# Highly Regio- and Stereoselective Hydrogermylation of Fluorinated Alkyl Propiolate

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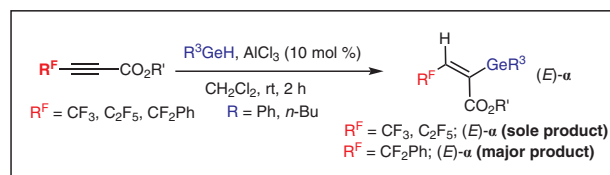
Abstract The selective introduction of fluoroalkylated vinylmetals in controlled strategies is a challenging process for many chemists. This study reports the highly regio- and stereoselective synthesis of functionalized vinylgermanes bearing a perfluoroalkyl group from perfluoroalkylated acetylenic esters via $AlCl_3$-catalyzed hydrogermylation. Regio- and stereoselectivity are highly dependent on the nature of the catalyst and the nature of the fluoroalkyl group of alkyne.

The field of organofluorine chemistry plays an important role in various applications including agrochemicals, soft materials, and especially pharmaceuticals, for which they are widely used as anticancer, antiarrhythmic, antihypertensive agents, anti-inflammatory, antidepressant, and antibiotics.[1–3] In fact, the unique properties of fluorine has an exceptional impact on the electronic, lipophilic, and steric parameters, and on the acidity or basicity of organofluorinated molecules. Accordingly, the incorporation of fluorine atoms and perfluoroalkyl groups into organic compounds can modify their physiochemical properties, improve their metabolic stability, and change their biological activities.[4] Therefore, the introduction of fluorinated building blocks in controlled strategies is considered an interesting challenge for many researchers, particularly those studying fluoroalkylated vinyl metals.[5,6] However, the selective introduction of (E) and (Z) fluoroalkylated alkenes in the structure of natural products is still daunting.

There are a few synthetic strategies that enable such an operation including the direct sp^2 C–H bond functionalization,[7] and olefination reactions.[8] However, these methods suffer from limitations and stereoselectivity issues. Provided that regio- and stereoselectivity of the hydrometallation could be controlled, an efficient approach that would afford a straightforward entry to the selective preparation of low toxic fluoro-polysubstituted alkenes would rely on the hydrogermylation/cross coupling sequences from alkynes bearing fluorinated moieties. Although, germanium is slightly more expensive than tin, it is closer to silicon in its organic chemistry. Furthermore, germanium has a higher thermal stability,[9] and a lower toxicity than tin.[10]

The addition of organogermanes to alkynes is the best method for the direct synthesis of vinylgermanes.[11,12] However, hydrogermylation of carbonyl functionalized fluorinated alkynes, which provides a new entry to a wide range of functional fluorinated compounds, is still under investigation. To our knowledge, no hydrogermylation reaction of fluorinated alkynes type **1a**[13] has been described in the open literature. It is worth mentioning that we recently reported the first highly regio- and stereoselective free-metal hydrostannylation of ethyl 4,4,4-trifluorobut-2-ynoate (**1a**) leading to the synthesis of α and β-tributylstannyl-4,4,4-trifluorobut-2-enoates without any additives (Scheme 1).[14]
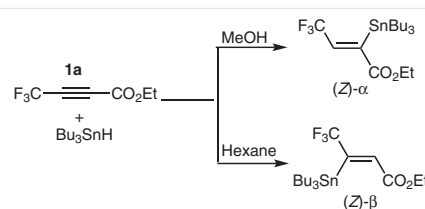

Scheme 1 Previously described hydrostannylation of ethyl 4,4,4-trifluorobutenoate (**1a**)

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As a continuation of our previous study on the hydro-metalation reaction of fluorinated alkynes for the preparation of new vinylmetals bearing a perfluoroalkyl group,[14,15] we report herein, for the first time, a highly regio- and stereoselective hydrogermylation reaction of fluorinated alkynes of type **1** using the inexpensive Lewis acid AlCl$_3$ as catalyst.

We first sought to determine the best conditions for a highly regio- and stereoselective hydrogermylation reaction of fluorinated ethyl propiolate **1a** with Ph$_3$GeH using different solvents and additives. The results are summarized in Table 1.

First, we examined the free-metal hydrogermylation of **1a** using triphenylgermanium hydride in different solvents. Importantly, and contrary to what is generally observed in the case of hydrostannylation of alkyne **1a**,[14] the regioselectivity of this hydrogermylation reaction is relatively independent of the nature of the solvent (Table 1, entries 1–3). Thus, using hexane, methanol or dichloromethane as solvent, the hydrogermylation of alkyne **1a** leads to the formation of the four possible isomers (Z)-**2α**, (E)-**2α**, (Z)-**2β** and (E)-**2β**. In all cases, the regioselectivity is greatly in favor of the β-regioisomer (>75 %). Although the ratio of formation of both α- and β-adducts is not exactly the same in each selected solvent, it is clear that the polarity of the solvents does not have a significant impact on the hydrogermylation reaction.

The regiochemistry of vinylgermanes was then deduced without ambiguity from NMR data, especially from the J_{H-F} coupling patterns (Figure 1). Indeed, in the case of the α-regioisomer, the coupling constant $^3J_{H-F}$ reaches a value of ca. 7–8 Hz, whereas in the case of the β-regioisomer the coupling constant $^4J_{H-F}$ is close to 1–2 Hz. These values are consistent with previously published work.[16]

Figure 1 $^3J_{H-F}$ and $^4J_{H-F}$ coupling constants of the two regioisomers α and β, respectively
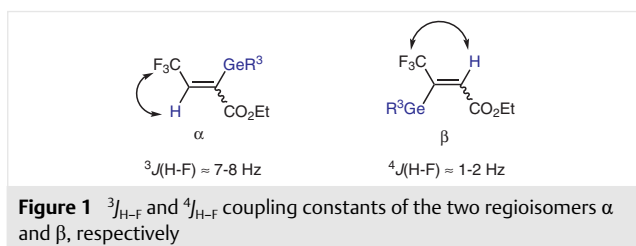
For further investigations, the hydrogermylation of alkyne **1a** was carried out under similar conditions in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a radical scavenger (Table 1, entry 4). Remarkably, the β-regioisomer was not formed and only the α-isomer was isolated in 21% yield as a 64:36 mixture of the geometric isomers (E)-**2α** and (Z)-**2α**, respectively. These results suggest that the reaction mechanism leading to the formation of the β-regioisomer takes place according to a radical process, while the α-isomer could be the product of an ionic pathway. Furthermore, these results indicate that the free-metal

hydrogermylation reaction proceeds mainly by a free radical mechanism. Organogermanium hydrides have been used for the radical and transition-metal-catalyzed hydrogermylation of alkynes since the mid-1950s, but such transformations still suffer from serious limitations such as low regio- and stereoselectivities.[17–19] However, Blanchard et al. developed two efficient stereocomplementary routes for nonfunctionalized (Z)- and (E)-α-trifluoromethylvinyl-germanes by regio- and stereoselective hydrogermylation of α-trifluoromethylated alkynes under transition-metal-catalyzed conditions or in presence of a radical initiator.[20] Inspired by these results, fluorinated alkyne **1a** was treated in dichloromethane with 1 equivalent of Ph$_3$GeH in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ (5 mol %). The ^{1}H and ^{19}F NMR spectra of the crude hydrogermylation product reveal a 60:40 mixture of the α and β regioisomers was formed, respectively (entry 5). The (E)-**2α** adduct, resulting from a cis-addition, constitutes the major product.

To explore more synthetic routes to perform the highly regio- and stereoselective hydrogermylation of alkyne **1a**, we next directed our attention to the radical hydrogermylation of alkyne **1a**. The treatment of alkyne **1a** with Ph$_3$GeH at room temperature using ammonium persulfate,[21] as radical initiator in aqueous acetonitrile, provides a mixture of the α- and β-regioisomers in a ratio of about 22:78, with a majority of the trans-addition product (Z)-**2β** (Table 1, entry 6). Similar results were obtained but with a lower yield when we used the known radical initiator triethylborane BEt$_3$[22] (entries 7). Another class of catalyzed hydrogermylation reaction of functionalized alkynes was reported in 2005 based on the use of an expensive Lewis acid such as B(C$_6$F$_5$)$_3$.[23] Gevorgyan et al. demonstrated that the stereochemistry of this hydrogermylation reaction depends on the nature of the alkyne used; the reaction proceeded via a trans-addition pathway with simple alkynes and cis-addition with ethyl propiolate. Applying the same conditions as Gevorgyan et al., by using BPh$_3$, a less expensive Lewis acid than B(C$_6$F$_5$)$_3$, the hydrogermylation of alkyne **1a** with Ph$_3$GeH proceeds mainly by trans-addition, yielding the major product (Z)-**2β** with a small amount of the α-adduct (entry 8).

Lewis acid AlCl$_3$ mediated hydrosilylation and hydrostannylation of alkynes have been reported,[24] but AlCl$_3$ has never been used in the case of the hydrogermylation of alkynes. We therefore decided to perform the hydrogermylation reaction of alkyne **1a** at room temperature in the presence of a catalytic amount of AlCl$_3$ (10 mol%) in toluene during 2 h. Remarkably, complete α-regioselectivity of the hydrogermylation of alkyne **1a** was observed, yielding α-triphenylgermylacrylate **2α** as the sole regioisomer in 74% yield (Table 1, entry 9). Furthermore, the stereoselectivity was also greatly in favor of the (E)-isomer (E > 93%). Surprisingly, complete regio- and stereoselectivity of the hydrogermylation reaction was observed in the presence of

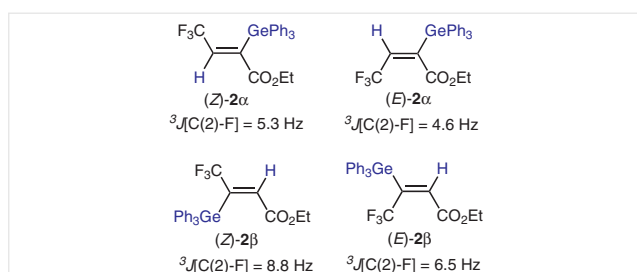**Table 1** Hydrogermylation Reaction Conditions for **1a**

Entry	Solvent	Additive (%)	α/β	(Z)-**2α** (%)	(E)-**2α** (%)	(Z)-**2β** (%)	(E)-**2β** (%)	Yield (%)
1	methanol	–	24:76	14.0	9.8	68.9	6.3	39[a]
2	hexane	–	24:76	13.2	10.4	68.3	7.8	35[a]
3	CH_2Cl_2	–	20:80	14.8	5.5	78.1	1.6	65[a]
4	CH_2Cl_2	TEMPO	100:0	36.0	64.0	0.0	0.0	21[b]
5	CH_2Cl_2	Pd(PPh₃)₄ (5)	60:40	0.7	59.5	29.7	10.1	31[a]
6	CH_3CN/H_2O	(NH₄)₂S₂O₈ (20)	22:78	18.4	3.9	76.9	0.8	83[a]
7	CH_2Cl_2	Et₃B (10)	32:68	25.6	7.0	63.5	4.1	50[a]
8	CH_2Cl_2	BPh₃ (10)	26:74	17.0	9.0	74.0	0.0	77[a]
9	toluene	AlCl₃ (10)	100:0	6.6	93.4	0.0	0.0	74[b]
10	CH_2Cl_2	AlCl₃ (10)	100:0	0.0	100.0	0.0	0.0	92[b]

[a] Evaluated by ^{1}H NMR and ^{19}F NMR.
[b] Yield of isolated product.

a catalytic amount of AlCl₃ (10 mol%) using CH_2Cl_2 as solvent, yielding (E)-**2α** as the sole product with excellent yield (entry 10).

In view of these results, we deduced that the optimum conditions for the hydrogermylation reaction of alkyne **1a** to produce the corresponding *trans*-vinylgermane (E)-**2α** in a complete regio- and *cis*-stereoselective manner is 1 mol of Ph₃GeH and 10 mol% of AlCl₃ in CH_2Cl_2 at room temperature for 2 h.

The *E*- and *Z*-configurations of the two regioisomers **2α** and **2β** were assigned based on the values of the coupling constant [³J(C(2)-F)]; for which ³J[C(2)-F] of the (Z)-isomer is higher than that of the (E)-isomer (Figure 2).[16,20]

Figure 2 *E*- and *Z*-configuration assignments of the two regioisomers α and β

To investigate the scope and limitations of the AlCl₃-catalyzed hydrogermylation reaction, we next tested the hydrogermylation reaction of alkyne **1a** using a less hindered organogermane compound such as Bu₃GeH. Remarkably, complete α-regioselectivity of the hydrogermylation of alkyne **1a** was observed. However, the reaction was found to be highly but not completely stereoselective, be-

cause traces of the *Z*-stereoisomer were observed (E/Z = 91:9). Therefore, it seems that the size of the R group on R₃GeH is at the origin of this result. To further investigate the regiochemistry of vinylgermane **3**, we then tested the radical hydrogermylation of alkyne **1a** using Bu₃GeH in the presence of Et₃B as a radical initiator and CH_2Cl_2 as solvent, providing a mixture of the four possible isomers (Z)-**3α**, (E)-**3α**, (Z)-**3β** and (E)-**3β** with the majority being the *trans*-addition product (Z)-**3β** (Scheme 2).
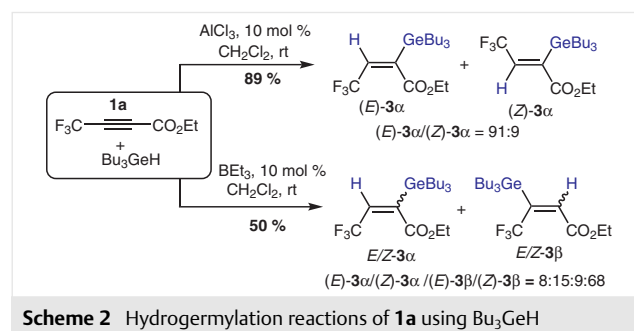

Scheme 2 Hydrogermylation reactions of **1a** using Bu₃GeH

Another fluorinated α,β-acetylenic ester, ethyl 4,4,5,5,5-pentafluoropent-2-ynoate (**1b**),[13] was then treated under the same conditions as those described above. The results obtained were very similar to those obtained in the case of alkyne **1a**. The hydrogermylation of alkyne **1b** using AlCl₃ as catalyst in CH_2Cl_2 and Ph₃GeH yields exclusively the *cis*-addition product (E)-**4α** in 91% yield. Likewise, as observed in the case of alkyne **1a**, there was a slight loss of stereoselectivity when triphenylgermane was substituted with the less bulky tributylgermane, but the regioselectivity remained complete. Similarly, radical hydrogermylation of

alkyne **1b** using Bu$_3$GeH or Ph$_3$GeH in the presence of Et$_3$B was performed, yielding a mixture of α- and β-regioisomers in a ratio of ca. 33:67, respectively, with the majority of the *trans*-addition product (*Z*)-**4β** and (*Z*)-**5β** (Scheme 3).

**Scheme 3** Hydrogermylation of **1b** using Ph$_3$GeH and Bu$_3$GeH
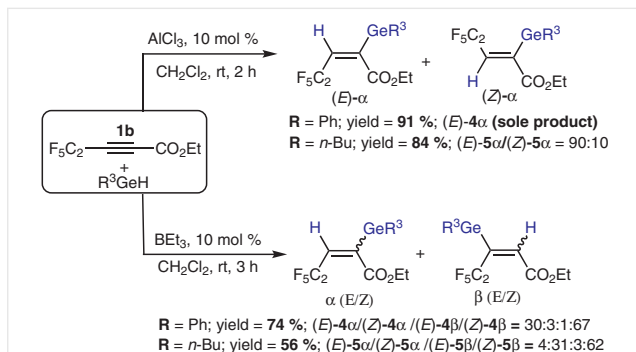
To better understand the role of the fluorinated group of the alkyne in the orientation of the regioselectivity of the AlCl$_3$-catalyzed hydrogermylation reaction, hydrogermylation of methyl 4,4-difluoro-4-phenylbut-2-ynoate (**1c**)[25] using Ph$_3$GeH was performed under the conditions described above (Scheme 4). Although the reaction gave the (*E*)-**6α** adduct as the major isomer, it was accompanied by the formation of the other three isomers in the proportions: (*Z*)-**6α** (7%), (*E*)-**6α** (55%), (*Z*)-**6β** (34%) and (*E*)-**6β** (4%).
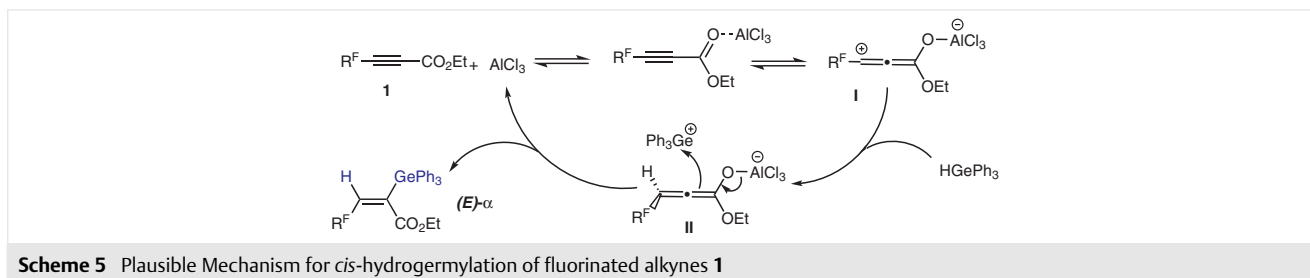

Scheme 4 AlCl$_3$-catalyzed hydrogermylation of **1c** using Ph$_3$GeH
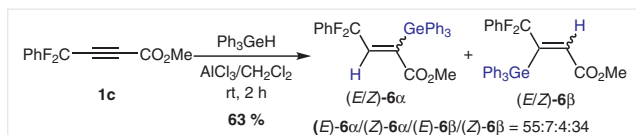
It is worth mentioning that the regio- and stereochemistry for the vinylgermanes **3**, **4**, **5** and **6** were deduced from the $^3J_{H–F}$, $^4J_{H–F}$ and $^3J_{C–F}$ coupling patterns by following the analyses described above in case of vinylgermane **2**.

Despite the limited number of fluorinated alkynes used, it seems that the regioselectivity of this hydrogermylation reaction is also very dependent on the nature of the fluorinated group of the alkyne. This dependence may be related

to the difference of the partial charges on sp-carbon atoms of the alkyne. To investigate this in greater detail, ab initio calculations were carried out (full minimization of the structure realized using the HF/6-311G* level of theory followed by a single-point calculation with the basic set DFT/B3-LYP/def-TZVP within Turbomole 7.2) to determine the partial charge of these two sp-carbon atoms (Scheme 5), thanks to the Natural Population Analysis approach.[26] A larger difference on the partial charges (Δ = δC$_3$–δC$_2$) was observed in the cases of alkynes **1a** and **1b** than in alkyne **1c** (Figure 3). Furthermore, changing a -CF$_3$ (or -C$_2$F$_5$) group with a PhF$_2$C induces a significant charge inversion on sp-carbon atoms. To further understand the origin of the regioselectivity of this hydrogermylation reaction by using AlCl$_3$ as catalyst, a similar charge analysis was carried out on intermediates (**1a′**, **1b′** and **1c′**). By looking at the partial charge of each carbocation, it seems that C3 of **1c′** is less electrophile than those of **1a′** and **1b′**. This may explain the higher regioselectivity observed in the case of alkynes **1a** and **1b** (Figure 3).

Figure 3 Partial charges on the sp-carbon atoms
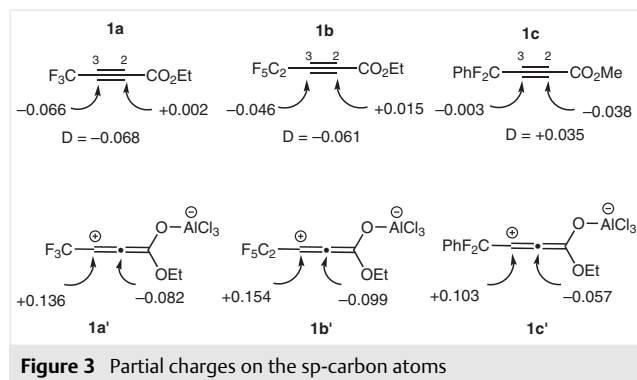
By taking into consideration the charge distribution of these two sp-carbon atoms, a plausible ionic mechanism for the AlCl$_3$-catalyzed *cis* hydrogermylation of fluorinated alkynes type **1** is shown in Scheme 5. The coordination of the ester-carbonyl group of alkynes of type **1** to AlCl$_3$ produces the zwitterionic intermediate **I**, which is transformed into allenoate **II** through hydride transfer from Ph$_3$GeH to the cationic center of **I**. Trapping of intermediate **II** with germylium-type species occurs from the less hindered face, *cis* to H, thus providing the *cis*-hydrogermylation (*E*)-α products and regenerating the AlCl$_3$ catalyst.

Scheme 5 Plausible Mechanism for *cis*-hydrogermylation of fluorinated alkynes **1**

In summary, the AlCl₃-catalyzed hydrogermylation reaction of ethyl propiolate bearing a perfluoroalkyl group can be achieved under very mild conditions. This reaction proceeds in a highly regio- and stereocontrolled manner, providing functionalized vinylgermane products with excellent yields. Studies are now under way to delineate the synthetic utility of these reagents and the results of these investigations will be reported in due course.

Most reagents were obtained from commercial sources and used as received. All reactions were carried out under inert atmosphere. Petroleum ether (PE) used had a boiling range 40–60 °C, CH₂Cl₂ was distilled from calcium hydride and stored under Argon. Thin-layer chromatography (TLC) was performed on Merck 60F254 plates. Column chromatography was carried out with Merck silica gel 60 (0.040–0.063 mm, 230–400 mesh). All ¹H, ¹³C, and ¹⁹F NMR spectra were recorded with a 300 MHz Bruker Avance FT NMR spectrometer (300 MHz, 75 or 282 MHz, respectively). All chemical shifts are given as δ values (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The coupling constants J are reported in Hertz (Hz). Electrospray ionization high-resolution mass spectrometry experiments (HRMS) were performed with a hybrid tandem quadrupole/time-of flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, U.K.) operated in positive mode.

AlCl₃-Catalyzed Hydrogermylation Reaction: Synthesis of (E)-α Adduct; General Procedure A

Alkyne **1a** (143 mg, 0.86 mmol) was placed in a vial containing a magnetic stirring bar. AlCl₃ (12 mg, 0.09 mmol, 10 mol%) in CH₂Cl₂ (0.5 mL) was added to the vial. The vial was sealed with a Teflon-coated silicon rubber septum, evacuated and filled with argon. The reaction mixture was set at 0 °C. After 5 min stirring, Ph₃GeH (220 mg, 0.72 mmol) was then added. The mixture was stirred for 1 hour at 0 °C, then Et₃N (37 mg, 0.36 mmol) was added. The reaction mixture was allowed to warm to r.t. then hexane was added and the mixture was filtered through Celite. The solvent was evaporated under vacuum and column chromatography through silica gel afforded the purified (E)-**2α**-isomer (290 mg, 92%) with complete regio- and stereoselectivity.

Radical Hydrogermylation using BEt₃: Synthesis of Mixture of Isomers (E)-β, (Z)-β, (E)-α, (Z)-α; General Procedure B

Triethylborane (6 mg, 0.1 equiv, 0.06 mmol), Bu₃GeH (177 mg, 1.2 equiv, 0.72 mmol) and CH₂Cl₂ (0.4 mL) were placed in a vial containing a magnetic stirring bar. The vial was sealed with a teflon-coated silicon rubber septum, evacuated and filled with argon. Alkyne **1a** (100 mg, 1 equiv, 0.60 mmol) was added slowly to the reaction mixture. The reaction mixture was left for 3 hours under agitation at r.t. then the solvent was evaporated under vacuum. Column chromatography through silica gel using PE as eluent afforded the four isomers (247 mg, 50% overall yield).

(E)-**2α**, (E)-**3α**, (E)-**4α** and (E)-**5α** were characterized by ¹H, ¹³C, and ¹⁹F NMR and HRMS; whereas, all other products obtained in the form of a mixture of isomers were characterized at least by ¹H NMR and ¹⁹F NMR spectroscopy.

(E)-Ethyl 4,4,4-Trifluoro-2-(triphenylgermyl)but-2-enoate [(E)-2α]

(E)-**2α** was obtained as the sole product by following general procedure A.

Yield: 92%; white solid; mp 85–86 °C.

¹H NMR (300 MHz, CDCl₃): δ = 7.67–7.46 (m, 15 H), 5.88 (q, J_{H-F} = 7.2 Hz, 1 H), 4.07 (q, J = 7.1 Hz, 2 H), 1.02 (t, J = 7.1 Hz, 3 H).

¹³C NMR (CDCl₃, 75 MHz): δ = 168.3, 146.4 (q, J_{C-F} = 4.7 Hz), 135.3 (6C), 132.9 (3C), 130.1 (3C), 129.5 (q, J_{C-F} = 35.2 Hz), 128.7 (6C), 121.3 (q, J_{C-F} = 272.5 Hz), 61.4, 13.8.

¹⁹F NMR (CDCl₃, 282 MHz): δ = –61.84.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₄H₂₂F₃GeO₂: 473.02904; found: 473.02710.

(E)-Ethyl 4,4,4-Trifluoro-3-(triphenylgermyl)but-2-enoate [(E)-2β]

(E)-**2β** was obtained as a mixture with the other three isomers by following general procedure B.

¹H NMR (CDCl₃, 300 MHz): δ = 7.66–7.34 (m, 15 H), 6.41 (bs, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 1.30 (t, J = 7.1 Hz, 3 H).

¹⁹F NMR (CDCl₃, 282 MHz): δ = –54.58.

(Z)-Ethyl 4,4,4-Trifluoro-2-(triphenylgermyl)but-2-enoate [(Z)-2α]

(Z)-**2α** was obtained as a mixture with the other three isomers by following general procedure B.

¹H NMR (CDCl₃, 300 MHz): δ = 7.67–7.46 (m, 15 H), 6.99 (q, J_{H-F} = 7.9 Hz, 1 H), 3.72 (q, J = 7.1 Hz, 2 H), 0.87 (t, J = 7.1 Hz, 3 H).

¹³C NMR (CDCl₃, 75 MHz): δ = 169.6, 146.9 (q, J_{C-F} = 5.3 Hz), 135.7 (6C), 134.3 (q, J_{C-F} = 35.8 Hz), 133.2 (3C), 129.5 (3C), 128.7 (6C), 121.3 (q, J_{C-F} = 272.5 Hz), 61.4, 13.8.

¹⁹F NMR (CDCl₃, 282 MHz): δ = –60.5.

(Z)-Ethyl 4,4,4-Trifluoro-3-(triphenylgermyl)but-2-enoate [(Z)-2β]

(Z)-**2β** was obtained as a mixture with the other three isomers by following general procedure B.

¹H NMR (CDCl₃, 300 MHz): δ = 7.66–7.34 (m, 15 H), 7.26 (q, J_{H-F} = 2.2 Hz, 1 H), 3.50 (q, J = 7.1 Hz, 2 H), 0.77 (t, J = 7.1 Hz, 3 H).

¹³C NMR (CDCl₃, 75 MHz): δ = 164.5, 144.6 (q, J_{C-F} = 31.1 Hz), 137.8 (q, J_{C-F} = 8.8 Hz), 134.9 (6C), 129.3 (3C), 128.4 (6C), 128.4 (3C), 125.0 (q, J_{C-F} = 272.8 Hz), 61.3, 13.4.

¹⁹F NMR (CDCl₃, 282 MHz): δ = –60.7.

(E)-Ethyl 4,4,4-Trifluoro-2-(tributylgermyl)but-2-enoate [(E)-3α]

(E)-**3α** was obtained as a mixture with (Z)-**3α** by following general procedure A.

Yield: 89%; colorless oil.

¹H NMR (CDCl₃, 300 MHz): δ = 5.71 (q, J_{H-F} = 7.23 Hz, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 1.38–1.28 (m, 18 H), 0.95–0.87 (m, 12 H).

¹³C NMR (CDCl₃, 75 MHz): δ = 169.3, 149.2 (q, J_{C-F} = 4.6 Hz), 125.3 (q, J_{C-F} = 33.6 Hz), 121.4 (q, J_{C-F} = 272.3 Hz), 68.1, 26.8 (3C), 26.4 (3C), 14.2, 13.7 (3C), 12.6 (3C).

¹⁹F NMR (CDCl₃, 282 MHz): δ = –61.93.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₈H₃₄F₃GeO₂: 413.02930; found: 413.02721.

(E)-Ethyl 4,4,4-Trifluoro-3-(tributylgermyl)but-2-enoate [(E)-3β]

(E)-**3β** was obtained as a mixture with the other three isomers by following general procedure B.

¹H NMR (CDCl₃, 300 MHz): δ = 6.35 (q, J_{H-F} = 1.7 Hz, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 1.38–1.28 (m, 18 H), 0.95–0.87 (m, 12 H).

¹⁹F NMR (CDCl₃, 282 MHz): δ = –61.63.

(Z)-Ethyl 4,4,4-Trifluoro-2-(tributylgermyl)but-2-enoate [(Z)-3α]

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(Z)-3α was obtained as a mixture with **(E)-3α** by following general procedure A.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 6.61 (q, J_{H-F} = 8.5 Hz, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 1.38–1.28 (m, 18 H), 0.95–0.87 (m, 12 H).

^{13}C NMR (CDCl$_3$, 75 MHz): δ = 170.6, 150.3 (q, J_{C-F} = 5.5 Hz), 132.6 (q, J_{C-F} = 35.5 Hz), 122.9 (q, J_{C-F} = 269.8 Hz), 61.5, 27.1 (3C), 25.7 (3C), 14.2 (3C), 14.0, 13.9 (3C).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –60.50.

(Z)-Ethyl 4,4,4-Trifluoro-3-(tributylgermyl)but-2-enoate [(Z)-3β]

(Z)-3β was obtained as a mixture with the other three isomers by following general procedure B.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 6.89 (q, J_{H-F} = 2.3 Hz, 1 H), 4.23 (q, J = 7.1 Hz, 2 H), 1.38–1.28 (m, 18 H), 0.95–0.87 (m, 12 H).

^{13}C NMR (CDCl$_3$, 75 MHz): δ = 165.4, 150.2 (q, J_{C-F} = 31.3 Hz), 134.5 (q, J_{C-F} = 9.6 Hz), 125.6 (q, J_{C-F} = 272.5 Hz), 61.1, 27.1 (3C), 26.3 (3C), 14.1, 13.6 (3C), 13.4 (3C).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –61.76.

(E)-Ethyl 4,4,5,5,5-Pentafluoro-2-(triphenylgermyl)pent-2-enoate [(E)-4α]

(E)-4α was obtained as a sole product by following general procedure A.

Yield: 91%; white solid; mp 85–86 °C.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.54–7.39 (m, 15 H), 5.80 (t, J_{H-F} = 13.3 Hz, 1 H), 3.95 (q, J = 7.1 Hz, 2 H), 1.0 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (CDCl$_3$, 75 MHz): δ = 168.3, 145.2 (t, J_{C-F} = 4.8 Hz), 135.6 (6C), 132.7 (3C), 130.1 (3), 128.7 (6C), 126.8 (t, J_{C-F} = 23.4 Hz), 118.8 (qt, J_{C-F} = 284.7 Hz, 36.7 Hz), 111.6 (tq, J_{C-F} = 252.8 Hz, 38.8 Hz), 61.3, 13.8.

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –84.55 (t, J_{F-F} = 2.0 Hz, CF$_3$), –113.96 (q, J_{F-F} = 2.0 Hz, CF$_2$).

HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{25}$H$_{22}$F$_5$GeO$_2$: 523.07463; found: 523.07265.

(E)-Ethyl 4,4,5,5,5-Pentafluoro-3-(triphenylgermyl)pent-2-enoate [(E)-4β]

(E)-4β was obtained as a mixture with the other three isomers by following general procedure B.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.66–7.3 (m, 15 H), 6.66 (t, J_{H-F} = 1.7 Hz, 1 H), 4.28 (q, J = 7.1 Hz, 2 H), 0.86 (t, J = 7.1 Hz, 3 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –81.61 (t, J_{F-F} = 2.2 Hz, CF$_3$), –102.14 (q, J_{F-F} = 2.2 Hz, CF$_2$).

(Z)-Ethyl 4,4,5,5,5-Pentafluoro-2-(triphenylgermyl)pent-2-enoate [(Z)-4α]

(Z)-4α was obtained as a mixture with the other three isomers by following general procedure B.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.66–7.3 (m, 15 H), 5.89 (t, J_{H-F} = 14.2 Hz, 1 H), 4.03 (q, J = 7.1 Hz, 2 H), 1.06 (t, J = 7.1 Hz, 3 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –84.59 (t, J_{F-F} = 2.2 Hz, CF$_3$), –113.89 (q, J_{F-F} = 2.2 Hz, CF$_2$).

(Z)-Ethyl 4,4,5,5,5-Pentafluoro-3-(triphenylgermyl)pent-2-enoate [(Z)-4β]

(Z)-4β was obtained as a mixture with the other three isomers by following general procedure B.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.66–7.3 (m, 15 H), 7.32 (t, J_{H-F} = 1.9 Hz, 1 H), 3.48 (q, J = 7.1 Hz, 2 H), 1.01 (t, J = 7.1 Hz, 3 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –82.06 (t, J_{F-F} = 2.3 Hz, CF$_3$), –104.78 (q, J_{F-F} = 2.3 Hz, CF$_2$).

(E)-Ethyl 4,4,5,5,5-Pentafluoro-2-(tributylgermyl)pent-2-enoate [(E)-5α]

(E)-5α was obtained as a mixture with **(Z)-5α** by following general procedure A.

Yield: 84%; colorless oil.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 5.60 (t, J_{H-F} = 13.3 Hz, 1 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.38–1.25 (m, 12 H), 0.97–0.86 (m, 18 H).

^{13}C NMR (CDCl$_3$, 75 MHz): δ = 169.4, 152.2 (t, J_{C-F} = 4.7 Hz), 122.4 (t, J_{C-F} = 23.5 Hz), 111.6 (tq, J_{C-F} = 252/ 38.5 Hz), 118.9 (qt, J_{C-F} = 284.5/ 37.1 Hz), 61.0, 26.8 (3C), 26.3 (3C), 14.2, 13.7 (3C), 12.6 (3C).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –84.91 (t, J_{F-F} = 2.2 Hz, CF$_3$), –113.95 (q, J_{F-F} = 2.2 Hz, CF$_2$).

HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{19}$H$_{34}$F$_5$GeO$_2$: 463.16853; found: 463.16643.

(E)-Ethyl 4,4,5,5,5-Pentafluoro-3-(tributylgermyl)pent-2-enoate [(E)-5β]

(E)-5β was obtained as a mixture with the other three isomers by following general procedure B.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 6.31 (bs, 1 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.38–1.25 (m, 18 H), 0.97–0.86 (m, 12 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –82.76 (t, J_{F-F} = 1.8 Hz, CF$_3$), –113.91 (q, J_{F-F} = 1.8 Hz, CF$_2$).

(Z)-Ethyl 4,4,5,5,5-Pentafluoro-2-(tributylgermyl)pent-2-enoate [(Z)-5α]

(Z)-5α was obtained as a mixture with **(E)-5α** by following general procedure A.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 6.50 (t, J_{H-F} = 14.8 Hz, 1 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.38–1.25 (m, 18 H), 0.97–0.86 (m, 12 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –84.95 (t, J_{F-F} = 2.5 Hz, CF$_3$), –113.46 (q, J_{F-F} = 2.5 Hz, CF$_2$).

(Z)-Ethyl 4,4,5,5,5-Pentafluoro-3-(tributylgermyl)pent-2-enoate [(Z)-5β]

(Z)-5β was obtained as a mixture with the other three isomers by following general procedure B.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 6.84 (t, J_{H-F} = 2.0 Hz, 1 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.38–1.25 (m, 18 H), 0.97–0.86 (m, 12 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –82.29 (t, J_{F-F} = 1.5 Hz, CF$_3$), –105.48 (q, J_{F-F} = 1.5 Hz, CF$_2$).

(E)-Methyl 4,4-Difluoro-4-phenyl-2-(triphenylgermyl)but-2-enoate [(E)-6α]

(E)-6α was obtained as a mixture with the other three isomers by following general procedure A.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.61–7.25 (m, 15 H), 7.23–7.17 (m, 2 H), 7.19–7.09 (m, 2 H), 7.08 (t, J = 14.0 Hz, 1 H), 6.88–6.86 (m, 1 H), 3.04 (s, 3 H).

^{13}C NMR (CDCl$_3$, 75 MHz): δ = 165.8, 152.7 (t, J_{C-F} = 29.5 Hz), 142.2 (t, J_{C-F} = 29.8 Hz), 135.9 (t, J_{C-F} = 2.4 Hz, 2C), 134.9 (6C), 129.9 (t, J_{C-F} = 1.3 Hz, 2C), 129.6, 129.1 (3C), 128.1 (3C), 127.9 (6C), 125.7 (t, J_{C-F} = 5.6 Hz, 1C), 122.23 (t, J_{C-F} = 242.2 Hz, 1C, CF$_2$), 51.4.

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –85.31.

(E)-Methyl 4,4-Difluoro-4-phenyl-3-(triphenylgermyl)but-2-enoate [(E)-6β]

(E)-6β was obtained as a mixture with the other three isomers by following general procedure A.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.61–7.25 (m, 15 H), 7.23–7.17 (m, 2 H), (m, 2 H), 7.19–7.09 (m, 2 H), 6.40 (t, J = 1.7 Hz, 1 H), 6.88–6.86 (m, 1 H), 3.59 (s, 3 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –91.30.

(Z)-Methyl 4,4-Difluoro-4-phenyl-2-(triphenylgermyl)but-2-enoate [(Z)-6α]

(Z)-**6α** was obtained as a mixture with the other three isomers by following general procedure A.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.61–7.25 (m, 15 H), 7.23–7.17 (m, 2 H), (m, 2 H), 7.19–7.09 (m, 2 H), 6.05 (t, J = 12.1 Hz, 1 H), 6.88–6.86 (m, 1 H), 3.46 (s, 3 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –78.11.

(Z)-Methyl 4,4-Difluoro-4-phenyl-3-(triphenylgermyl)but-2-enoate [(Z)-6β]

(Z)-**6β** was obtained as a mixture with the other three isomers by following general procedure A.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.61–7.25 (m, 15 H), 7.23–7.17 (m, 2 H), (m, 2 H), 7.19–7.09 (m, 2 H), 7.13 (t, J = 2.7 Hz, 1 H), 6.88–6.86 (m, 1 H), 3.20 (s, 3 H).

^{19}F NMR (CDCl$_3$, 282 MHz): δ = –90.26.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611666.

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