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.

Key words regio- and stereoselective hydrogermylation, fluorinated ethyl propiolate, AlCl\(_3\), triphenyl- and tributylgermanes, fluorinated vinylgermanes

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, anti-hypertensive agents, anti-inflammatory, antidepressant, and antibiotics.\textsuperscript{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 group into organic compounds can modify their physicochemical properties, improve their metabolic stability, and change their biological activities.\textsuperscript{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.\textsuperscript{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,\textsuperscript{7} and olefination reactions.\textsuperscript{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,\textsuperscript{9} and a lower toxicity than tin.\textsuperscript{10}

The addition of organogermanes to alkynes is the best method for the direct synthesis of vinylgermanes.\textsuperscript{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 \textsuperscript{1a}\textsuperscript{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 \(\alpha\)- and \(\beta\)-tributylstannyl-4,4,4-trifluorobut-2-enoates without any additives (Scheme 1).\textsuperscript{14}

\begin{center}
\textbf{Scheme 1} Previously described hydrostannylation of ethyl 4,4,4-trifluorobutenoate (1a)
\end{center}
As a continuation of our previous study on the hydro-
metallation reaction of fluorinated alkynes for the prepa-
ratio of new vinylmetals bearing a perfluoroalkyl group,\textsuperscript{14,15} we report herein, for the first time, a highly regio- and stereo-
selective hydrogermylation reaction of fluorinated
alkynes of type 1 using the inexpensive Lewis acid AlCl\textsubscript{3} as
catalyst.

We first sought to determine the best conditions for a
highly regio- and stereoselective hydrogermylation reac-
tion of fluorinated ethyl propiolate 1a with Ph\textsubscript{3}GeH using
different solvents and additives. The results are summa-
rized 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,\textsuperscript{14} the regio-
selectivity of this hydrogermylation reaction is relatively inde-
pendent of the nature of the solvent (Table 1, entries 1–3).
Thus, using hexane, methanol or dichloromethane as sol-
vent, the hydrogermylation of alkyne 1a leads to the for-
mation of the four possible isomers (Z)-2\textsubscript{a}, (E)-2\textsubscript{a}, (Z)-2\textsubscript{b}
and (E)-2\textsubscript{b}. 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 se-
lected 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 \(J_{H-F}\) reaches a value of ca. 7–8 Hz, whereas in the case of the β-regioisomer the
coupling constant \(J_{H-F}\) is close to 1–2 Hz. These values are
consistent with previously published work.\textsuperscript{16}

![Figure 1 - \(J_{H-F}\) and \(J_{H-F}\) coupling constants of the two regioisomers α and β, respectively](image)

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 iso-
lated in 21% yield as a 64:36 mixture of the geometric iso-
mers (E)-2\textsubscript{a} and (Z)-2\textsubscript{a}, 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 path-
way. Furthermore, these results indicate that the free-metal
hydrogermylation reaction proceeds mainly by a free radi-
cal mechanism. Organogeranium hydrides have been
used for the radical and transition-metal-catalyzed hydro-
germylation of alkynes since the mid-1950s, but such
transformations still suffer from serious limitations such as
low regio- and stereoselectivities.\textsuperscript{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.\textsuperscript{10}

Inspired by these results, fluorinated alkyne 1a was treated
in dichloromethane with 1 equivalent of Ph\textsubscript{3}GeH in the
presence of a catalytic amount of Pd(PPPh\textsubscript{3})\textsubscript{4} (5 mol \%). The
\(^1\text{H}\) and \(^19\text{F}\) 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)-2\textsubscript{a} adduct, re-
sulting 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 hydrogermyla-
tion of alkyne 1a. The treatment of alkyne 1a with Ph\textsubscript{3}GeH at
room temperature using ammonium persulfate,\textsuperscript{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)-2\textsubscript{b} (Table 1, entry 6). Similar results were obtained but with a lower
yield when we used the known radical initiator triethylbor-
rane BEt\textsubscript{3},\textsuperscript{22} (entries 7). Another class of catalyzed hydro-
germylation reaction of functionalized alkynes was report-
ed in 2005 based on the use of an expensive Lewis acid such
as B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}.\textsuperscript{23} Gevorgyan et al. demonstrated that the stereo-
chemistry 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-addi-
tion with ethyl propiolate. Applying the same conditions as
Gevorgyan et al., by using BPh\textsubscript{3}, a less expensive Lewis acid
than B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, the hydrogermylation of alkyne 1a with
Ph\textsubscript{3}GeH proceeds mainly by trans-addition, yielding the
major product (Z)-2\textsubscript{b} with a small amount of the α-adduct
(entry 8).

Lewis acid AlCl\textsubscript{3} mediated hydroxsilylation and hydro-
stannylation of alkynes have been reported,\textsuperscript{24} but AlCl\textsubscript{3} has
never been used in the case of the hydrogermylation of
alkynes. We therefore decided to perform the hydrogermy-
lation reaction of alkyne 1a at room temperature in the
presence of a catalytic amount of AlCl\textsubscript{3} (10 mol \%) in toluene
during 2 h. Remarkably, complete α-regioselectivity of the
hydrogermylation of alkyne 1a was observed, yielding α-
triphenylgermylacrylate 2a 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%). Sur-
prisingly, complete regio- and stereoselectivity of the
hydrogermylation reaction was observed in the presence of
a catalytic amount of AlCl₃ (10 mol%) using CH₂Cl₂ 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 CH₂Cl₂ 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 \( J(C(2)-F) \); for which \( J(C(2)-F) \) of the (Z)-isomer is higher than that of the (E)-isomer (Figure 2).\(^{16,20}\)

![Figure 2](image)

**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, because 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 CH₂Cl₂ as solvent, providing a mixture of the four possible isomers (Z)-3a, (E)-3a, (Z)-3β and (E)-3β with the majority being the trans-addition product (Z)-3β (Scheme 2).

![Scheme 2](image)

**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 CH₂Cl₂ 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

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Additive (%)</th>
<th>α/β (Z)-2α (%)</th>
<th>α/β (E)-2α (%)</th>
<th>α/β (Z)-2β (%)</th>
<th>α/β (E)-2β (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>methanol-</td>
<td>-</td>
<td>24:76</td>
<td>14:0</td>
<td>9.8</td>
<td>68.9</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>hexane-</td>
<td>-</td>
<td>24:76</td>
<td>13:2</td>
<td>10.4</td>
<td>68.3</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>CH₂Cl₂-</td>
<td>-</td>
<td>20:80</td>
<td>14:8</td>
<td>5.5</td>
<td>78.1</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>CH₂Cl₂-</td>
<td>TEMPO</td>
<td>100:0</td>
<td>36:0</td>
<td>64.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>5</td>
<td>CH₂Cl₂-</td>
<td>Pd(PPh₃)₅ (5)</td>
<td>60:40</td>
<td>0.7</td>
<td>59.5</td>
<td>29.7</td>
<td>10.1</td>
</tr>
<tr>
<td>6</td>
<td>CH₂CN/H₂O (NH₄)₂S₂O₈ (20)</td>
<td>22:78</td>
<td>18.4</td>
<td>3.9</td>
<td>76.9</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>CH₂Cl₂-</td>
<td>Et₃B (10)</td>
<td>32:68</td>
<td>25:6</td>
<td>7.0</td>
<td>63.5</td>
<td>4.1</td>
</tr>
<tr>
<td>8</td>
<td>CH₂Cl₂-</td>
<td>BPh₃ (10)</td>
<td>26:74</td>
<td>17.0</td>
<td>9.0</td>
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<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>toluene-</td>
<td>AlCl₃ (10)</td>
<td>100:0</td>
<td>6.6</td>
<td>93.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>CH₂Cl₂-</td>
<td>AlCl₃ (10)</td>
<td>100:0</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\(^{a}\) Yield of isolated product.

\(^{b}\) Yield of isolated product.

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alkyne 1b using Bu3GeH or Ph3GeH in the presence of Et3B was performed, yielding a mixture of α- and β-regiosomers in a ratio of ca. 33:67, respectively, with the majority of the trans-addition product (Z)-4β and (Z)-5β (Scheme 3).

To better understand the role of the fluorinated group of the alkyne in the orientation of the regioselectivity of the AlCl3-catalyzed hydrogermylation reaction, hydrogermylation of methyl 4,4-difluoro-4-phenylbut-2-ynoate (1c) using Ph3GeH 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%).

It is worth mentioning that the regio- and stereochemistry for the vinylermanes 3, 4, 5 and 6 were deduced from the 3JH-F, 3JH-F and 3Jc-F coupling patterns by following the analyses described above in case of vinylermane 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. A larger difference on the partial charges (Δ = δC3-δC2) was observed in the cases of alkynes 1a and 1b than in alkyne 1c (Figure 3). Furthermore, changing a -CF3 (or -C2F5) group with a PhF2C induces a significant charge inversion on sp-carbon atoms. To further understand the origin of the regioselectivity of this hydrogermylation reaction by using AlCl3 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).

By taking into consideration the charge distribution of these two sp-carbon atoms, a plausible ionic mechanism for the AlCl3-catalyzed cis hydrogermylation of fluorinated alkynes type I is shown in Scheme 5. The coordination of the ester-carbonyl group of alkynes of type I to AlCl3 produces the zwitterionic intermediate I, which is transformed into allenolate II through hydride transfer from Ph3GeH to the cationic center of I. Trapping of intermediate II with germium-type species occurs from the less hindered face, cis to H, thus providing the cis-hydrogermylation (E)-α products and regenerating the AlCl3 catalyst.
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)-a 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 stirred for 1 hour at 0 °C, then Et₃N (37 mg, 0.36 mmol) was then 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)-2a-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)-2a, (E)-3a, (E)-4a and (E)-5a 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-(tributylgermyl)but-2-enoate [(E)-2a] (E)-2a 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=Jₓ₋ₓ = 7.2 Hz, 1 H), 4.07 (q, J = 7.1 Hz, 2 H), 1.02 (t, J = 7.1 Hz, 3 H).

¹C NMR (CDCl₃, 75 MHz): δ = 168.3, 146.4 (q, Jₓ₋ₓ = 4.7 Hz), 135.3 (6C), 132.9 (3C), 130.1 (3C), 129.5 (q, Jₓ₋ₓ = 35.2 Hz), 128.7 (6C), 121.3 (q, Jₓ₋ₓ = 272.5 Hz), 61.4, 13.8.

¹⁹F NMR (CDCl₃, 282 MHz): δ = –61.84.


(E)-Ethyl 4,4,4-Trifluoro-3-(tribenzyldimethylgermyl)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), 6.42 (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 = –54.58.

(Z)-Ethyl 4,4,4-Trifluoro-2-(tribenzyldimethylgermyl)but-2-enoate [(Z)-2a]

(Z)-2a 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, Jₓ₋ₓ = 7.9 Hz, 1 H), 3.72 (q, J = 7.1 Hz, 2 H), 0.87 (t, J = 7.1 Hz, 3 H).

¹⁹F NMR (CDCl₃, 282 MHz): δ = –60.5.

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

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

Yield: 89%; colorless oil.

¹H NMR (CDCl₃, 300 MHz): δ = 5.71 (q, Jₓ₋ₓ = 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).

¹⁹F NMR (CDCl₃, 282 MHz): δ = –61.93.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₈H₃₄F₃GeO₂: 413.02930; found: 413.0272.

(E)-Ethyl 4,4,4-Trifluoro-3-(tribenzyldimethylgermyl)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, Jₓ₋ₓ = 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-(tribenzyldimethylgermyl)but-2-enoate [(Z)-3α]

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

Yield: 89%; colorless oil.

¹H NMR (CDCl₃, 300 MHz): δ = 5.71 (q, Jₓ₋ₓ = 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).

¹⁹F NMR (CDCl₃, 282 MHz): δ = –61.93.

HRMS (ESI): m/z [M + H]⁺ calcd for C₁₈H₃₄F₃GeO₂: 413.02930; found: 413.0272.
(Z)-3a was obtained as a mixture with (E)-3a by following general procedure A.

1H NMR (CDCl3, 300 MHz): δ = 6.61 (q, J_{J-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).

13C NMR (CDCl3, 75 MHz): δ = 163.5, 150.2 (q, J_{C-F} = 31.3 Hz), 134.5 (q, J_{C-F} = 9.6 Hz), 125.6 (q, J_{C-F} = 27.25 Hz), 61.1, 27.1 (3C), 26.3 (3C), 14.1, 13.6 (3C), 13.4 (3C).

19F NMR (CDCl3, 282 MHz): δ = –61.76.

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

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

Yield: 91%; white solid; mp 85–86 °C.

1H NMR (CDCl3, 300 MHz): δ = 7.54–7.39 (m, 15 H), 5.80 (t, J_{J-F} = 13.3 Hz, 1 H), 3.95 (q, J = 7.1 Hz, 2 H), 1.0 (t, J = 7.1 Hz, 3 H).

13C NMR (CDCl3, 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 (qt, J_{C-F} = 252.8 Hz, 38.8 Hz), 61.3, 13.8.

19F NMR (CDCl3, 282 MHz): δ = –84.55 (t, J_{J-F} = 2.0 Hz, CF3), –113.96 (q, J_{J-F} = 2.0 Hz, CF3).

HRMS (ESI): m/z [M + H]+ calcd for C_{19}H_{34}F_{5}GeO_{2}: 463.16643; found: 463.16643.

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

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

1H NMR (CDCl3, 300 MHz): δ = 6.50 (t, J_{J-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).

19F NMR (CDCl3, 282 MHz): δ = –84.95 (t, J_{J-F} = 2.2 Hz, CF3), –113.91 (q, J_{J-F} = 1.8 Hz, CF3).

HRMS (ESI): m/z [M + H]+ calcd for C_{19}H_{34}F_{5}GeO_{2}: 463.16643; found: 463.16643.

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

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

Yield: 84%; colorless oil.

1H NMR (CDCl3, 300 MHz): δ = 5.60 (t, J_{J-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).

13C NMR (CDCl3, 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 (qt, J_{C-F} = 252) 38.5 Hz), 118.9 (qt, J_{C-F} = 284.5/37.1 Hz), 61.0, 26.0 (3C), 26.3 (3C), 14.2, 13.7 (3C), 12.6 (3C).

19F NMR (CDCl3, 282 MHz): δ = –84.91 (t, J_{J-F} = 2.2 Hz, CF3), –113.95 (q, J_{J-F} = 1.8 Hz, CF3).

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 [(Z)-5p]

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

1H NMR (CDCl3, 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).

19F NMR (CDCl3, 282 MHz): δ = –82.76 (t, J_{J-F} = 1.8 Hz, CF3), –113.91 (q, J_{J-F} = 1.8 Hz, CF3).

HRMS (ESI): m/z [M + H]+ calcd for C_{19}H_{34}F_{5}GeO_{2}: 463.17090; found: 463.17095.

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

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

1H NMR (CDCl3, 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).

13C NMR (CDCl3, 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, CF3), 51.4.

19F NMR (CDCl3, 282 MHz): δ = –85.31.

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

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

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References


