemes 5 to 9, we explored the corresponding transition-metal-catalyzed hydrogermylation of α-CF_3-alkynes **8** (Scheme 10). Once again, 1,1,1-trifluorotridec-2-yne (**20a**) was elected as a model compound and screening of reaction conditions identified $Pd(PPh_3)_4$ as the optimal catalyst at a loading of 1 mol% in THF at 20 °C. Inspection of the crude reaction mixture by ^1H and ^{19}F NMR revealed that the major α-CF_3-vinylgermane **30a** was indeed the anticipated (*E*)-α-CF_3-isomer (74% isolated yield), and that only traces (4%) of the (*E*)-β-CF_3-vinyl were obtained.

Upon investigation of the scope of this palladium-catalyzed process, it was found that only alkyl-substituted alkynes were reactive. Even under forcing conditions (100 °C in THF, microwave irradiation), the aryl-substituted derivatives were unreactive, although the reasons are unclear at present. Nevertheless, alkyl-substituted α-CF_3-alkynes (**30b**,**d**–**f**) and enyne (**30c**) were good partners as demonstrated in Scheme 10. The desired (*E*)-α-CF_3-vinylgermanes **30** were obtained in 43–91% with only traces of the β-vinylgermanes. Worthy of note is the functional group tolerance of the reaction since silyl ethers, *p*-methoxybenzyl ether, and 1,2-disubstituted cyclopropanes were tolerated.



Scheme 10 Regio- and stereoselective hydrogermylation of α-CF_3-alkynes **8**. [a] Method A. [b] Method B. [c] 20 °C, 12 h. [d] 50 °C, 2 h. [e] 100 °C (microwave irradiation), 2 h.

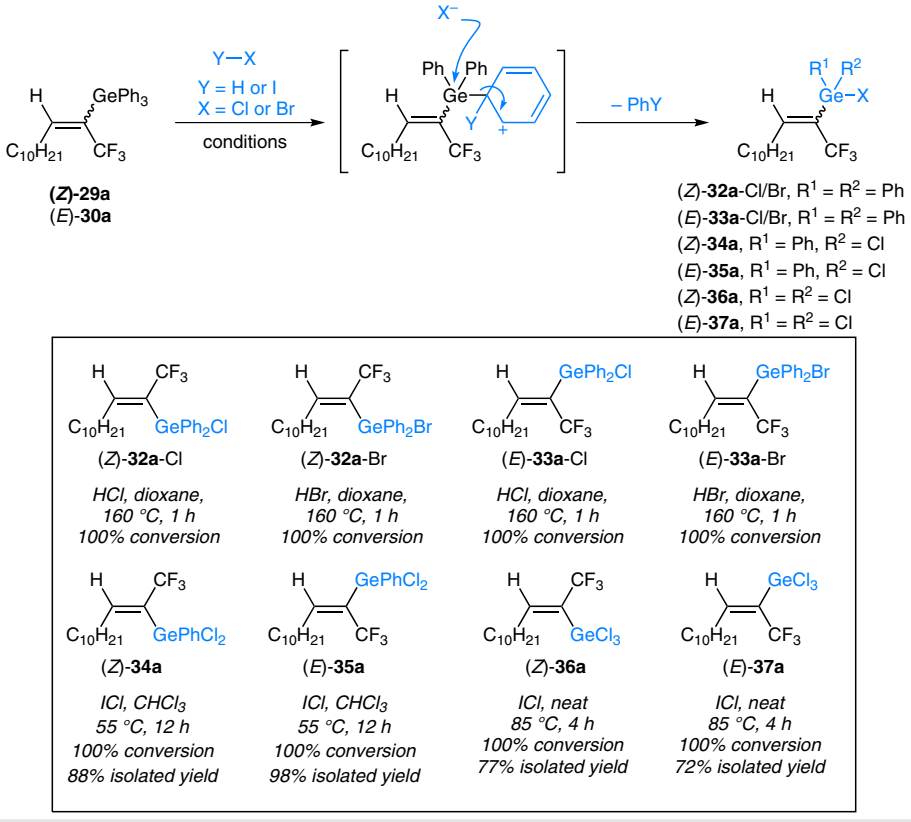


Scheme 11 Lack of reactivity of (*Z*)-**29a** in the iodolysis reaction

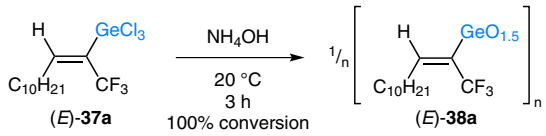
As with α-CF_3-vinylstannane (*E*)-**24b**, the iododemetalation of (*Z*)-**29a** with iodine in dichloromethane was explored. However, no reaction took place even in the absence of solvent (Scheme 11). In addition, neither Abarbri's conditions (CuI, I_2, up to 100 °C)[23] nor ICl at room temperature were able to convert (*Z*)-**29a** into the desired α-CF_3-vinyl iodide (*Z*)-**31a**. This lack of reactivity is reminiscent of the previously investigated iodolysis of α-CF_3-vinylsilane **21a**. Overall in this series, only the α-CF_3-vinylstannane (*E*)-**24b** underwent smooth iodolysis, thus stressing the enhanced reactivity of stannane derivatives toward iodolysis reactions.

In a last part of our investigations, we focused on the synthetic use of these unique (*Z*)- and (*E*)-α-CF_3-vinylgermanes **29** and **30** in cross-coupling reactions with aryl halides. The prerequisite for such a process is to finely tune the electronics of the germanium center to render it sufficiently electron-deficient.[34] To achieve this goal, various electrophiles potentially able to promote a preferential reaction on the phenyl substituent of the germanium [versus the more electron-deficient (trifluoromethyl)alkene] were screened (Scheme 12). Mineral acids such as HCl and HBr proved to be the most efficient in this regard. Indeed, when α-CF_3-vinylgermanes (*Z*)-**29a** and (*E*)-**30a** were treated with HCl (37% in water) or HBr (48% in water) in dioxane at 160 °C for 1 h, quantitative conversion to the moisture sensitive mono-chloro (*Z*)-**32a**-Cl/Br and mono-bromo (*E*)-**33a**-Cl/Br derivatives was observed.

On the other hand, the replacement of two phenyl substituents on the germanium center by two chlorine atoms was cleanly promoted by iodine monochloride in chloroform at 55 °C for 12 hours, thus leading to (*Z*)-**34a** (88%) and (*E*)-**35a** (98%). Running the reaction neat at 85 °C delivered exclusively the α-CF_3-trichloro(vinyl)germanes (*Z*)-**36a** (77%) and (*E*)-**37a** (72%). Although the latter derivatives proved to be readily hydrolyzed to the corresponding trihydroxygermanes in the presence of traces of water, they could be converted into the bench-stable germanium sesquioxides when treated with aqueous ammonia, as shown in Scheme 13.[36]



Scheme 12 Electronic tuning of the germanium center of (*Z*)-**29a** and (*E*)-**30a**

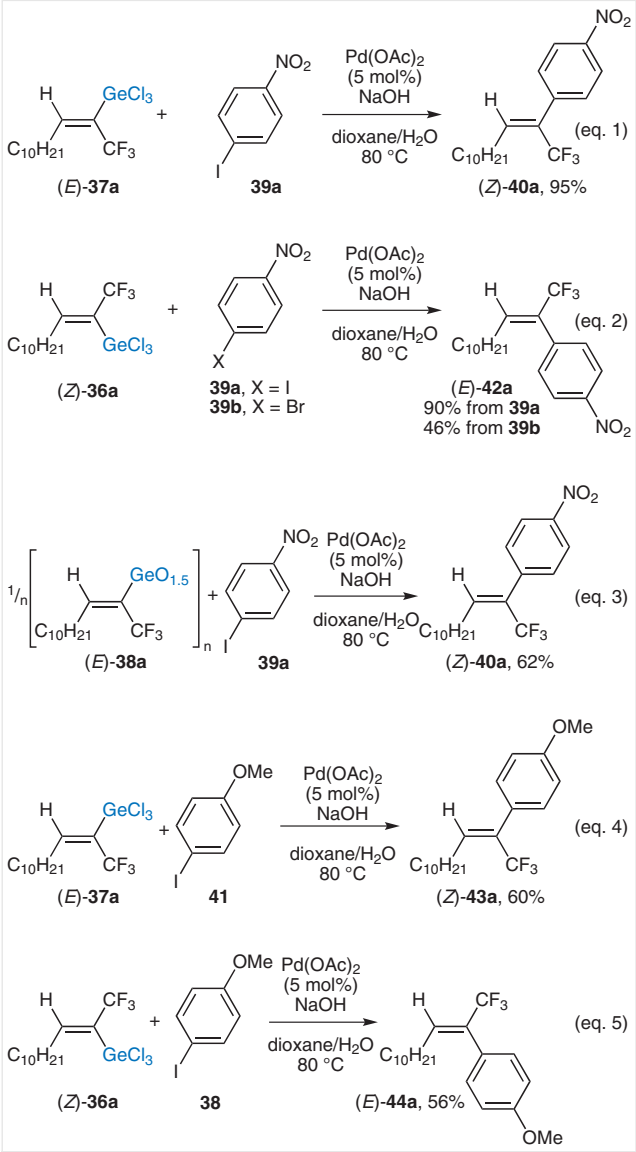


Scheme 13 Synthesis of germanium sesquioxide (*E*)-**38a** from (*E*)-**37a**

We next turned our attention to the use of these electron-deficient vinylgermanes in palladium-catalyzed cross-couplings with aryl iodides and bromides under the conditions reported by Fugami and Kosugi in the cases of aromatic trichlorogermanes and aromatic germanium sesquioxides.[34] It should be noted that only α-CF_3-trichlorogermanes (*Z*)-**36a** and (*E*)-**37a** and sesquioxide (*E*)-**38a** proved to be reactive under these conditions. In a first series of cross-couplings, 1-iodo-4-nitrobenzene (**39a**) was reacted with (*E*)-α-CF_3-trichlorogermane (*E*)-**37a** (Scheme 14, eq. 1), the corresponding (*Z*)-isomer (*Z*)-**36a** (Scheme 14, eq. 2) and the (*E*)-sesquioxide **38a** (Scheme 14, eq. 3), thus delivering the α-CF_3-styrene derivatives (*Z*)-**40a** and (*E*)-**42a** as single isomers in 95%, 90%, and 62% yields, respectively. Use of the 1-bromo-4-nitrobenzene (**39b**) was less efficient, styrene (*E*)-**42a** being obtained only in 46% yield (Scheme 14, eq. 2).

Finally, 4-iodoanisole (**41**) was employed as the electrophile in these palladium-catalyzed cross-couplings with (*E*)-**37a** and (*Z*)-**36a** (Scheme 14, eqs. 4 and 5). The expected α-CF_3-styrenes (*Z*)-**43a** and (*E*)-**44a** were obtained in moderate yields (60% and 56%, respectively), but as single isomers as shown by inspection of the crude reaction mixture by ^{19}F NMR.

In conclusion, we have demonstrated that α-CF_3-alkynes are reactive partners in regio- and stereoselective hydrosilylation, hydrostannylation, and hydrogermylation reactions. The corresponding α-CF_3-vinylmetals are stable derivatives that could be further transformed into the corresponding α-CF_3-vinyl halides (in the case of the stannane series) or engaged in palladium-catalyzed cross-couplings with aryl halides, thus delivering valuable fluorinated building blocks that were previously difficult to access.



Scheme 14 Cross-coupling reactions of (*E*)- and (*Z*)-α-CF_3-vinylgermanes and (*E*)-vinylgermane sesquioxide with aryl halides

NMR spectra were recorded on Bruker AV 300 or AV 400 spectrometers at 300 or 400 MHz for ^1H NMR, 75 or 100 MHz for ^{13}C NMR, and 376 or 282 MHz for ^{19}F NMR. The spectra were calibrated using undeuterated solvent as the internal reference, unless otherwise indicated. HRMS in positive mode were recorded using a 6520 series quadrupole time-of-flight (Q-TOF) mass spectrometer (Agilent) fitted with a multimode ion source (in mixed mode that enables both electrospray ionization, ESI, and atmospheric pressure chemical ionization, APCI). Samples were directly infused into the source using MeOH/0.2% aq HCO_2H 50:50. The HRMS of **24a**, **29e**, **29g**, **30c**, and **40a** could not be obtained despite our efforts; they do not ionize under either ESI or APCI techniques. Melting points were recorded on a Büchi 510 melting point apparatus. THF was distilled under N_2 from Na/benzophenone. Reagents were purchased from Aldrich or Alfa Aesar and used without further purification, unless otherwise noted. All α-CF_3-alkynes were synthesized from the corresponding terminal alkynes according to the literature.[29a] Microwave reactions were performed in a CEM Intelligent Explorer (Model 541416) microwave. Yields refer to chromatographically and spectroscopically (^1H and ^{19}F NMR) homogeneous materials, unless otherwise noted. Reactions were monitored by TLC carried out on Merck TLC silica gel 60 F_{254} aluminum plates, using UV light or $KMnO_4$ as visualizing agents. All separations were performed by chromatography on Merck silica gel 60 (40–63 μm), on a Combiflash Companion from Teledyne Isco or by preparative TLC chromatography (layer thickness of 500 μm).

For the sake of completeness, experimental procedures leading to compounds **29a**–**g**, **30a**–**f**, **32a**–**37a**, **40a** and **42a**–**44a** that have been published in the preliminary communication[28] are reproduced here. Detailed procedures for the synthesis of **21a**, **22**, **26a**,**b**, **27b**, **28**, **32a-Cl**/**Br**, **38a**, **42a**, **44a** and the hydrolyzed organogermanes from **32a-Cl**/**Br** and **33a-Cl**/**Br** can be found in the Supporting Information.

Tributyl[(*E*)-1,1,1-trifluorotridec-2-en-2-yl]stannane [(*E*)-24a] and Tributyl[(*E*)-1,1,1-trifluorotridec-2-en-3-yl]stannane [(*E*)-25a]; Typical Procedure A (TP A)

A round-bottom flask equipped with a magnetic stirring bar, a dry N_2 inlet and a septum, was successively charged with **20a** (100 mg, 0.43 mmol), THF (2.1 mL, 0.2 M), Bu_3SnH (126 µL, 0.47 mmol, 1.1 equiv), and $Pd(PPh_3)_4$ (5.0 mg, 4.3 µmol, 1 mol%). The mixture was then stirred under N_2 atmosphere at 20 °C for 2 h. The solvent was removed under reduced pressure and analysis of the crude mixture by ^{19}F NMR revealed a ratio of **24a**/**25a** of 89:11. After purification of the crude material by column chromatography (100% cyclohexane), **24a** (223 mg, 0.425 mmol, 99%) was isolated as a pale yellow oil. Due to the weak proportion of **25a**, this compound was not fully characterized. However, diagnostic signals are given.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.98 (t, J = 7.4 Hz, J^1H-^{117}Sn = 55.1 Hz, J^1H-^{119}Sn = 57.4 Hz, 1 H, diagnostic signal of minor isomer), 5.64 (q, J = 8.5 Hz, 1 H, diagnostic signal of minor isomer), 2.37–2.28 (m, 2 H), 1.56–1.39 (8 H), 1.34–1.26 (20 H), 1.06–0.93 (6 H), 0.93–0.86 (12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8 (q, J = 7.8 Hz), 132.7 (q, J = 33.2 Hz), 127.1 (q, J = 274.8 Hz), 125.5 (q, J = 31.0 Hz, diagnostic signal of minor isomer), 31.9, 31.3 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 35.3 Hz), 29.6, 29.5, 29.4, 29.3, 29.2 (2 C), 28.7 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 19.8 Hz, 3 C), 27.2 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 59.1 Hz, 3 C), 22.7, 14.1, 13.6 (3 C), 10.2 ($J^{13}C$-^{117}Sn = 344.7 Hz, $J^{13}C$-^{119}Sn = 352.5 Hz, 3 C).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –47.9 (s, $J^{19}F$-^{117}Sn = $J^{19}F$-^{119}Sn = 21.3 Hz, CF_3), –52.5 (d, J = 8.2 Hz, CF_3, minor isomer).

Tributyl[(*E*)-1,1,1-trifluoro-5-(4-methoxybenzyloxy)-6-methylhept-2-en-2-yl]stannane [(*E*)-24b]

Obtained from **20b** (100 mg, 0.33 mmol) following TP A (at –30 °C), which led to a separable mixture of **24b** and **25b**. After purification of the crude material by preparative TLC (cyclohexane/toluene 7:3), **24b** (189 mg, 0.32 mmol, 96%) was isolated as a pale yellow oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, J = 8.7 Hz, 2 H), 6.90 (d, J = 8.7 Hz, 2 H), 6.24 (t, J = 7.0 Hz, J^1H-^{117}Sn = 56.3 Hz, J^1H-^{119}Sn = 57.3 Hz, 1 H), 4.47 (s, 2 H), 3.82 (s, 3 H), 3.27 (m, 1 H), 2.60 (m, 2 H), 1.92 (sept d, J = 6.8, 5.3 Hz, 1 H), 1.61–1.45 (6 H), 1.41–1.26 (6 H), 1.04–0.87 (21 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 149.1 (q, J = 7.8 Hz), 134.2 (q, J = 33.2 Hz), 130.9, 129.2 (2 C), 127.1 (q, J = 274.7 Hz), 113.7 (2 C), 88.3, 71.3, 55.2, 32.0 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 34.6 Hz), 31.0, 28.7 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 19.8 Hz, 3 C), 27.2 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 60.7 Hz, 3 C), 18.3, 17.8, 13.6 (3 C), 10.2 ($J^{13}C$-^{117}Sn = 344.7 Hz, $J^{13}C$-^{119}Sn = 352.5 Hz, 3 C).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –48.1 (br s, $J^{19}F$-^{117}Sn = $J^{19}F$-^{119}Sn = 20.6 Hz, CF_3).

HRMS-ESI: m/z [M + H]$^+$ calcd for $C_{28}H_{48}F_3O_2Sn$: 593.2628; found: 593.2625.

Tributyl[(*E*)-1,1,1-trifluoro-5-(4-methoxybenzyloxy)-6-methylhept-2-en-3-yl]stannane [(*E*)-25b]

Obtained from **20b** (100 mg, 0.33 mmol) following a slight modification of TP A (the mixture was heated to reflux for 1 h), which led to a ratio of **24b**/**25b** of 73:27. After separation of the two isomers by preparative TLC (cyclohexane/toluene 7:3), **25b** (41 mg, 0.069 mmol, 21%) was isolated as a pale yellow oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.7 Hz, 2 H), 6.87 (d, J = 8.7 Hz, 2 H), 5.75 (q, J = 8.6 Hz, J^1H-^{117}Sn = 61.4 Hz, J^1H-^{119}Sn = 62.8 Hz, 1 H), 4.47 (d, J = 11.3 Hz, 1 H), 4.41 (d, J = 11.3 Hz, 1 H), 3.81 (s, 3 H), 3.37 (m, 1 H), 2.73 (m, 2 H), 1.93 (m, 1 H), 1.54–1.40 (6 H), 1.38–1.25 (6 H), 1.00–0.85 (21 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8 (q, J = 4.9 Hz), 158.9, 131.1, 128.8 (2 C), 127.1 (q, J = 31.1 Hz), 121.9 (q, J = 276.5 Hz), 113.5 (2 C), 84.1, 70.9, 55.2, 30.1 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 21.9 Hz), 30.3, 28.9 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 19.8 Hz, 3 C), 27.3 ($J^{13}C$-^{117}Sn = $J^{13}C$-^{119}Sn = 60.7 Hz, 3 C), 17.7, 17.5, 13.6 (3 C), 10.4 ($J^{13}C$-^{117}Sn = 332.0 Hz, $J^{13}C$-^{119}Sn = 339.1 Hz, 3 C).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –52.5 (d, J = 8.6 Hz, CF_3).

Triphenyl[(*Z*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*Z*)-29a]; Typical Procedure B (TP B)

A round-bottom flask equipped with a magnetic stirring bar and a septum was successively charged with **20a** (21 mg, 0.09 mmol), MeCN (450 µL), and H_2O (180 µL). After addition of Ph_3GeH (27.4 mg, 0.09 mmol) and ammonium persulfate (20.5 mg, 0.09 mmol), the mixture was stirred under air (balloon) at 20 °C for 12 h. Sat. aq $NaHCO_3$ solution was then added and the mixture was extracted with EtOAc (2 ×); the combined organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated under reduced pressure. After purification of the crude material by column chromatography (cyclohexane/EtOAc 95:5), (*Z*)-**29a** (42 mg, 87%) was isolated as white crystals; mp 63–64 °C.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.55 (m, 6 H), 7.43–7.37 (m, 9 H), 7.13–7.06 (m, 1 H), 1.95–1.85 (m, 2 H), 1.34–1.18 (m, 6 H), 1.17–1.05 (m, 6 H), 1.01–0.83 [m, 7 H, including 0.90 (t, J = 6.8 Hz, 3 H)].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1 (q, J = 8.9 Hz, *C*H), 135.5, 135.1, 129.4, 128.4, 125.6 (q, J = 273 Hz, CF_3), 32.7, 32.0, 29.6, 29.5, 29.4, 29.3, 29.2, 28.3, 22.8, 14.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –54.6 (d, J = 2.1 Hz, CF_3).

HRMS-APCI: m/z [M – C_6H_5]$^+$ calcd for $C_{25}H_{32}F_3Ge$: 461.1674; found: 461.1691.

[(*Z*)-5-(*tert*-Butyldiphenylsiloxy)-1,1,1-trifluoropent-2-en-2-yl]triphenylgermane [(*Z*)-29b]

Obtained from the corresponding α-CF_3-alkyne (34 mg, 0.09 mmol) following TP B. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 9:1), (*Z*)-**29b** (44 mg, 71%) was isolated as a white powder; mp 107–108 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.56 (m, 4 H), 7.52–7.50 (m, 6 H), 7.45–7.31 (m, 16 H), 3.40 (t, J = 6.0 Hz, 2 H), 2.16–2.10 (m, 2 H), 1.03 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4 (q, J = 9.2 Hz, *C*H), 135.7, 135.3, 135.0, 133.5, 129.8, 129.7, 128.5, 127.8, 125.5 (q, J = 273 Hz, CF_3), 62.1, 35.3, 26.9, 19.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –54.9 (d, J = 2.4 Hz, CF_3).

HRMS-APCI: m/z [M – C_6H_5]$^+$ calcd for $C_{33}H_{34}F_3GeOSi$: 605.1544; found: 605.1558.

[(*Z*)-3-(Biphenyl-4-yl)-1,1,1-trifluoroprop-2-en-2-yl]triphenylgermane [(*Z*)-29c]; Typical Procedure C (TP C)

A round-bottom flask equipped with a magnetic stirring bar and a septum was successively charged with **20c** (20 mg, 0.08 mmol) and DMF (400 µL). After the addition of Ph_3GeH (24.4 mg, 0.08 mmol) and ammonium persulfate (18.3 mg, 0.08 mmol), the mixture was stirred under air (balloon) at 20 °C for 4 h. Sat. aq $NaHCO_3$ solution was then added and the mixture was extracted with cyclohexane/CH_2Cl_2 (9:1, 2 ×); the combined organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated under reduced pressure. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 9:1), (*Z*)-**29c** (37 mg, 84%) was isolated as a white powder; mp 176–177 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 2.0 Hz, 1 H), 7.50 (dd, *J* = 7.8, 1.8 Hz, 6 H), 7.40–7.28 (m, 14 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 7.04 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4 (q, *J* = 9.2 Hz, *C*H), 141.6, 140.5, 135.4, 135.2, 133.7, 129.7, 129.2, 128.8, 128.3, 127.6, 127.1, 126.3, 126.2 (q, *J* = 273 Hz, *C*F_3).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –53.0 (d, *J* = 2.1 Hz, C*F*$_3$).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{27}H_{20}F_3Ge$: 475.0729; found: 475.0736.

[(*Z*)-3-(4-Bromophenyl)-1,1,1-trifluoroprop-2-en-2-yl]triphenylgermane [(*Z*)-29d]

Obtained from **20d** (20 mg, 0.08 mmol) following TP C. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 95:5), (*Z*)-**29d** (32 mg, 72%) was isolated as a white powder; mp 135–136 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 2.3 Hz, 1 H), 7.45 (dd, *J* = 7.8, 1.2 Hz, 6 H), 7.37–7.27 (m, 9 H), 6.95–6.89 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6 (q, *J* = 9.2 Hz, *C*H), 135.1, 133.6, 130.8, 130.6, 129.3, 128.4, 126.0 (q, *J* = 273 Hz, *C*F_3), 123.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –53.4 (d, *J* = 2.4 Hz, C*F*$_3$).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{21}H_{15}BrF_3Ge$: 476.9514; found: 476.9524.

Triphenyl[(*Z*)-1,1,1-trifluoro-3-(4-methoxyphenyl)prop-2-en-2-yl]germane [(*Z*)-29e]

Obtained from **20e** (16 mg, 0.08 mmol) following TP C. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 8:2), (*Z*)-**29e** (33 mg, 82%); was isolated as a white powder; mp 107–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 2.3 Hz, 1 H), 7.50 (dd, *J* = 7.8, 1.5 Hz, 6 H), 7.35–7.27 (m, 9 H), 7.07 (d, *J* = 8.8 Hz, 2 H), 6.37 (d, *J* = 8.8 Hz, 2 H), 3.61 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 148.2 (q, *J* = 9.2 Hz, *C*H), 135.6, 135.2, 131.3, 129.2, 128.2, 127.1, 126.4 (q, *J* = 273 Hz, *C*F_3), 126.1 (q, *J* = 30 Hz, *C*), 113.1, 55.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –52.6 (d, *J* = 2.1 Hz, C*F*$_3$).

Triphenyl[(*Z*)-1,1,1-trifluoro-3-(2-methoxyphenyl)prop-2-en-2-yl]germane [(*Z*)-29f]

Obtained from **20f** (16 mg, 0.08 mmol) following TP C. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 9:1), (*Z*)-**29f** (33 mg, 82%) was isolated as a white powder; mp 83 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 2.3 Hz, 1 H), 7.47 (dd, *J* = 7.8, 1.5 Hz, 6 H), 7.32–7.24 (m, 9 H), 6.90 (t, *J* = 7.8 Hz, 1 H), 6.89 (d, *J* = 7.8 Hz, 1 H), 6.44 (d, *J* = 7.8 Hz, 1 H), 6.27 (t, *J* = 7.8 Hz, 1 H), 3.66 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 146.0 (q, *J* = 9.2 Hz, *C*H), 135.8, 135.1, 130.4, 129.8, 129.0, 128.9 (q, *J* = 30 Hz, *C*), 128.0, 126.2 (q, *J* = 273 Hz, *C*F_3), 124.5, 119.6, 109.7, 55.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –52.7 (d, *J* = 2.1 Hz, C*F*$_3$).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{22}H_{18}F_3GeO$: 429.0520; found: 429.0532.

Triphenyl[(*Z*)-1,1,1-trifluoro-3-(4-phenoxyphenyl)prop-2-en-2-yl]germane [(*Z*)-29g]

Obtained from **20g** (21 mg, 0.08 mmol) following TP C. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 9:1), (*Z*)-**29g** (37 mg, 82%) was isolated as a white powder; mp 113 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 2.3 Hz, 1 H), 7.49 (dd, *J* = 7.8, 1.2 Hz, 6 H), 7.38–7.27 (m, 11 H), 7.11–7.06 (m, 3 H), 6.76 (dd, *J* = 8.8, 1.0 Hz, 2 H), 6.46 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.6, 148.0 (q, *J* = 9.2 Hz, *C*H), 135.5, 135.2, 131.1, 129.8, 129.6, 129.3, 128.3, 127.8 (q, *J* = 30 Hz, *C*), 126.3 (q, *J* = 273 Hz, *C*F_3), 123.7, 119.3, 117.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –52.9 (d, *J* = 2.4 Hz, C*F*$_3$).

Triphenyl[(*E*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*E*)-30a]; Typical Procedure D (TP D)

A round-bottom flask equipped with a magnetic stirring bar, a dry N_2 inlet, and a septum was successively charged with **20a** (1.0 g, 4.27 mmol), THF (21.4 mL, 0.2 M), Ph_3GeH (1.30 g, 4.27 mmol), and $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol, 1 mol%). The mixture was stirred at 20 °C for 12 h. After purification of the crude material by column chromatography (cyclohexane), (*E*)-**30a** (1.7 g, 74%) was isolated as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 6 H), 7.43–7.36 (m, 9 H), 6.19 (t, *J* = 7.7 Hz, 1 H), 2.45–2.36 (m, 2 H), 1.39–1.25 m, 16 H), 0.89 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8 (q, *J* = 6.4 Hz, *C*H), 135.3, 135.2, 129.6, 129.1 (q, *J* = 31 Hz, *C*), 128.5, 126.1 (q, *J* = 276 Hz, *C*F_3), 32.0, 31.2, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 22.8, 14.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –47.3 (s, C*F*$_3$).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{25}H_{32}F_3Ge$: 463.1667; found: 463.1682.

[(*E*)-5-(*tert*-Butyldiphenylsiloxy)-1,1,1-trifluoropent-2-en-2-yl]triphenylgermane [(*E*)-30b]

Obtained from the corresponding α-CF_3-alkyne (34 mg, 0.09 mmol) following TP D. The mixture was stirred at 50 °C for 2 h. After purification of the crude material by preparative TLC chromatography (cyclohexane/CH_2Cl_2 8:2), (*E*)-**30b** (35 mg, 57%) was isolated as a white powder; mp 87–88 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.52 (m, 10 H), 7.44–7.31 (m, 15 H), 6.49 (t, *J* = 7.2 Hz, 1 H), 3.69 (t, *J* = 5.8 Hz, 2 H), 2.71–2.66 (m, 2 H), 0.96 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6 (q, *J* = 6.4 Hz, *C*H), 135.6, 135.3, 135.0, 133.6, 130.7 (q, *J* = 31 Hz, *C*), 129.8, 129.5, 128.5, 127.8, 126.1 (q, *J* = 276 Hz, *C*F_3), 62.5, 34.3, 26.9, 19.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –47.4 (s, C*F*$_3$).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{33}H_{34}F_3GeOSi$: 606.1569; found: 606.1558.

[(*E*)-6-(*tert*-Butyldiphenylsiloxy)-1,1,1-trifluorohexa-2,4-dien-2-yl]triphenylgermane [(*E*)-30c]

Obtained from the corresponding α-CF_3-alkyne (34 mg, 0.09 mmol) following TP D. The mixture was stirred at 50 °C for 2 h. After purification of the crude material by preparative TLC chromatography (cyclohexane/CH_2Cl_2 8:2), (*E*)-**30c** (27 mg, 43%) was isolated as a white solid; mp 82 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 7.6, 1.2 Hz, 4 H), 7.55–7.53 (m, 6 H), 7.45–7.37 (m, 15 H), 7.08–7–00 (m, 1 H), 6.61 (d, *J* = 11.6 Hz, 1 H), 5.89 (dt, *J* = 14.8, 4.0 Hz, 1 H), 4.30 (d, *J* = 1.8 Hz, 2 H), 1.08 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9 (q, *J* = 6.4 Hz, *C*H), 142.2, 135.7, 135.3, 135.0, 133.4, 129.9, 129.5, 128.5, 127.4 (q, *J* = 31 Hz, *C*), 127.9, 126.2 (q, *J* = 276 Hz, *C*F_3), 124.9, 63.5, 26.9, 19.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –46.7 (d, *J* = 1.3 Hz, CF_3).

Triphenyl[(*E*)-1,1,1-trifluoro-5-(4-methoxybenzyloxy)-6-methylhept-2-en-2-yl]germane [(*E*)-30d]

Obtained from the corresponding α-CF_3-alkyne (27 mg, 0.09 mmol) following TP D. The mixture was stirred at 20 °C for 12 h. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 9:1), (*E*)-**30d** (50 mg, 91%) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 7.6, 1.6 Hz, 6 H), 7.44–7.33 (m, 9 H), 7.02 (d, *J* = 8.6 Hz, 2 H), 6.77 (d, *J* = 8.6 Hz, 2 H), 6.46 (t, *J* = 7.1 Hz, 1 H), 4.34 (d, *J* = 10.9 Hz, 1 H), 4.24 (d, *J* = 10.9 Hz, 1 H), 3.79 (s, 3 H), 3.23–3.18 (m, 1 H), 2.72–2.65 (m, 1 H), 2.60–2.52 (m, 1 H), 1.92–1.80 (m, 1 H), 0.90 (t, *J* = 6.7 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 154.0 (q, *J* = 6.4 Hz, *C*H), 135.5, 135.3, 135.1, 130.8, 130.1 (q, *J* = 31 Hz, *C*), 129.5, 129.2, 128.5, 126.1 (q, *J* = 276 Hz, *C*F_3), 113.8, 83.3, 71.7, 55.4, 32.4, 31.3, 18.4, 17.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –47.5 (s, CF_3).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{28}H_{30}F_3GeO_2$: 529.1363; found: 529.1362.

Triphenyl[(*E*)-*trans*-1,1,1-trifluoro-3-(2-phenylcyclopropyl)prop-2-en-2-yl]germane [(*E*)-30e]

Obtained from the corresponding α-CF_3-alkyne (19 mg, 0.09 mmol) following TP D. The mixture was stirred at 50 °C for 2 h. After purification of the crude material by preparative TLC chromatography (cyclohexane/CH_2Cl_2 8:2), (*E*)-**30e** (30 mg, 65%) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 6 H), 7.45–7.37 (m, 9 H), 7.28 (t, *J* = 7.3 Hz, 2 H), 7.19 (t, *J* = 7.3 Hz, 1 H), 7.10 (d, *J* = 7.3 Hz, 2 H), 5.56 (d, *J* = 10.8 Hz, 1 H), 2.40–2.32 (m, 1 H), 2.01–1.96 (m, 1 H), 1.41–1.36 (m, 1 H), 1.10–1.05 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9 (q, *J* = 6.4 Hz, *C*H), 140.5, 135.3, 135.1, 129.5, 128.6, 128.5, 126.5 (q, *J* = 276 Hz, *C*F_3), 126.4, 126.4 (q, *J* = 31 Hz, *C*), 27.0, 25.0, 18.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –47.1 (d, *J* = 1.3 Hz, CF_3).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{24}H_{20}F_3Ge$: 439.0728; found: 439.0726.

{(*E*)-*cis*-3-[2-(*tert*-Butyldiphenylsiloxymethyl)cyclopropyl]-1,1,1-trifluoroprop-2-en-2-yl]triphenylgermane [(*E*)-30f]

Obtained from the corresponding α-CF_3-alkyne (44 mg, 0.11 mmol) following TP D. The mixture was stirred under MW at 100 °C for 1 h. After purification of the crude material by column chromatography (cyclohexane/CH_2Cl_2 95:5), (*E*)-**30f** (65 mg, 83%) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.59 (m, 4 H), 7.48 (d, *J* = 6.5 Hz, 6 H), 7.38–7.29 (m, 15 H), 5.75 (d, *J* = 11.3 Hz, 1 H), 3.59 (dd, *J* = 11.4, 6.8 Hz, 1 H), 3.43 (dd, *J* = 11.4, 8.2 Hz, 1 H), 2.22–2.13 (m, 1 H), 1.51–1.42 (m, 1 H), 1.11–1.06 (m, 1 H), 1.01 (s, 9 H), 0.31 (dd, *J* = 11.4, 5.3 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4 (q, *J* = 6.4 Hz, *C*H), 135.8, 135.7, 135.3, 135.2, 129.8, 129.4, 128.4, 127.8, 127.7, 126.6 (q, *J* = 276 Hz, *C*F_3), 64.0, 27.0, 23.9, 19.3, 18.0, 14.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –47.1 (s, CF_3).

HRMS-APCI: *m*/*z* [M – C_6H_5]$^+$ calcd for $C_{35}H_{36}F_3GeOSi$: 631.1805; found: 631.1813.

Chlorodiphenyl[(*E*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*E*)-33a-Cl]

A microwave tube was successively charged with (*E*)-**30a** (50 mg, 0.09 mmol), dioxane (0.3 mL), and concd HCl (37%, 0.3 mL), and the mixture was stirred under MW irradiation at 160 °C (internal pressure: 13 bar), for 1 h. The mixture was cooled to r.t., CH_2Cl_2 (10 mL) and water (10 mL) were added, and the two resulting phases were separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL) and the combined organic layers were washed with brine and dried ($MgSO_4$). After filtration and evaporation of the solvents under reduced pressure, the crude material (*E*)-**33a**-Cl was obtained with 100% conversion as a brown oil. This compound was not fully characterized due to its extreme moisture sensitivity; the corresponding hydroxy-germanium derivative is very easily obtained upon exposure to ambient atmosphere (see the Supporting Information for details).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.57 (m, 3 H), 7.50–7.41 (m, 7 H), 6.65 (t, *J* = 7.6 Hz, 1 H), 2.49–2.2.41 (m, 2 H), 1.48–1.23 (m, 16 H), 0.87 (t, *J* = 6.9 Hz, 3 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –52.0 (t, *J* = 2.7 Hz, CF_3).

Bromodiphenyl[(*E*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*E*)-33a-Br]

A microwave tube was successively charged with (*E*)-**30a** (50 mg, 0.09 mmol), dioxane (0.3 mL), and concd HBr (48%, 0.3 mL), and the mixture was stirred under MW at 160 °C (internal pressure: 13 bar), for 1 h. The mixture was cooled to r.t., CH_2Cl_2 (10 mL) and water (10 mL) were added, and the two resulting phases were separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL) and the combined organic layers were washed with brine and dried ($MgSO_4$). After filtration and evaporation of the solvents under reduced pressure, the crude material (*E*)-**33a**-Br was obtained with 100% conversion as a brown oil. This compound was not fully characterized due to its extreme moisture sensitivity; the corresponding hydroxy-germanium derivative is very easily obtained upon exposure to ambient atmosphere (see the Supporting Information for details).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.59 (m, 3 H), 7.51–7.42 (m, 7 H), 6.66 (t, *J* = 7.7 Hz, 1 H), 2.50–2.41 (m, 2 H), 1.50–1.23 (m, 16 H), 0.88 (t, *J* = 6.7 Hz, 3 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –52.0 (t, *J* = 2.1 Hz, CF_3).

Dichlorophenyl[(*E*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*E*)-35a]

In a two-necked round-bottom flask equipped with a condenser and dry N_2 inlet, a solution of ICl (301 mg, 1.85 mmol) in $CHCl_3$ (3.5 mL) was added at 0 °C to a solution of (*E*)-**30a** (200 mg, 0.37 mmol) in $CHCl_3$ (4 mL). The red mixture was stirred at 50 °C for 4 h to provide 100% conversion of (*E*)-**30a** (as monitored by ^{19}F NMR). The mixture was cooled, the solvent was removed under reduced pressure, and the crude material was purified by distillation of PhI and excess ICl under reduced pressure (60 °C, 0.133 mbar) to provide (*E*)-**35a** (166 mg, 98%) as a colorless residual oil. This compound was not fully characterized due to its extreme moisture sensitivity; the corresponding hydroxy-germanium derivative is very easily obtained upon exposure to ambient atmosphere.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.67 (m, 2 H), 7.58–7.49 (m, 3 H), 6.90 (t, *J* = 7.7 Hz, 1 H), 2.53–2.46 (m, 2 H), 1.56–1.48 (m, 2 H), 1.35–1.24 (m, 14 H), 0.88 (t, *J* = 6.7 Hz, 3 H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –47.9 (m, CF_3).

Dichlorophenyl[(*Z*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*Z*)-34a]

In a two-necked round-bottom flask equipped with a condenser and dry N_2 inlet, a solution of ICl (226 mg, 1.40 mmol) in $CHCl_3$ (2.5 mL) was added at 0 °C to a solution of (*Z*)-**29a** (150 mg, 0.28 mmol) in $CHCl_3$ (3 mL). The red mixture was stirred at 55 °C for 12 h to provide 100% conversion of (*Z*)-**29a** (as monitored by ^{19}F NMR). The mixture was cooled, the solvent was removed under reduced pressure, and the crude material was purified by distillation of PhI and excess ICl under reduced pressure (60 °C, 0.133 mbar) to provide (*Z*)-**34a** (112 mg, 88%) as a colorless residual oil. This compound was not fully characterized due to its extreme moisture sensitivity; the corresponding hydroxy-germanium derivative is very easily obtained upon exposure to ambient atmosphere.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.70 (m, 2 H), 7.57–7.49 (m, 3 H), 6.90 (tq, *J* = 7.9, 2.0 Hz, 1 H), 2.38–2.30 (m, 2 H), 1.43–1.36 (m, 2 H), 1.30–1.16 (m, 14 H), 0.88 (t, *J* = 7.7 Hz, 3 H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –54.5 (q, *J* = 2.1 Hz, CF_3).

Trichloro[(*Z*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*Z*)-36a]

A round-bottom flask equipped with a magnetic stirring bar, dry N_2 inlet and a septum was charged with (*Z*)-**29a** (1.6 g, 2.97 mmol). At 0 °C, ICl (4.8 g, 29.7 mmol) was added in one portion, and the resulting dark red mixture was stirred under N_2 at 85 °C for 4 h to provide 100% conversion of the (*Z*)-**29a** (as monitored by ^{19}F NMR). The crude material was then purified by distillation of byproducts (PhI and 1,4-diiodobenzene) under reduced pressure (90 °C, 0.133 mbar) to provide (*Z*)-**36a** (950 mg, 77%) as a brown residual oil. This compound was not fully characterized due to its extreme moisture sensitivity; the corresponding hydroxy-germanium derivative is very easily obtained upon exposure to ambient atmosphere.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (tq app. td, *J* = 7.8, 1.8 Hz, 1 H), 2.59–2.52 (m, 2 H), 1.58–1.51 (m, 2 H), 1.39–1.26 (m, 14 H), 0.88 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (q, *J* = 7.1 Hz, *C*H), 128.4 (q, *J* = 33 Hz, *C*), 122.6 (q, *J* = 274 Hz, *C*F_3), 32.0, 31.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.3, 22.8, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –54.7 (d, *J* = 1.8 Hz, CF_3).

Trichloro[(*E*)-1,1,1-trifluorotridec-2-en-2-yl]germane [(*E*)-37a]

A round-bottom flask equipped with a magnetic stirring bar, dry N_2 inlet and a septum was charged with (*E*)-**30a** (1.5 g, 2.78 mmol). At 0 °C, ICl (3.6 g, 22.2 mmol) was added in one portion, and the resulting dark red mixture was stirred under N_2 at 85 °C for 2 h to provide 100% conversion of the (*E*)-**30a** (as monitored by ^{19}F NMR). The crude material was then purified by distillation of byproducts (PhI and 1,4-diiodobenzene) under reduced pressure (90 °C, 0.133 mbar) to provide (*E*)-**37a** (830 mg, 72%) as a brown residual oil. This compound was not fully characterized due to its extreme moisture sensitivity; the corresponding hydroxy-germanium derivative is very easily obtained upon exposure to ambient atmosphere.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.94 (t, *J* = 7.7 Hz, 1 H), 2.55–2.48 (m, 2 H), 1.58–1.50 (m, 2 H), 1.38–1.23 (m, 14 H), 0.88 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8 (q, *J* = 5.0 Hz, *C*H), 128.7 (q, *J* = 35 Hz, *C*), 123.0 (q, *J* = 275 Hz, *C*F_3), 32.0, 31.0, 29.7, 29.5, 29.4, 29.3, 29.3, 28.4, 22.8, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –48.2 (s, CF_3).

Synthesis of α-Trifluoromethylated Styrenes 40a and 43a; General Coupling Procedure

A round-bottom flask equipped with a magnetic stirring bar, a dry N_2 inlet and a septum was successively charged with (*Z*)-**36a** or (*E*)-**37a** (100 mg, 0.24 mmol) and dioxane (1.5 mL). 2 M aq NaOH solution (960 µL, 1.92 mmol) and H_2O (540 µL) were then successively added and the solution was stirred at r.t. for 10 min. After addition of aryl halide (0.12 mmol) and $Pd(OAc)_2$ (2.7 mg, 5 mol%), the mixture was stirred under N_2 at 80 °C for 1 h. The mixture was cooled and H_2O was added, and the mixture was extracted with EtOAc (2 ×). The combined organic layers were washed with brine, dried ($MgSO_4$) and filtered, and the solvents were removed under reduced pressure. The crude material was purified by chromatography to provide the desired α-trifluoromethylated styrene.

(*Z*)-1,1,1-Trifluoro-2-(4-nitrophenyl)tridec-2-ene [(*Z*)-40a]

*From (E)-**37a***: obtained from the reaction of (*E*)-**37a** (100 mg, 0.24 mmol) with 1-iodo-4-nitrobenzene (30 mg, 0.12 mmol) following the general coupling procedure. After purification of the crude material by preparative TLC chromatography (cyclohexane/EtOAc 95:5), (*Z*)-**40a** (41 mg, 95%) was isolated as a colorless oil.

*From (E)-**38a***: Obtained from the reaction of (*E*)-**38a** (40 mg, 0.06 mmol) with 1-iodo-4-nitrobenzene (30 mg, 0.12 mmol) following the general coupling procedure and heating at 80 °C for 15 h. After purification of the crude material by preparative TLC chromatography (cyclohexane/EtOAc 95:5), (*Z*)-**40a** (27 mg, 62%) was isolated as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.5 Hz, 2 H), 7.46 (d, *J* = 8.5 Hz, 2 H), 6.16 (t, *J* = 7.7 Hz, 1 H), 2.51–2.44 (m, 2 H), 1.55–1.48 (m, 2 H), 1.38–1.23 (m, 14 H), 0.88 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6, 145.3 (q, *J* = 3.0 Hz, *C*H), 143.2 (q, *J* = 1.5 Hz, *C*Ar), 130.2 (q, *J* = 30 Hz, *C*), 129.2, 123.7, 123.6 (q, *J* = 276 Hz, *C*F_3), 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 29.1, 22.8, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –52.5 (s, CF_3).

(*Z*)-1,1,1-Trifluoro-2-(4-methoxyphenyl)tridec-2-ene [(*Z*)-43a]

Obtained from the reaction of (*E*)-**37a** (100 mg, 0.24 mmol) with 4-iodoanisole (28 mg, 0.12 mmol) following the general coupling procedure. After purification of the crude material by preparative TLC chromatography (cyclohexane/EtOAc 95:5), (*Z*)-**43a** (26 mg, 60%) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, *J* = 8.7 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 5.96 (t, *J* = 7.7 Hz, 1 H), 3.81 (s, 3 H), 2.44–2.37 (m, 2 H), 1.51–1.46 (m, 2 H), 1.32–1.24 (m, 14 H), 0.88 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 141.6 (q, *J* = 3.1 Hz, *C*H), 131.0 (q, *J* = 30 Hz, *C*), 129.6, 128.0, 124.3 (q, *J* = 275 Hz, *C*F$_3$), 113.7, 55.4, 32.0, 29.7, 29.7, 29.5, 29.5, 29.4, 29.3, 22.8, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –52.8 (s, *C*F$_3$).

HRMS-APCI: *m*/*z* [M – H]$^+$ calcd for $C_{20}H_{30}F_3O$: 343.2243; found: 343.2247.

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Supporting Information

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