Supporting Information

Photoinduced decarboxylative germylation of α-fluoroacrylic acids: Access to germylated monofluoroalkenes

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I. General Information

(a). Materials

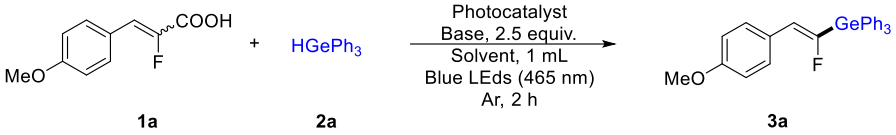
All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity ≥99.999%). *fac*-Ir(ppy)$_3$ (CAS: 94928-86-6), Ru(bpy)$_3$Cl$_2$·6H$_2$O (CAS: 50525-27-4), Eosin Y (CAS: 548-26-5), 4-CzIPN (CAS: 1416881-52-1), and TBPB (CAS: 614-45-9) were purchased from Adamas. Ph$_3$GeH (CAS: 2816-43-5), and *n*-Bu$_3$GeH (CAS: 998-39-0) were purchased from Sigma-Aldrich. The following chemicals were purchased and used as received: DABCO (Adamas). DMSO (Adamas) were stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle. All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

(b). Analytical methods

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in Chloroform-d unless otherwise noted; Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, AD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

II. General Experimental Procedures

(a). Optimization of the reaction conditions



1a **2a** **3a**

Entry	Catalyst	Base	Oxidant	Solvent	Yield%
1[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	CH_3CN	12
2[a]	*fac*-Ir(ppy)$_3$	DABCO	TBPB	CH_3CN	15
3[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	DMSO	76
4[a]	*fac*-Ir(ppy)$_3$	DABCO	TBPB	DMSO	10
5[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	DCE	< 10
6[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	Acetone	43
7[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	DMAc	41
8[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	THF	26
9[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	DCM	< 10
10[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPB	EtOAc	trace
11[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	DTBP	DMSO	trace
12[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	BPO	DMSO	trace
13[a]	$Ru(bpy)_3Cl_2·6H_2O$	DABCO	TBPA	DMSO	68
14[a]	$Ru(bpy)_3Cl_2·6H_2O$	Et_3N	TBPB	DMSO	trace
15[a]	$Ru(bpy)_3Cl_2·6H_2O$	DIPEA	TBPB	DMAc	trace
16[a]	$Ru(bpy)_3Cl_2·6H_2O$	Cs_2CO_3	TBPB	DMSO	30
17[a]	$Ru(bpy)_3Cl_2·6H_2O$	K_2CO_3	TBPB	DMSO	trace
18[a]	Eosin Y	DABCO	TBPB	DMSO	28
19[a]	4-CzIPN	DABCO	TBPB	DMSO	43
20[c]	w/o	DABCO	TBPB	DMSO	trace
21[d]	$Ru(bpy)_3Cl_2·6H_2O$	w/o	TBPB	DMSO	< 5

Reaction conditions: [a]**1a** (0.1 mmol, 1 equiv.), **2a** (0.3 mmol, 3 equiv.), base (2.5 equiv.), photoredox catalyst (5 mol%), oxidant (3 equiv.), and solvent (1.0 mL) irradiated by 20 W blue LEDs for 2 h under Ar atmosphere. [c]No photoredox catalyst. [c]No DABCO. Isolated yield. DABCO = Triethylenediamine. DIPEA = *N*,*N*-diisopropylethylamine. TBPB = *tert*-butyl benzoperoxoate. TBPA = *tert*-Butyl ethaneperoxoate. DTBP = Di-*tert*-butyl peroxide. BPO = Benzoyl peroxide.

(b). General procedure

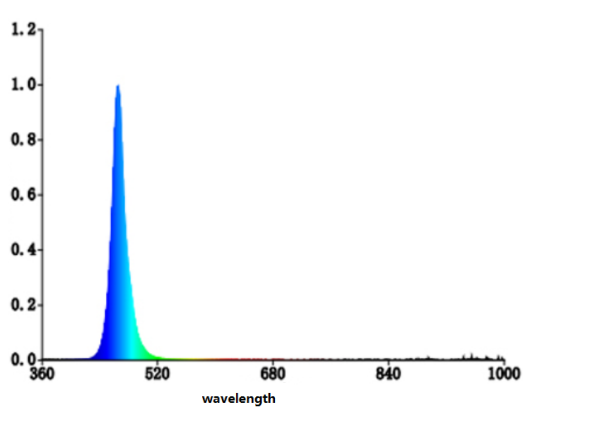
In air, fluoro acrylic acids (0.1 mmol, 1.0 equiv.), $Ru(bpy)_3Cl_2·6H_2O$ (3.1 mg, 5 mol%), Ph_3GeH (0.3 mmol, 91 mg, 3.0 equiv.), and DABCO (0.25 mmol, 28 mg, 2.5 equiv.) were

added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMSO (1.0 mL, 1 M), and TBPB (0.3 mmol, 3.0 equiv.) were added in turn by syringe. The resulting reaction mixture was irradiated by 20 W blue LEDs for 2 h under Ar. The residue was purified by silica gel (200-300 mesh) columun chromatography using petroleum ether and dichloromethane as eluent. The E/Z ratios were determined by ^{1}H NMR and ^{19}F NMR analyses.

(c). Experimental procedures of 1 mmol scale

In air, 2-fluoro-3-(4-methoxyphenyl)acrylic acid (196 mg, 1.0 mmol, 1.0 equiv.), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (30 mg, 5 mol%), and DABCO (280 mg, 2.5 mmol, 2.5 equiv.) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMSO (8.0 mL), and TBPB (3.0 equiv.) were added in turn by syringe. The resulting reaction mixture was irradiated by 20 W blue LEDs for 2 h under Ar. The residue was purified by silica gel (200-300 mesh) columun chromatography using petroleum ether and dichloromethane (30:1) as eluent (65%, E/Z > 50:1).

III. Experimental apparatus



Manufacturers：Jia-deng;

Model: HCB-SKDS-1000 (China);

Wavelength of peak intensity：465.4 nm;

Luminous flux: 1.854 lm; Photosynthetic efficiency: 32.39 lm/W;

Chromaticity coordinates: x = 0.1328; y = 0.0623/u' =0.1526; v' = 0.1610; duv = 1.610e-001;

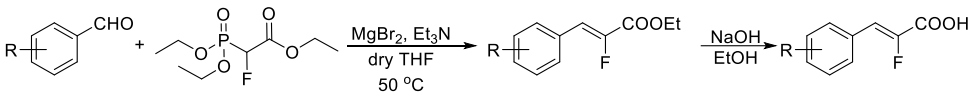
Color rendering index: Ra = -50.5;

The material of the irradiation vessel: ordinary glass.

IV. Preparation of Substrates

(a). Synthesis of E/Z mixture α-fluoroacrylic acids

Scheme S1.

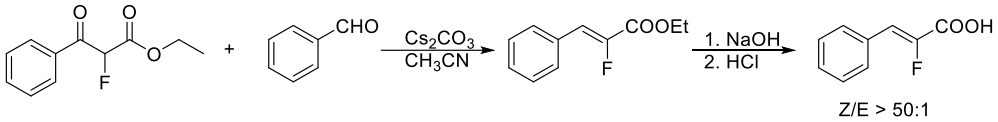


2-fluoro-triethylphosphonoacetate (2.42 g, 10 mmol, 1.0 equiv) was dissolved in dry THF (50 mL) at ambient temperature. Triethylamine (2.8 mL, 20 mmol, 2.0 equiv) was added, followed by magnesium bromide (1.84 g, 10 mmol, 1.0 equiv). An exotherm is observed, and while the reaction was hot (ca. 50 ℃), benzaldehyde (10 mmol, 1.0 equiv) was added. The reaction was stirred and monitored by TLC. Upon completion, the reaction was diluted with 50 mL diethyl ether, then filtered on a medium porosity fritted funnel. The filtrate was washed with saturated ammonium chloride solution, which was then extracted with ether (2 x 50 mL). The organic layers were combined, washed with brine, dried over magnesium sulfate, filtered and concentrated to give 1.95g of colorless oil, ethyl 2-fluoro-3-phenylacrylate as a mixture of olefin isomers. Spectral data for this compound matched literature, and it was carried to the next step without further purification[1].

To a stirred solution of ethyl 2-fluoro-3-phenylacrylate in EtOH (20 mL) was added 1 M aqueous NaOH (15 mL) and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated in vacuo. 50 mL water was added. The aqueous phase was acidified with 2 N HCl and extracted with ethyl acetate. The combined organic layers were dried over $NaSO_4$. The volatile compounds were removed in vacuo to afford 2-fluoro-3-phenylacrylic acid. The synthesis of α-fluoroacrylic acids refers to our previous literature, and all compounds have been characterized in our previous work.[1]

(b). Synthesis of (Z)-α-fluoroacrylic acids

Scheme S2

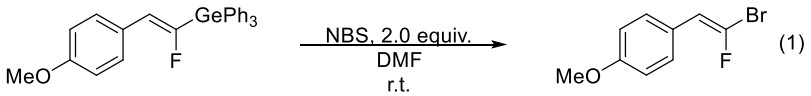


The reaction mixture of fluorinated substrates (5.5 mmol), aldehyde (5 mmol), cesium carbonate (10 mmol) and CH_3CN (15 mL) was stired at 40 ℃ for the indicated time until complete consumption of the starting material , which was monitored by TLC analysis (6-12 h).The solvents were removed by rotary evaporation to provide raw products. The residue was then chromatographied on silica gel, affording the desired product.[1]

(c). Synthesis of diphenylgermane (Ph_2GeH_2)

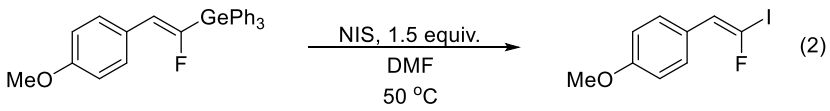
Solid $LiAlH_4$ (LAH) (0.26 g, 6.72 mmol, 2.0 equiv.) was added portionwise to the solution of diphenyldichlorogermane, Ph_2GeCl_2 (1.0 g, 3.35 mmol, 1.0 equiv.), in ether (15 mL). Then reaction mixture was refluxed for 6 h. For the workup the improved procedure for dissolution of products of LAH reduction was applied, including the sequential dropwise addition of water (1.0 mL), 15% aq. NaOH (0.5 mL), with time intervals of 10 to 15 min between additions. This procedure allows to obtain well separated alumina precipitate, easily removed by filtration or decantation. The inorganic solid was washed with ether (3 × 10 mL), organic phase was dried over anhydrous $NaSO_4$, and then all volatile materials were removed under reduced pressure; The residue was then chromatographied on silica gel, affording the desired product. These data are in agreement with those reported previously in the literature.[2]

V. Subsequent transformations of products



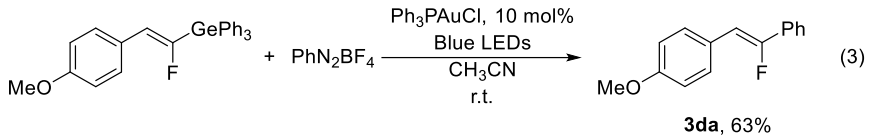
3ba, 95%

(E)-(1-fluoro-2-(4-methoxyphenyl)vinyl)triphenylgermane (**3a**, 0.1 mmol, 45 mg, 1.0 equiv.) and *N*-bromosuccinimide (NBS, 36 mg, 2.0 equiv.) were added to the reaction vial in air, dissolved in DMF (0.5 mL, 0.5 M) and stirred at room temperature for 6 h. After completion of reaction, the reaction was quenched by addition of aqueous solution of $Na_2S_2O_3$ (sat.), the organic phase was separated and the aqueous phase was extracted with DCM. The combined organic phases were dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by silica gel (200-300 mesh) columun chromatography using petroleum ether and EtOAc (50:1) as eluent.[3]

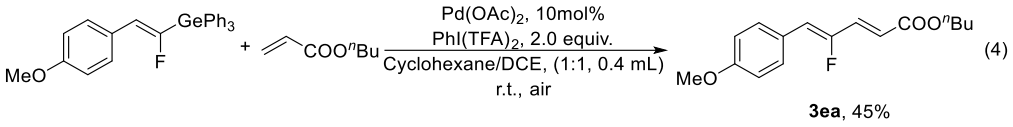


3ca, 72%

(E)-(1-fluoro-2-(4-methoxyphenyl)vinyl)triphenylgermane (**3a**, 0.1 mmol, 45 mg, 1.0 equiv.) and *N*-iodosuccinimide (NIS, 34 mg, 1.5 equiv.) were added to the reaction vial in air, dissolved in DMF (0.5 mL, 0.5 M) and stirred at 50 ℃. After completion of reaction (monitored by TLC), the reaction was quenched by addition of aqueous solution of $Na_2S_2O_3$ (sat.), the organic phase was separated and the aqueous phase was extracted with DCM. The combined organic phases were dried with $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by silica gel (200-300 mesh) columun chromatography using petroleum ether and EtOAc (50:1) as eluent.[3]



In an argon-filled glovebox, (E)-(1-fluoro-2-(4-methoxyphenyl) vinyl) triphenylgermane (3a, 0.1 mmol, 45 mg, 1.0 equiv.), phenyldiazonium tetra fluoroborate (0.15 mmol, 1.5 equiv.), and (Ph_3P)AuCl (0.01 mmol, 10 mol%) were placed in a screw top vial equipped with magnetic stir bar and dissolved in anhydrous and degassed CH_3CN (1 mL, 1 M). The vial with the solution was placed into the blue LED setup for irradiation. After the completion of reaction, the crude mixture was concentrated in vacuo, and the obtained residue was purified by silica gel column chromatography.[4]



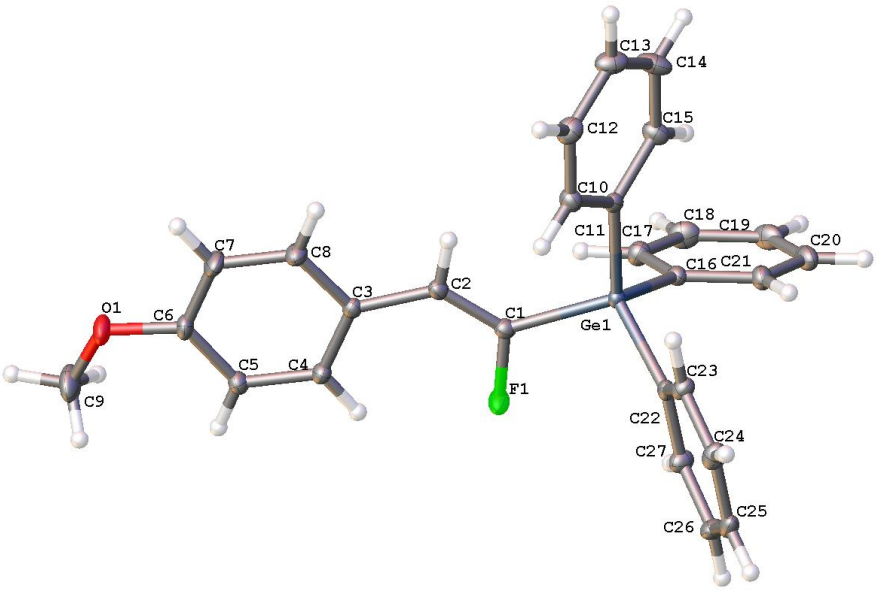
Under air, a 5 mL screw-capped glass vial equipped with a magnetic stir bar was charged with (E)-(1-fluoro-2-(4-methoxyphenyl) vinyl) triphenylgermane (**3a**, 0.1 mmol, 45 mg, 1.0 equiv.), butyl acrylate (28.5 μL, 0.20 mmol, 2.0 equiv.) and dissolved in the cyclohexane (0.4 mL, 0.4 M). $Pd(OAc)_2$ (0.01 mmol, 2.2 mg, 10 mol%) and $PhI(TFA)_2$ (0.2 mmol, 86.0 mg, 2.0 equiv.) were mixed in a separate vial and were then added to the reaction mixture. The reaction mixture was stirred for 2 h at room temperature. The residue was purified by flash chromatography on silica gel to give the expected compound.[5]

VI. X-ray diffraction analysis of the product 3a

Crystal of compound was obtained by dissolving the product in a mixture of ethyl acetate and PE and allowing the solvent to slowly evaporate at room temperature. The suitable single crystals for X-ray structural analysis were mounted at 170 K on a XtaLAB Synergy R, DW system, HyPix Diffractometer. Data reduction and empirical absorption correction were performed using the CrysAlisPro program. The structure was solved by using SHELXT program or Olex2. All nonhydrogen atoms could be located directly from the difference Fourier maps. Framework hydrogen atoms were placed geometrically and constrained using the riding model to the parent atoms. Final structure refinement was done using the SHELXL program by minimizing the sum of squared deviations of F2 using a full-matrix technique.

Refined structure and crystallographic parameters are summarized as below. The Diamond diagram was drawn by Olex 2-1.3

X-ray crystal structure of compound **3a**



CCDC[#] 2357268

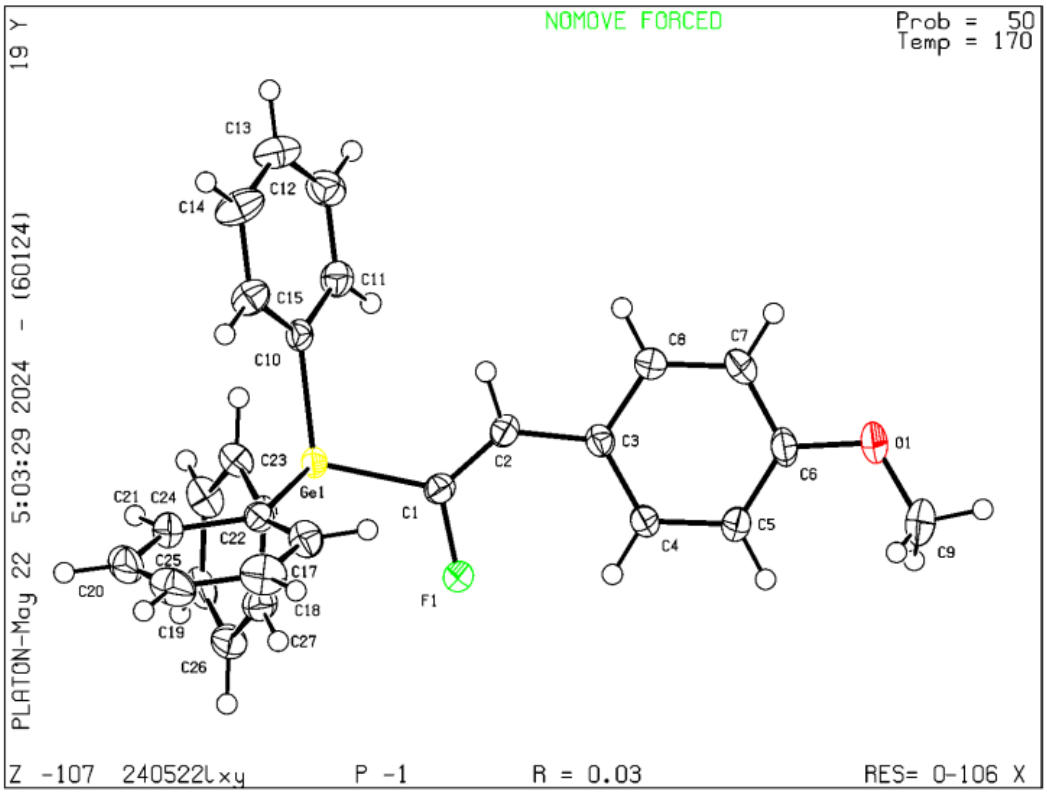
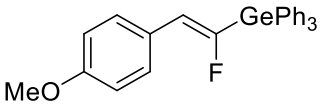


Table 1. Crystal data and structure refinement for **3a**.

Identification code	3a	
Empirical formula	$C_{27}H_{23}FGeO$	
Formula weight	455.04	
Temperature	170.00 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.87890(10) Å	α = 106.2010(10)°.
	b = 11.0575(2) Å	β = 104.2420(10)°.
	c = 11.8202(2) Å	γ = 105.0350(10)°.
Volume	1124.69(3) $Å^3$	
Z	2	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	1.337 mm^{-1}	
F(000)	468	
Crystal size	0.17 x 0.17 x 0.05 mm^3	
Theta range for data collection	3.870 to 54.949°.	
Index ranges	-11<=h<=12, -13<=k<=13, -13<=l<=14	

Reflections collected	17576
Independent reflections	4228 [R(int) = 0.0581]
Completeness to theta = 53.594°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5757
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4228 / 1 / 272
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0902
R indices (all data)	R1 = 0.0356, wR2 = 0.0914
Extinction coefficient	n/a
Largest diff. peak and hole	0.575 and -0.863 e.$Å^{-3}$

VII. Substrate Scope, Spectral Data and NMR Spectra



(E)-(1-fluoro-2-(4-methoxyphenyl)vinyl)triphenylgermane

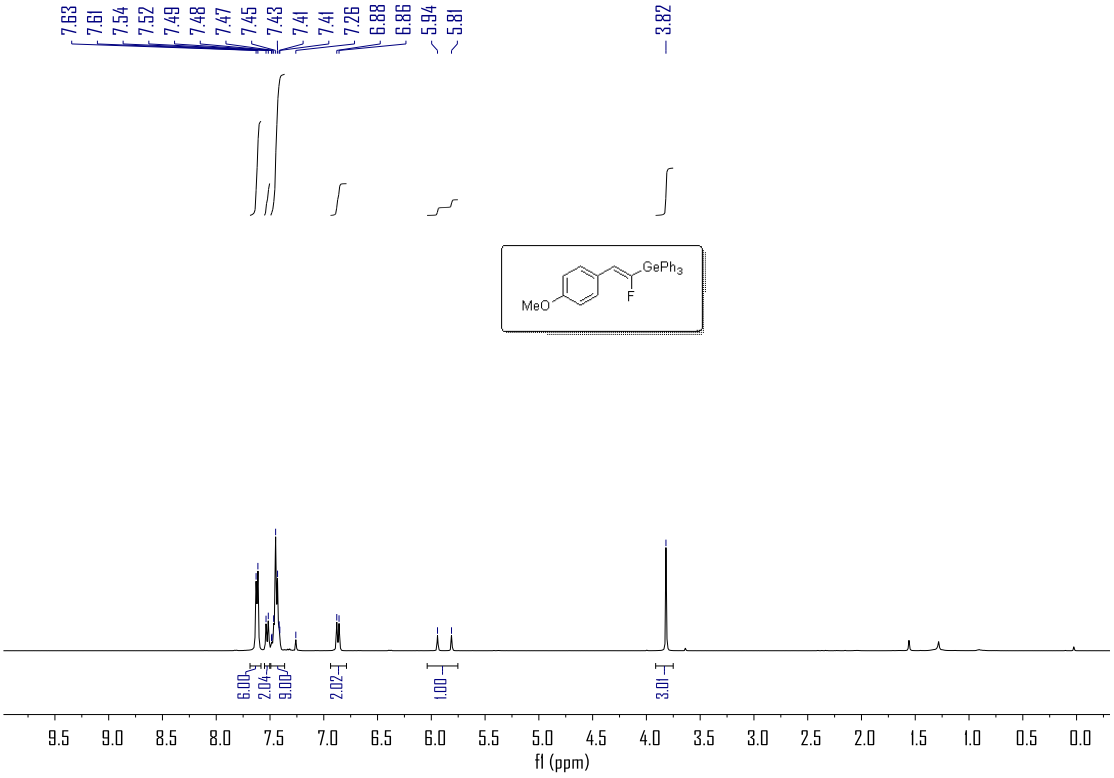
Following the general procedure (**3a**, pale-yellow liquid, after freezing, it turns into a solid. 34 mg, 76%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (20:1) as an eluent.

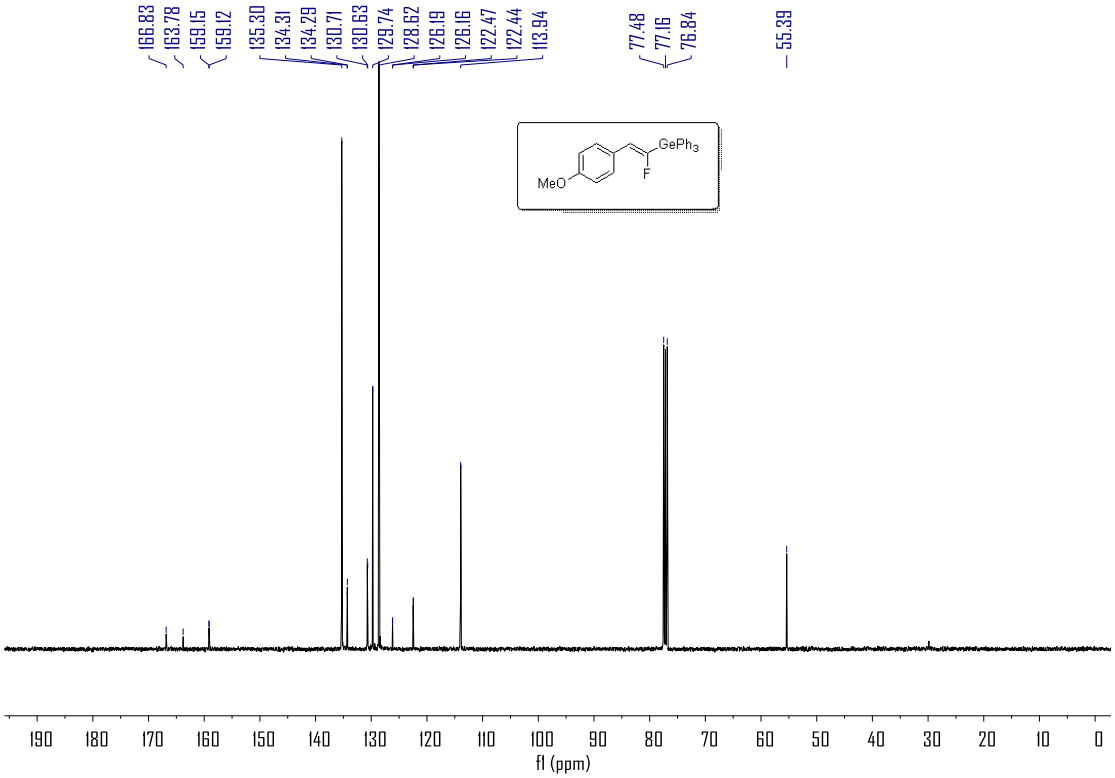
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 6.7 Hz, 6H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.40 (m, 9H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.88 (d, *J* = 52.1 Hz, 1H), 3.82 (s, 3H).

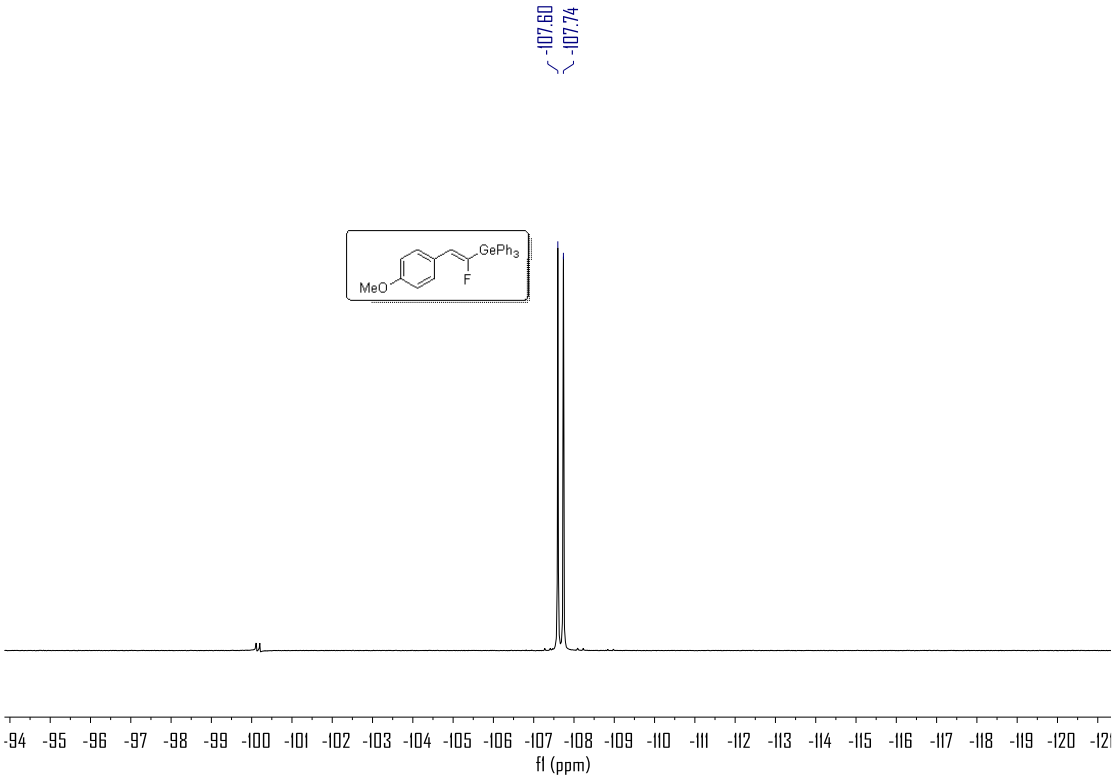
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.31 (d, *J* = 306.7 Hz), 159.13 (d, *J* = 3.1 Hz), 135.30, 134.30 (d, *J* = 2.1 Hz), 130.67 (d, *J* = 7.7 Hz), 129.74, 128.62, 126.18 (d, *J* = 2.8 Hz), 122.45 (d, *J* = 3.8 Hz), 113.94, 55.39.

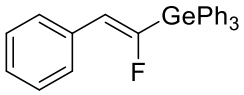
^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.67 (d, *J* = 52.3 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}FGeNaO$: 479.0837; found: 479.0835.




166.83
163.78
159.15
159.12
135.30
134.31
134.29
130.71
130.63
129.74
128.62
126.19
126.16
122.47
122.44
113.94
77.48
77.16
76.84
55.39
GePh3
F
MeO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-107.60
-107.74
GePh3
F
MeO
-94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120
f1 (ppm)



(E)-(1-fluoro-2-phenylvinyl)triphenylgermane

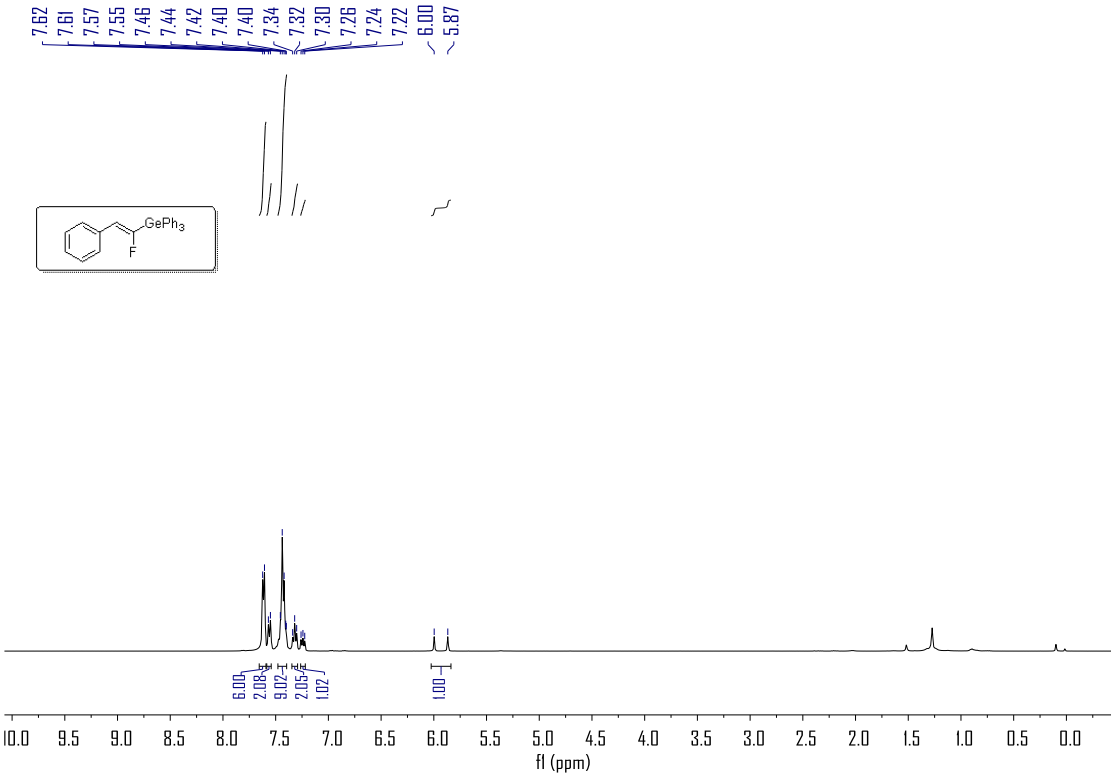
Following the general procedure (**3b**, pale-yellow solid, 31 mg, 73%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

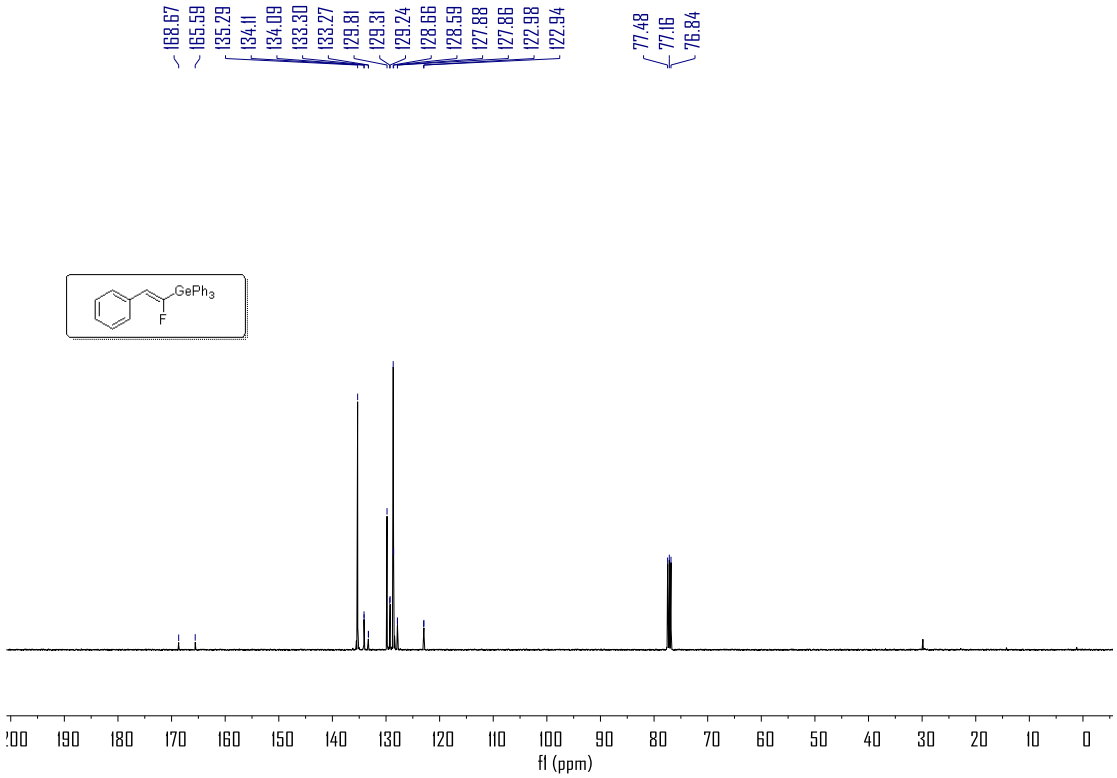
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 6.8 Hz, 6H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.50 – 7.39 (m, 9H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 5.93 (d, *J* = 51.6 Hz, 1H).

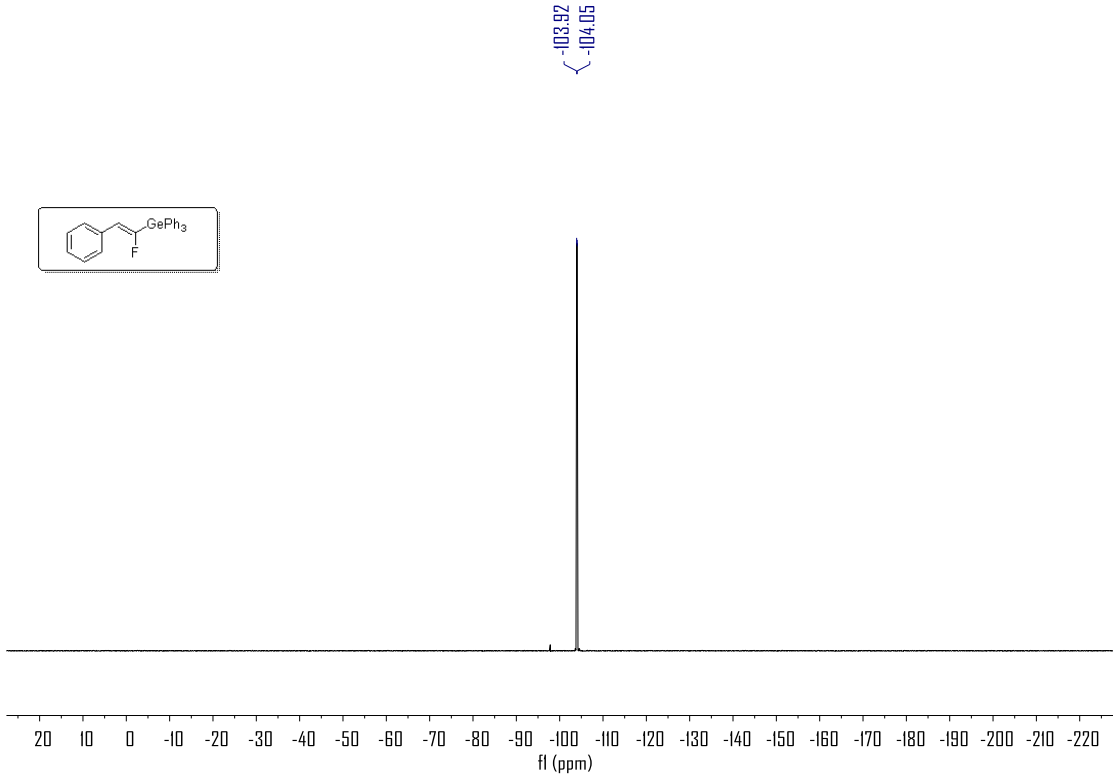
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.13 (d, *J* = 310.4 Hz), 135.29, 134.10 (d, *J* = 1.9 Hz), 133.28 (d, *J* = 2.8 Hz), 129.81, 129.27 (d, *J* = 7.3 Hz), 128.66, 128.59, 127.87 (d, *J* = 2.3 Hz), 122.96 (d, *J* = 4.3 Hz).

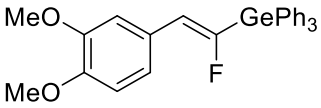
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.98 (d, *J* = 51.5 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}FGeNa$: 449.0731; found: 449.0735.




168.67
165.59
135.29
134.11
134.09
133.30
133.27
129.81
129.31
129.24
128.66
128.59
127.88
127.86
122.98
122.94
77.48
77.16
76.84
GePh3
F
f1 (ppm)


-103.92
-104.05
GePh3
F
f1 (ppm)



(E)-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)triphenylgermane

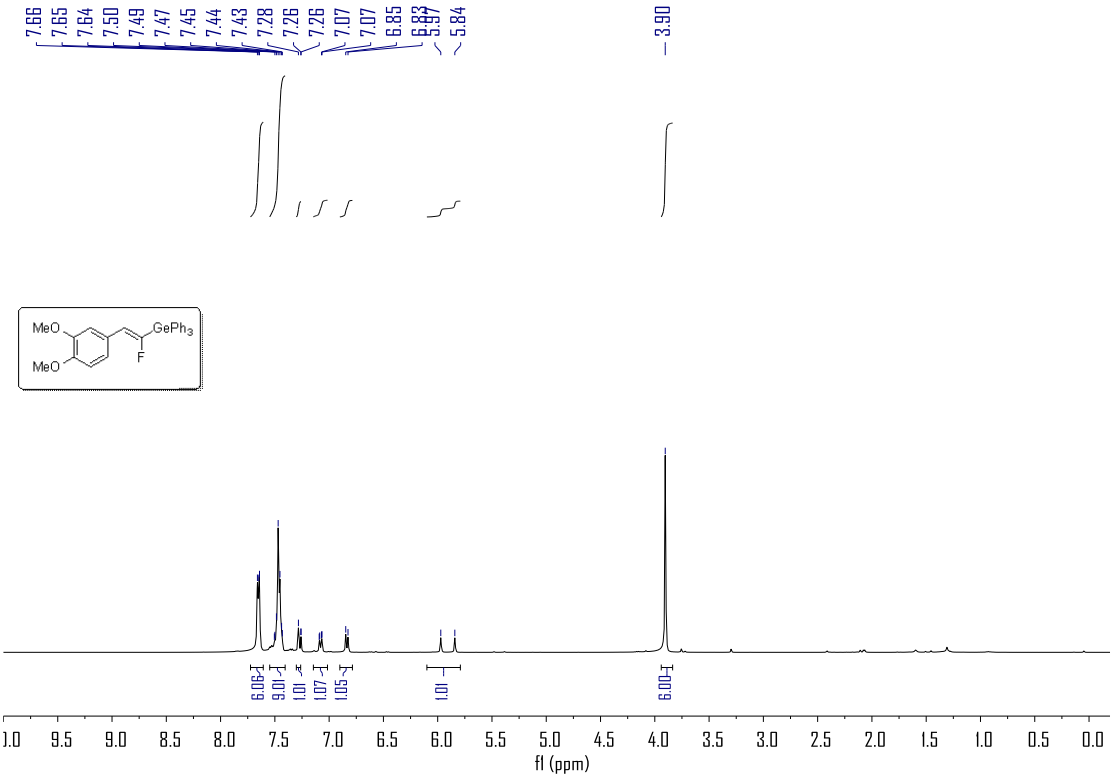
Following the general procedure (**3c**, pale-yellow solid, 30 mg, 62%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (10:1) as an eluent.

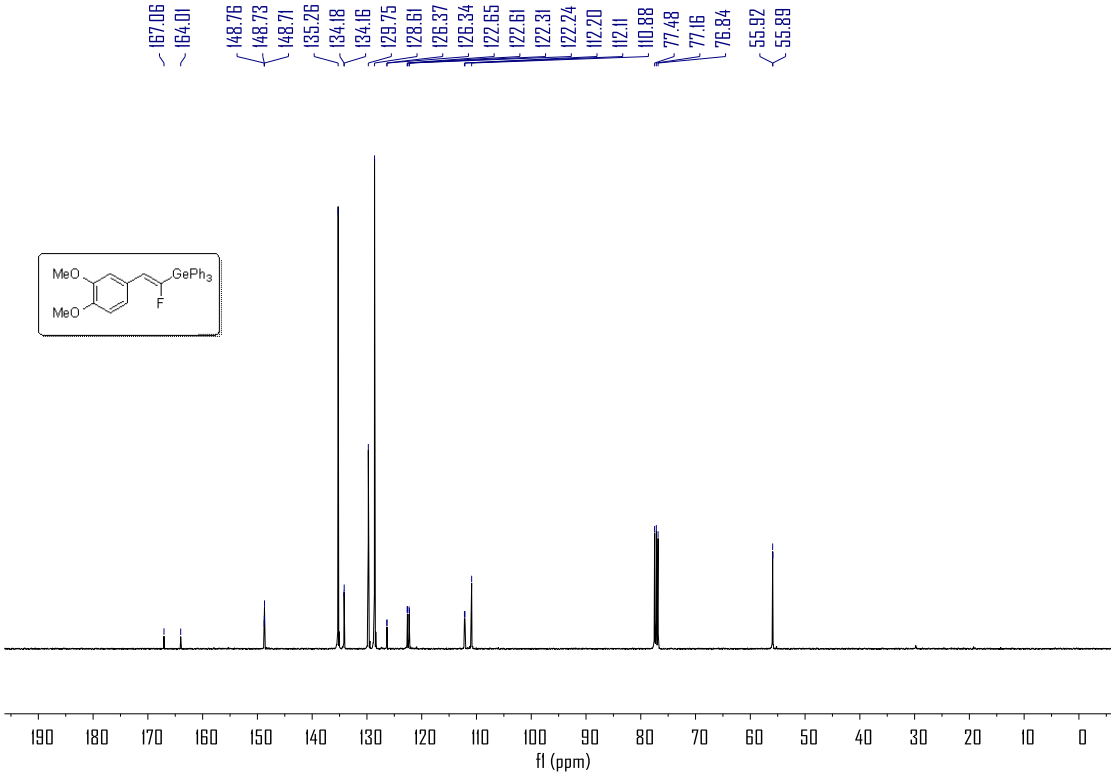
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.59 (m, 6H), 7.54 – 7.41 (m, 9H), 7.28 (s, 1H), 7.08 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 5.91 (d, *J* = 51.7 Hz, 1H), 3.90 (s, 6H).

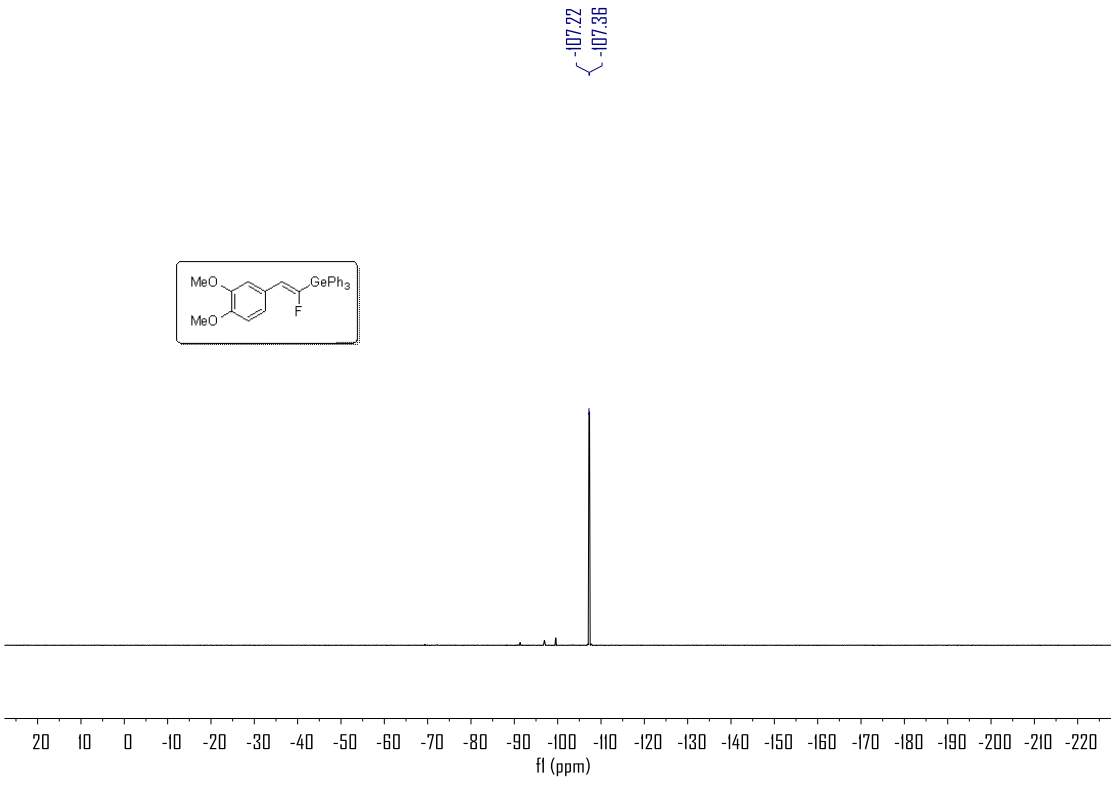
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.53 (d, *J* = 307.4 Hz), 148.75 (d, *J* = 3.0 Hz), 148.71, 135.26, 134.17 (d, *J* = 2.0 Hz), 129.75, 128.61, 126.35 (d, *J* = 2.6 Hz), 122.63 (d, *J* = 4.3 Hz), 122.28 (d, *J* = 6.5 Hz), 112.15 (d, *J* = 9.1 Hz), 110.88, 55.92, 55.89.

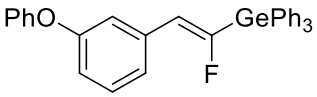
^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.29 (d, *J* = 52.0 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}FGeNaO_2$: 509.0943; found: 509.0939.




167.06
164.01
148.76
148.73
148.71
135.26
134.18
134.16
129.75
128.61
126.37
126.34
122.65
122.61
122.31
122.24
112.20
112.11
110.88
77.48
77.16
76.84
55.92
55.89
MeO
MeO
GePh3
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-107.22
-107.36
MeO
MeO
GePh3
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(1-fluoro-2-(3-phenoxyphenyl)vinyl)triphenylgermane

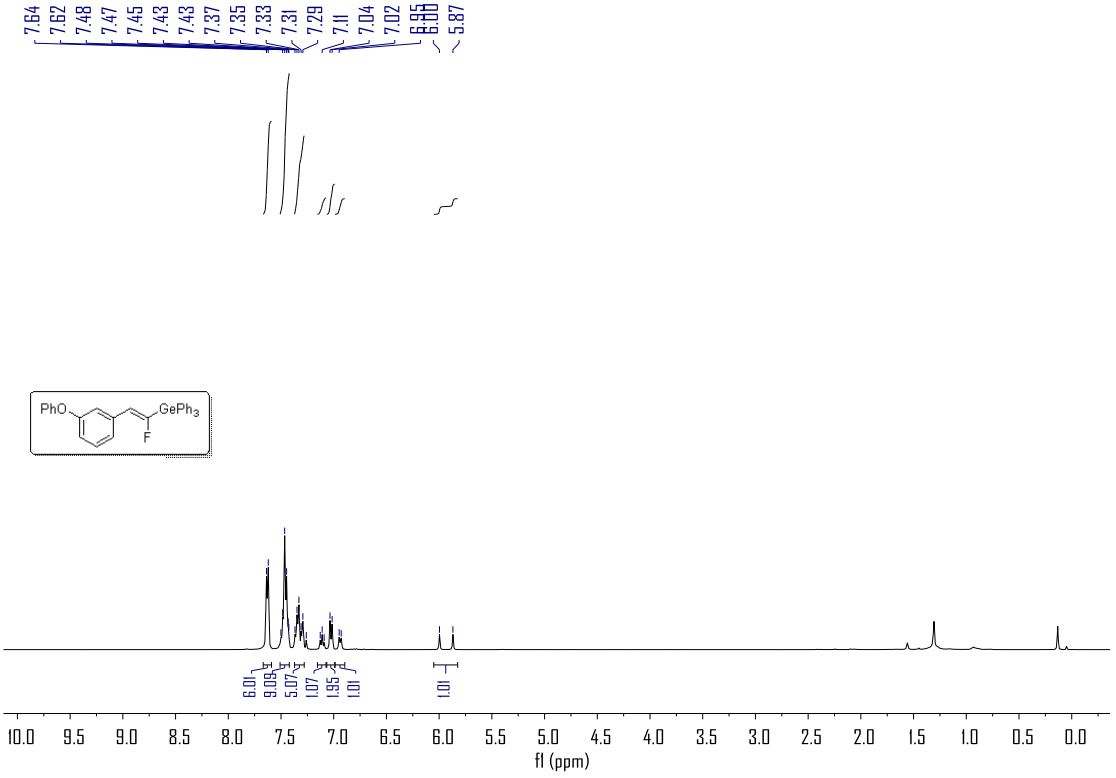
Following the general procedure (**3d**, pale-yellow solid, 35 mg, 68%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

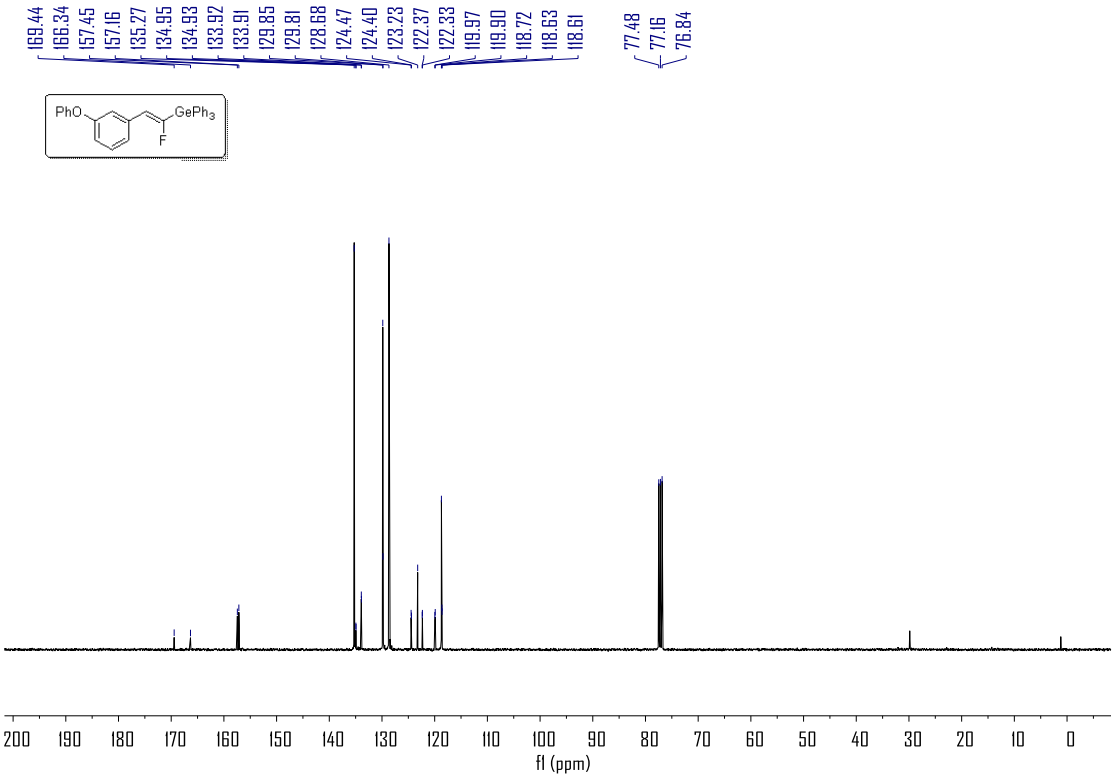
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 6.8 Hz, 6H), 7.46 (q, *J* = 7.0, 6.2 Hz, 9H), 7.38 – 7.27 (m, 5H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 5.93 (d, *J* = 50.8 Hz, 1H).

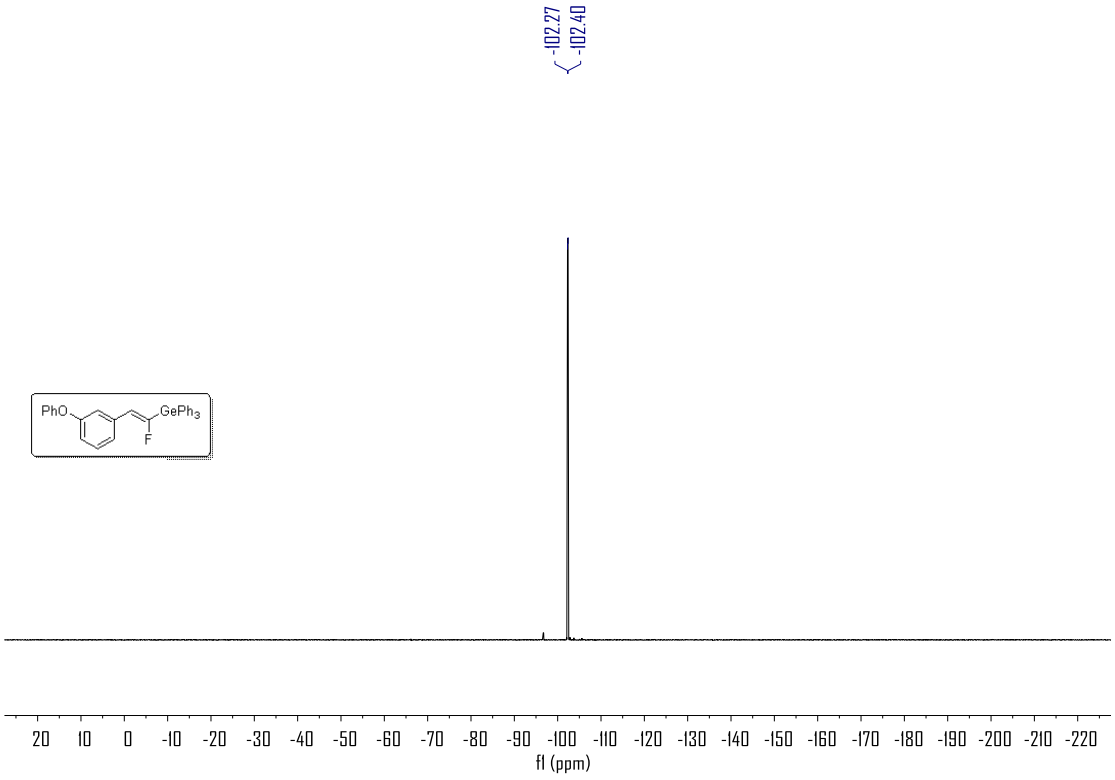
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.89 (d, *J* = 311.8 Hz), 157.45, 157.16, 135.27, 134.94 (d, *J* = 2.8 Hz), 133.91 (d, *J* = 1.8 Hz), 129.85, 129.81, 128.68, 124.44 (d, *J* = 7.4 Hz), 123.23, 122.35 (d, *J* = 4.1 Hz), 119.93 (d, *J* = 7.6 Hz), 118.72, 118.62 (d, *J* = 2.1 Hz).

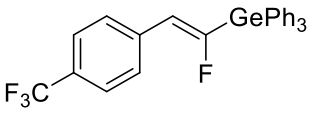
^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.34 (d, *J* = 50.6 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}FGeNaO$: 541.0993; found: 541.0995.




169.44
166.34
157.45
157.16
135.27
134.95
134.83
133.92
133.91
129.85
129.81
128.68
124.47
124.40
123.23
122.37
122.33
119.97
119.90
118.72
118.63
118.61
77.48
77.16
76.84
PhO
GePh3
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-102.27
-102.40
PhO
GePh3
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(1-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)triphenylgermane

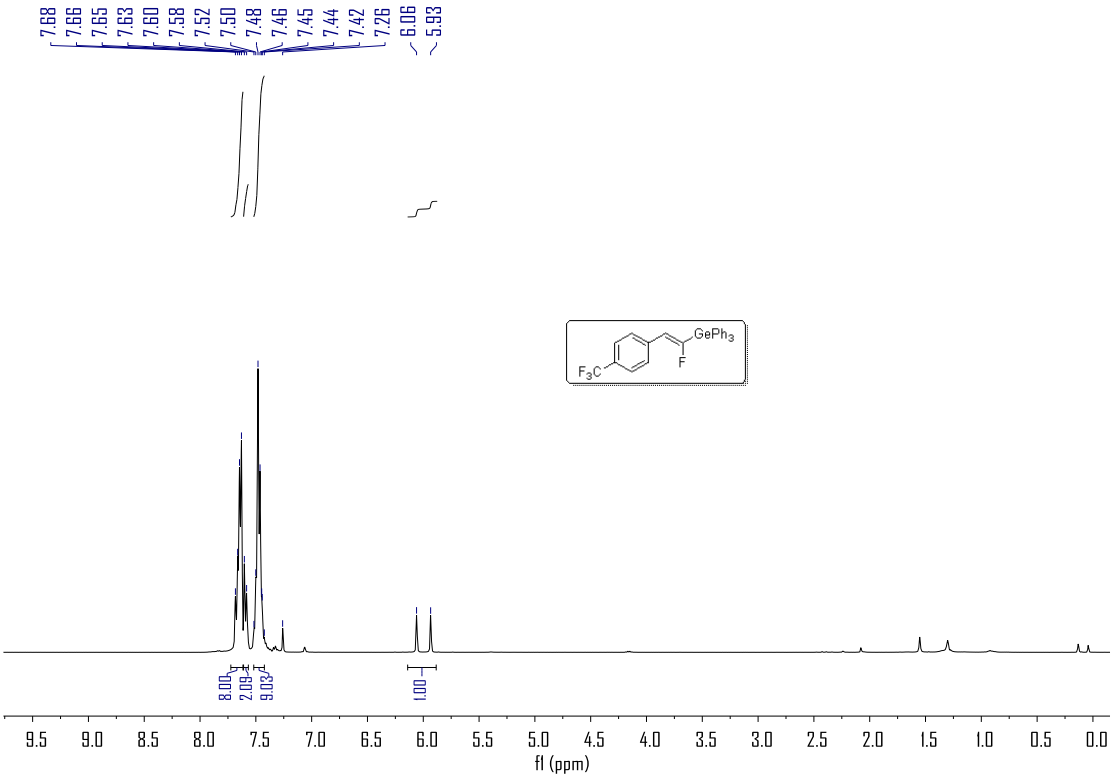
Following the general procedure (**3e**, pale-yellow solid, 37 mg, 75%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

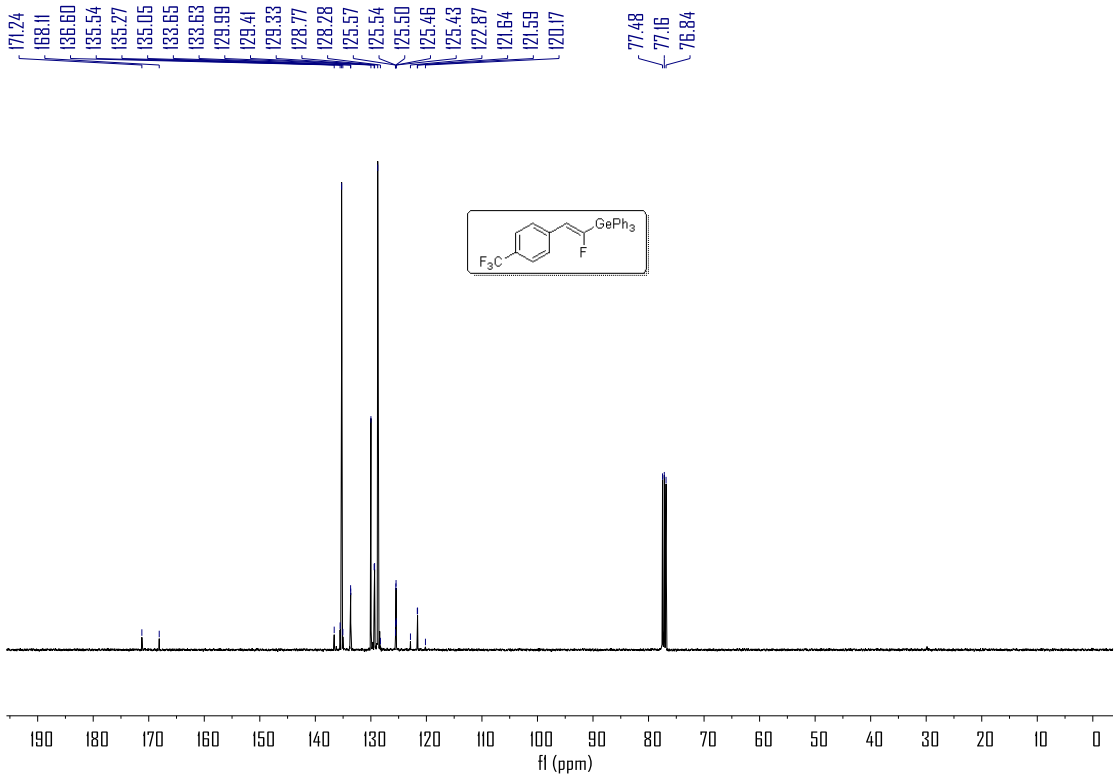
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.62 (m, 8H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.47 (q, *J* = 8.0 Hz, 9H), 6.00 (d, *J* = 50.5 Hz, 1H).

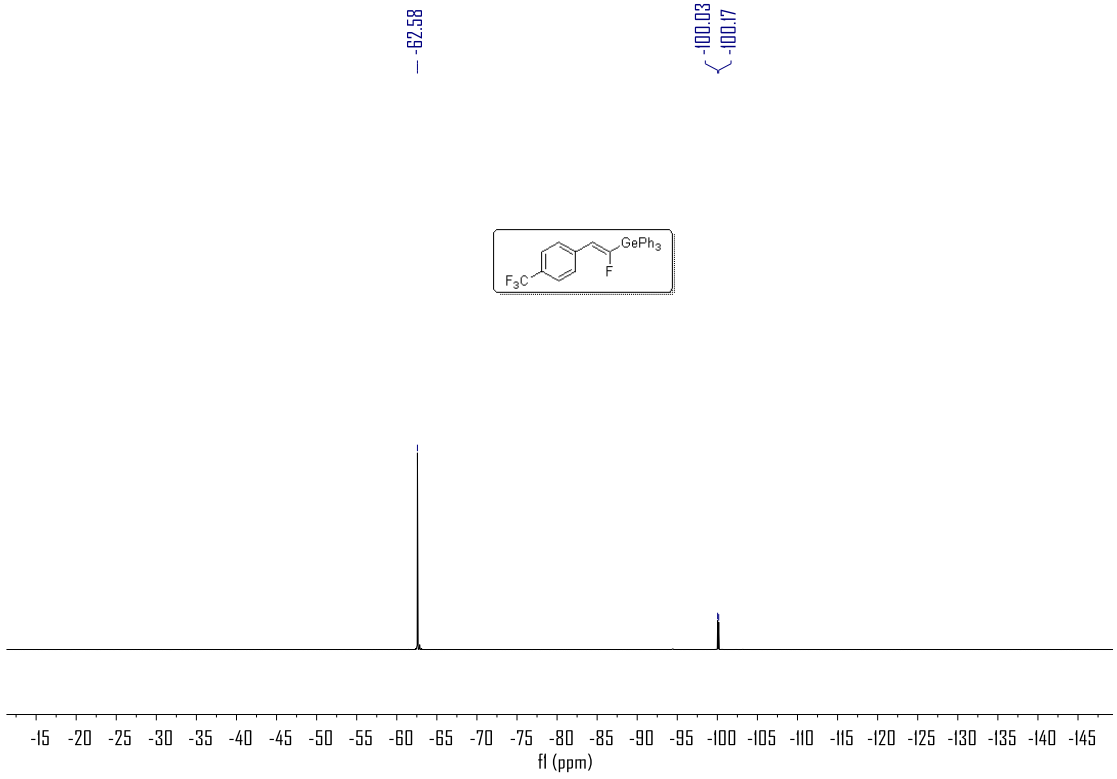
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.67 (d, *J* = 314.7 Hz), 136.60, 135.29 (q, *J* = 49.4 Hz), 135.27, 133.64 (d, *J* = 1.8 Hz), 129.99, 129.37 (d, *J* = 7.9 Hz), 128.77, 125.48 (q, *J* = 3.8 Hz), 124.22 (q, *J* = 271.5 Hz), 121.61 (d, *J* = 4.3 Hz).

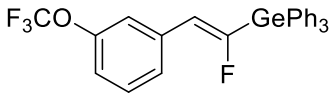
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.58, -100.10 (d, *J* = 50.5 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{20}F_4GeNa$: 517.0605; found: 517.0601.




171.24
168.11
136.60
135.54
135.27
135.05
133.65
133.63
129.99
129.41
129.33
128.77
128.28
125.57
125.54
125.50
125.46
125.43
122.87
121.64
121.59
120.17
77.48
77.16
76.84
GePh3
F3C
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.58
-100.03
-100.17
GePh3
F3C
F
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)



(E)-(1-fluoro-2-(3-(trifluoromethoxy)phenyl)vinyl)triphenylgermane

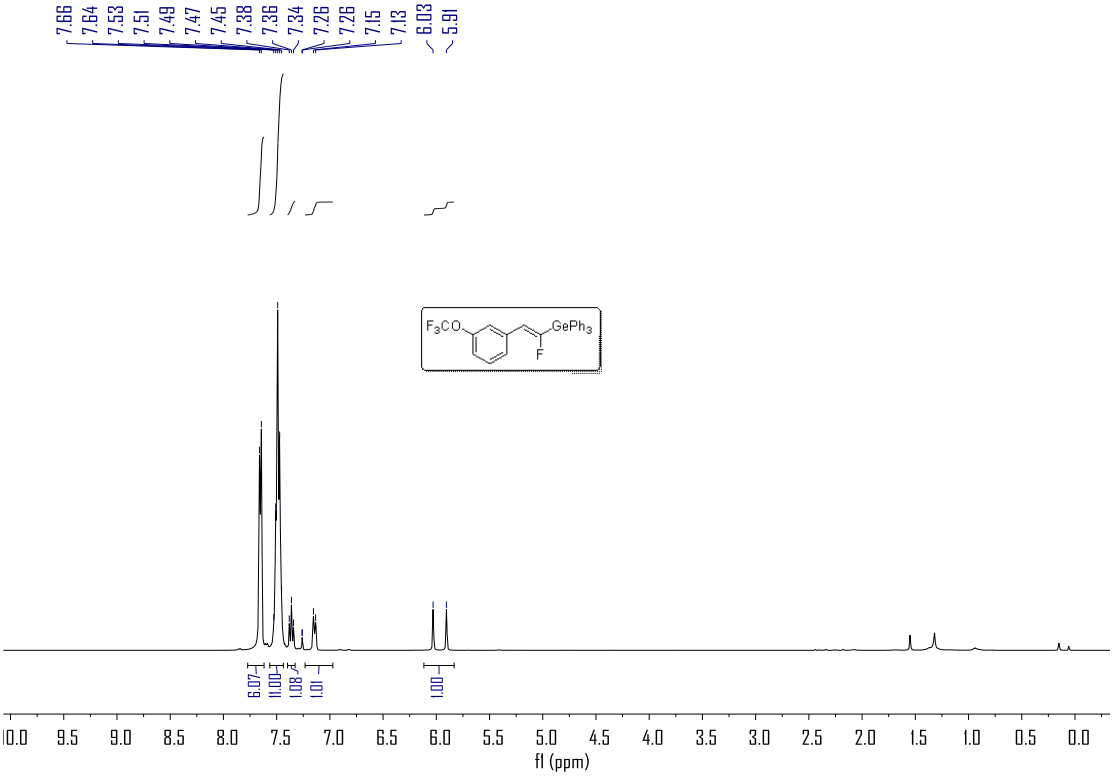
Following the general procedure (**3f**, pale-yellow solid, 37 mg, 73%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

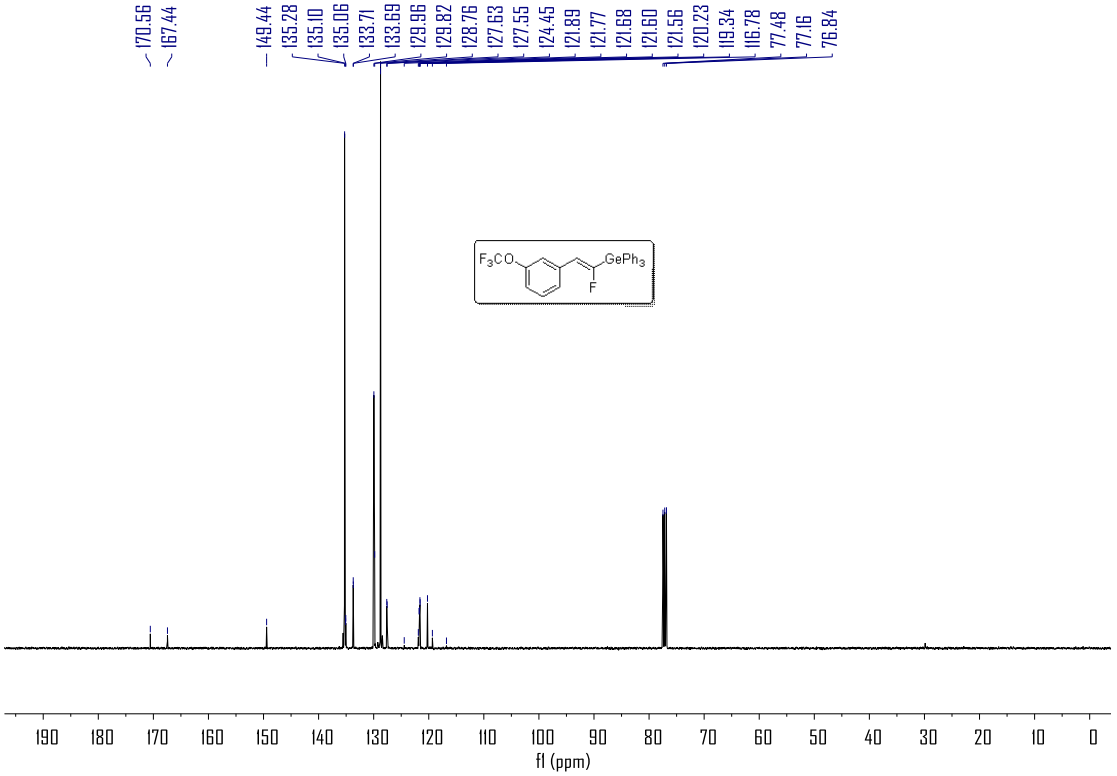
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 6.9 Hz, 6H), 7.55 – 7.43 (m, 11H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 5.97 (d, *J* = 50.0 Hz, 1H).

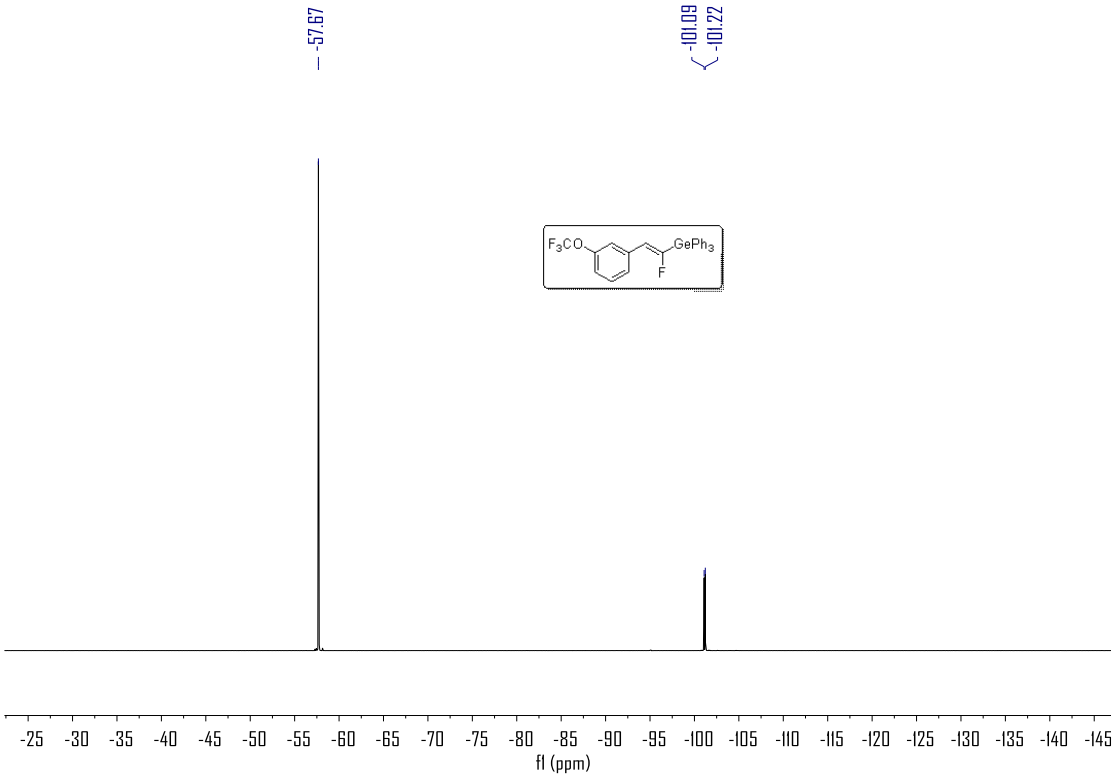
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.00 (d, *J* = 313.4 Hz), 149.44, 135.28, 135.08 (d, *J* = 3.4 Hz), 133.70 (d, *J* = 1.9 Hz), 129.96, 129.82, 128.76, 127.59 (d, *J* = 7.2 Hz), 121.72 (d, *J* = 8.4 Hz), 121.58 (d, *J* = 4.3 Hz), 120.62 (q, *J* = 256.9 Hz), 120.23.

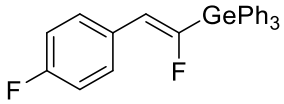
^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.67, -101.16 (d, *J* = 50.3 Hz).

HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{27}H_{20}F_4GeNaO$: 533.0554; found: 533.0552.




170.56
167.44
149.44
135.28
135.10
135.06
133.71
133.69
129.96
129.82
128.76
127.63
127.55
124.45
121.89
121.77
121.68
121.60
121.56
120.23
119.34
116.78
77.48
77.16
76.84
F3CO
GePh3
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-57.67
-101.09
-101.22
F3CO
GePh3
F
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)



(E)-(1-fluoro-2-(4-fluorophenyl)vinyl)triphenylgermane

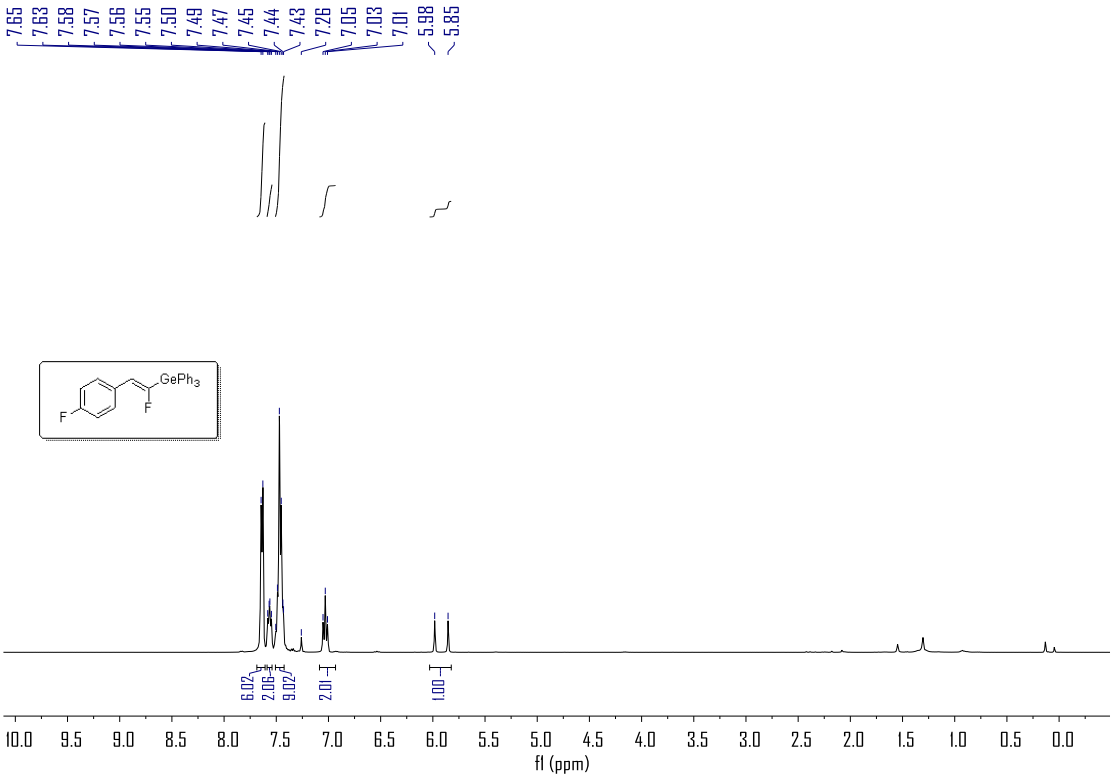
Following the general procedure (**3g**, pale-yellow liquid, 32 mg, 72%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

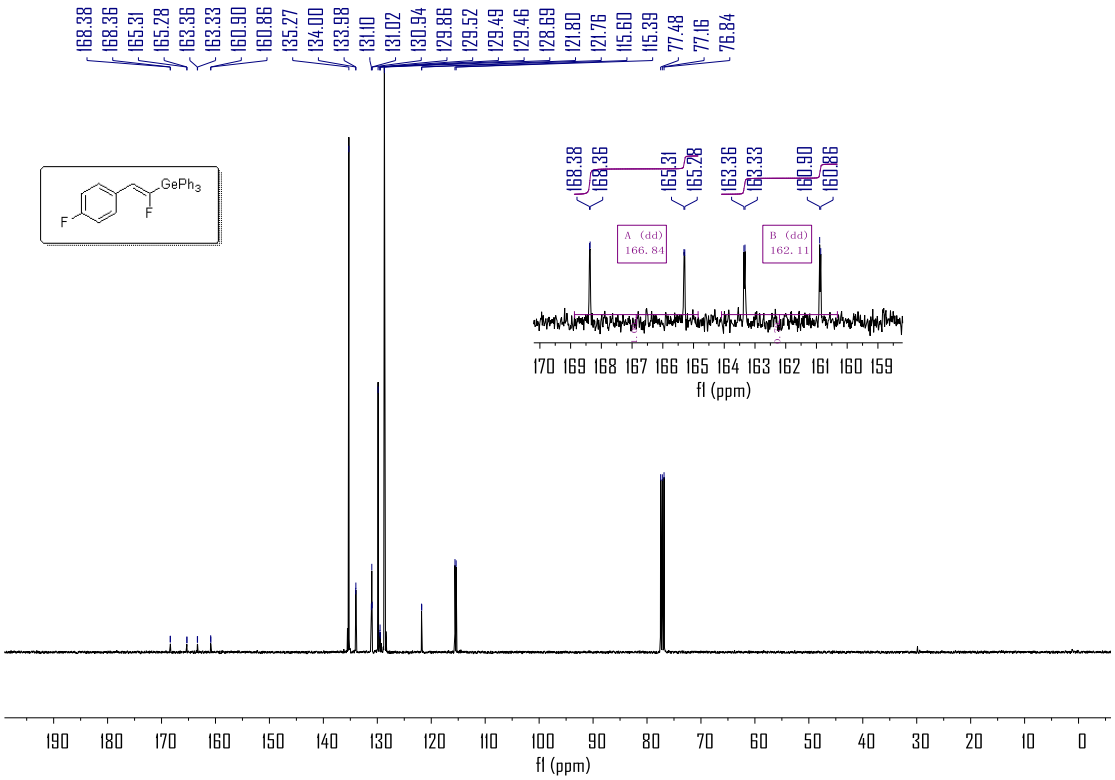
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 6.8 Hz, 6H), 7.56 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.52 – 7.42 (m, 9H), 7.03 (t, *J* = 8.6 Hz, 2H), 5.92 (d, *J* = 51.3 Hz, 1H).

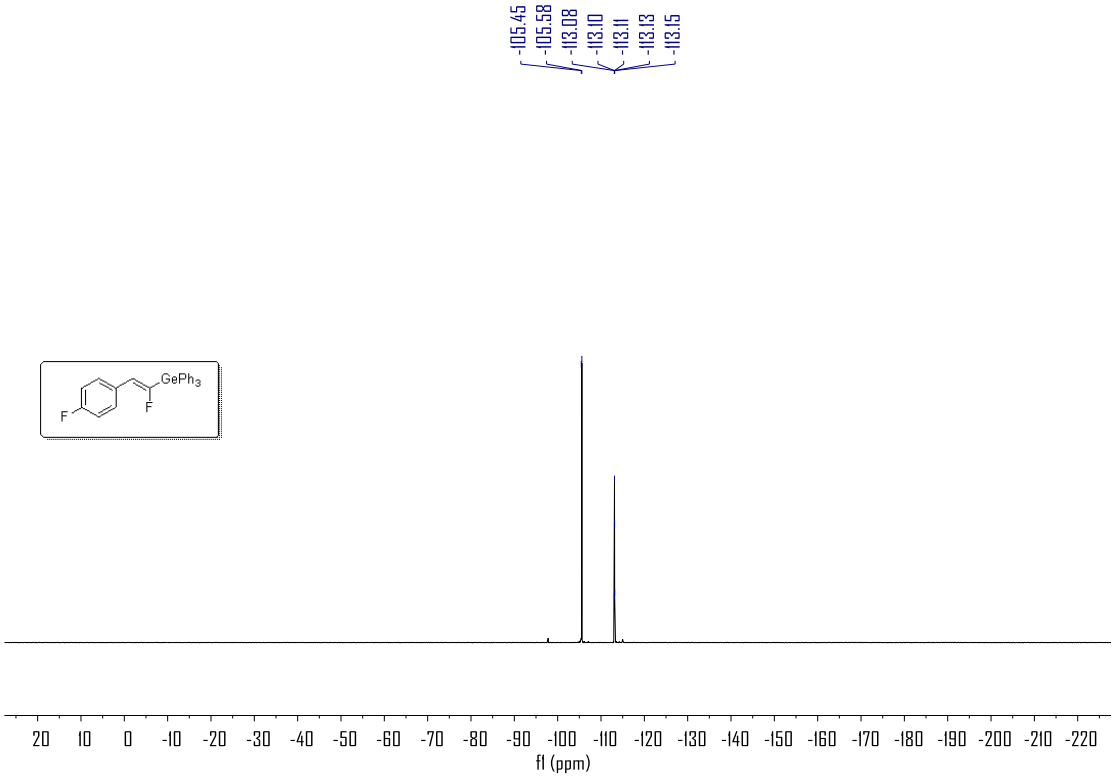
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.84 (dd, *J* = 309.5, 2.4 Hz), 162.11 (dd, *J* = 248.0, 3.5 Hz), 135.27, 133.99 (d, *J* = 2.0 Hz), 131.02 (t, *J* = 7.8 Hz), 129.86, 129.49 (t, *J* = 3.3 Hz), 128.69, 121.78 (d, *J* = 3.9 Hz), 115.49 (d, *J* = 21.6 Hz).

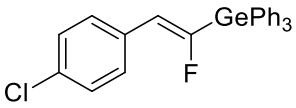
^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.52 (d, *J* = 51.2 Hz), -113.11 (p, *J* = 8.6 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{20}F_2GeNa$: 467.0637; found: 467.0642.




168.38
168.36
165.31
165.28
163.36
163.33
160.90
160.86
135.27
134.00
133.98
131.10
131.02
130.94
129.86
129.52
129.49
129.46
128.69
121.80
121.76
115.60
115.39
77.48
77.16
76.84
GePh3
F
F
A (dd)
166.84
B (dd)
162.11
170 169 168 167 166 165 164 163 162 161 160 159
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-105.45
-105.58
-113.08
-113.10
-113.11
-113.13
-113.15
GePh3
F
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(2-(4-chlorophenyl)-1-fluorovinyl)triphenylgermane

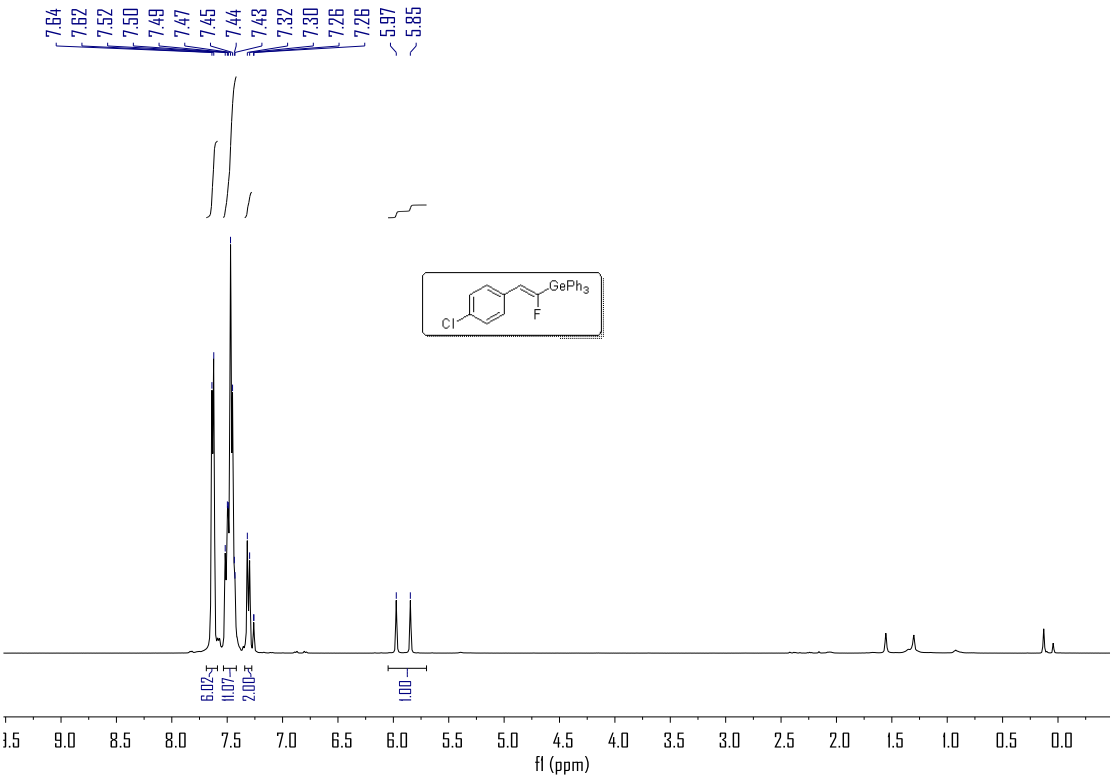
Following the general procedure (**3h**, pale-yellow liquid, 33 mg, 72%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

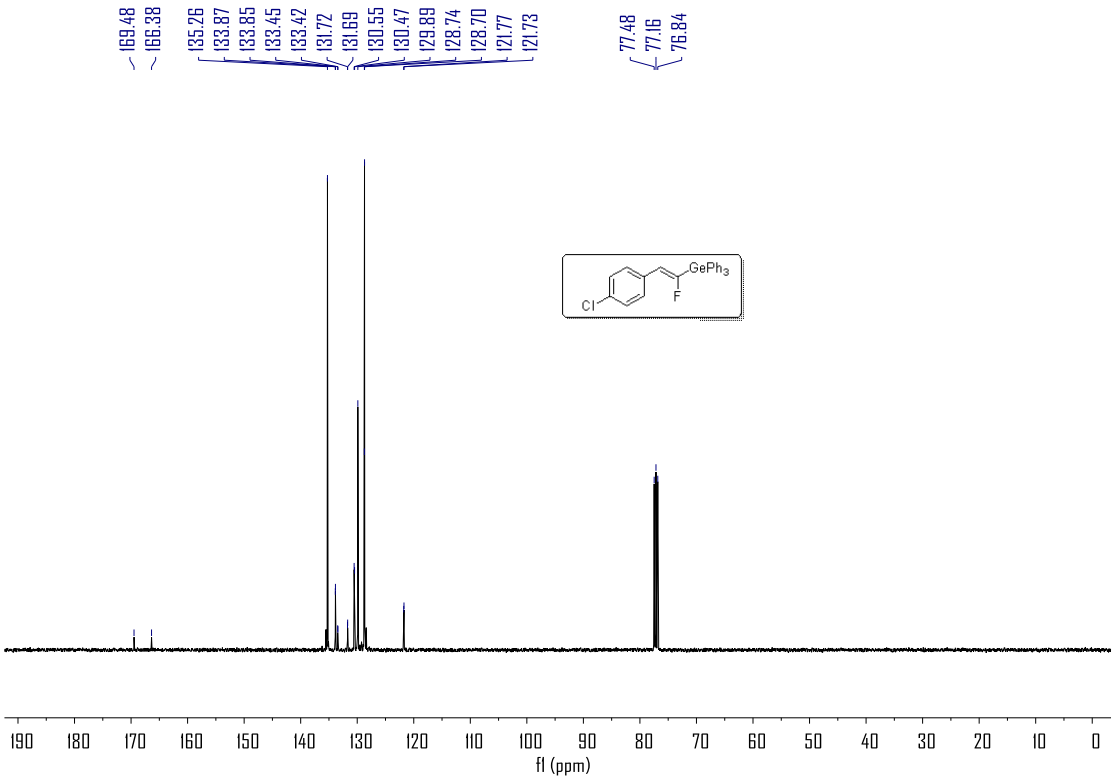
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 6.7 Hz, 6H), 7.48 (dq, *J* = 16.2, 8.9, 8.4 Hz, 11H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.91 (d, *J* = 50.8 Hz, 1H).

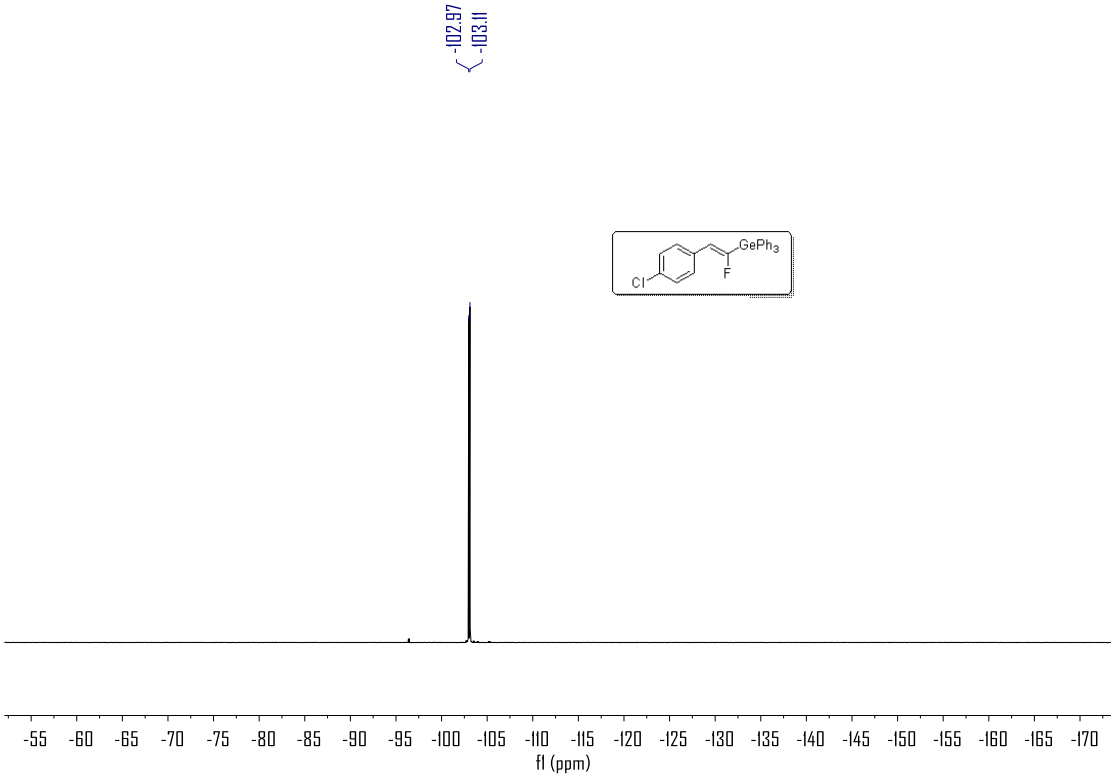
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.93 (d, *J* = 311.7 Hz), 135.26, 133.86 (d, *J* = 1.9 Hz), 133.43 (d, *J* = 3.8 Hz), 131.71 (d, *J* = 2.8 Hz), 130.51 (d, *J* = 7.8 Hz), 129.89, 128.74, 128.70, 121.75 (d, *J* = 4.1 Hz).

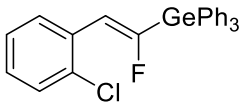
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.04 (d, *J* = 50.8 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{20}ClFGeNa$: 483.0342; found: 483.0336.




169.48
166.38
135.26
133.87
133.85
133.45
133.42
131.72
131.69
130.55
130.47
129.89
128.74
128.70
121.77
121.73
77.48
77.16
76.84
GePh3
Cl
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-102.97
-103.11
GePh3
Cl
F
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)



(E)-(2-(2-chlorophenyl)-1-fluorovinyl)triphenylgermane

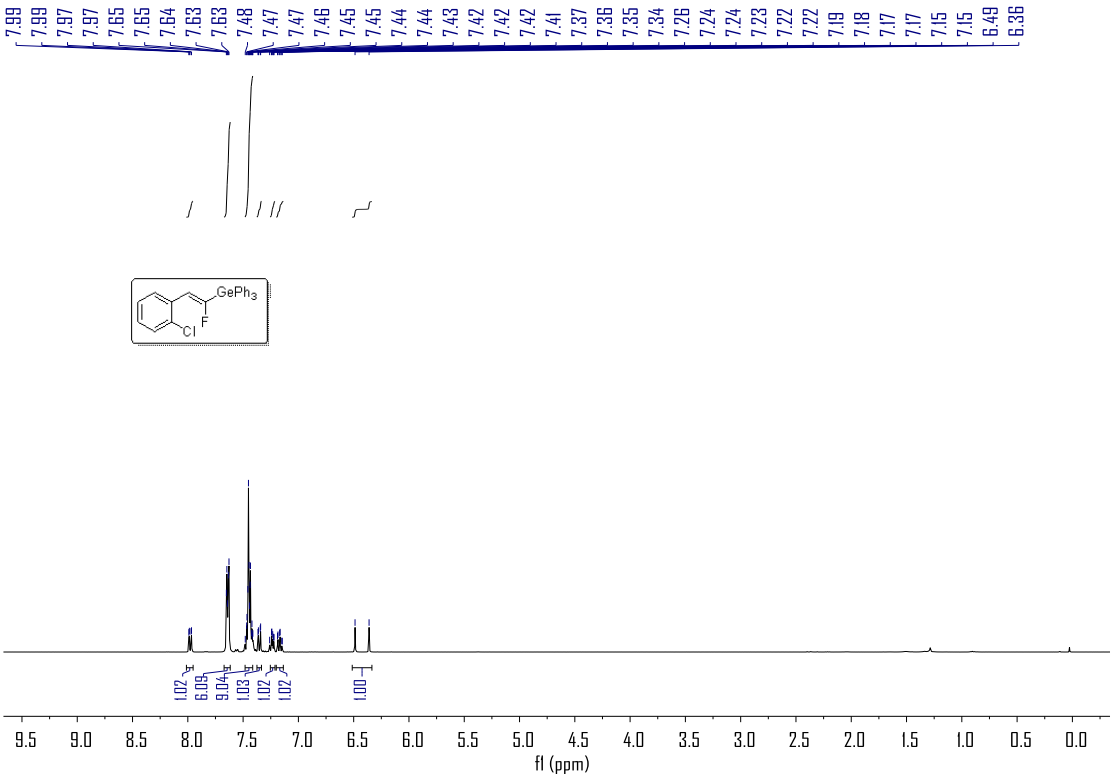
Following the general procedure (**3i**, pale-yellow solid, 35 mg, 77%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (20:1) as an eluent.

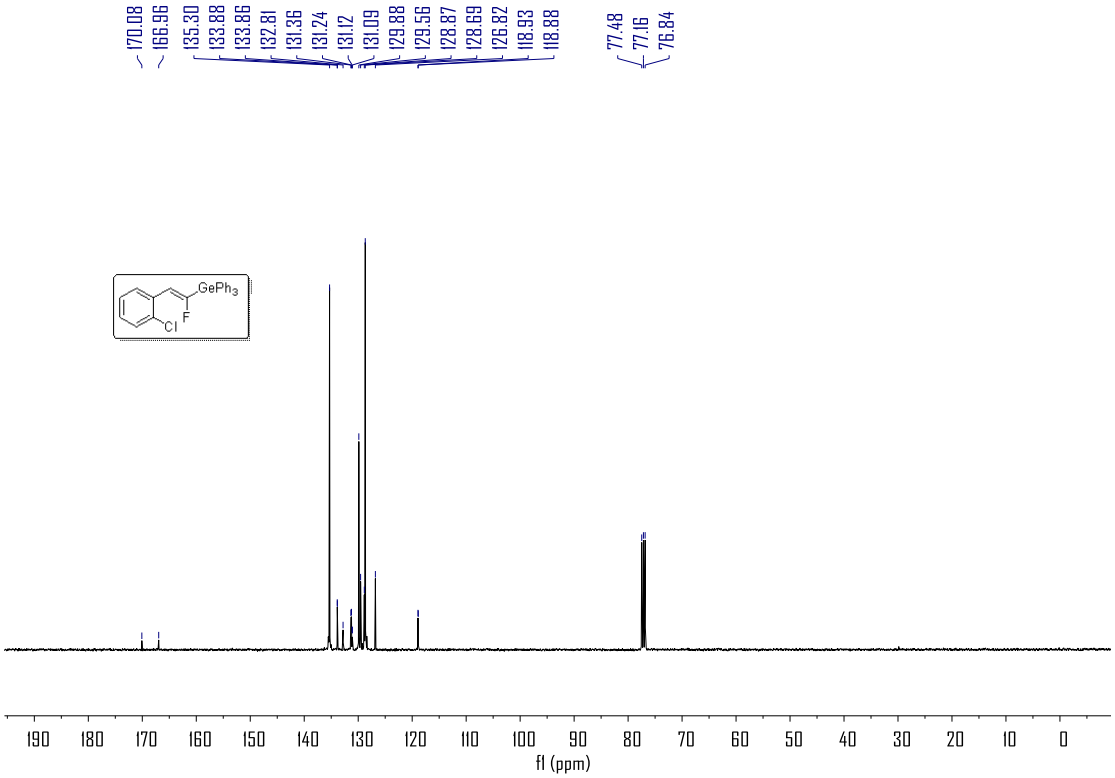
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.64 (dd, *J* = 7.4, 2.1 Hz, 6H), 7.49 – 7.40 (m, 9H), 7.35 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.17 (td, *J* = 7.7, 1.8 Hz, 1H), 6.42 (d, *J* = 50.8 Hz, 1H).

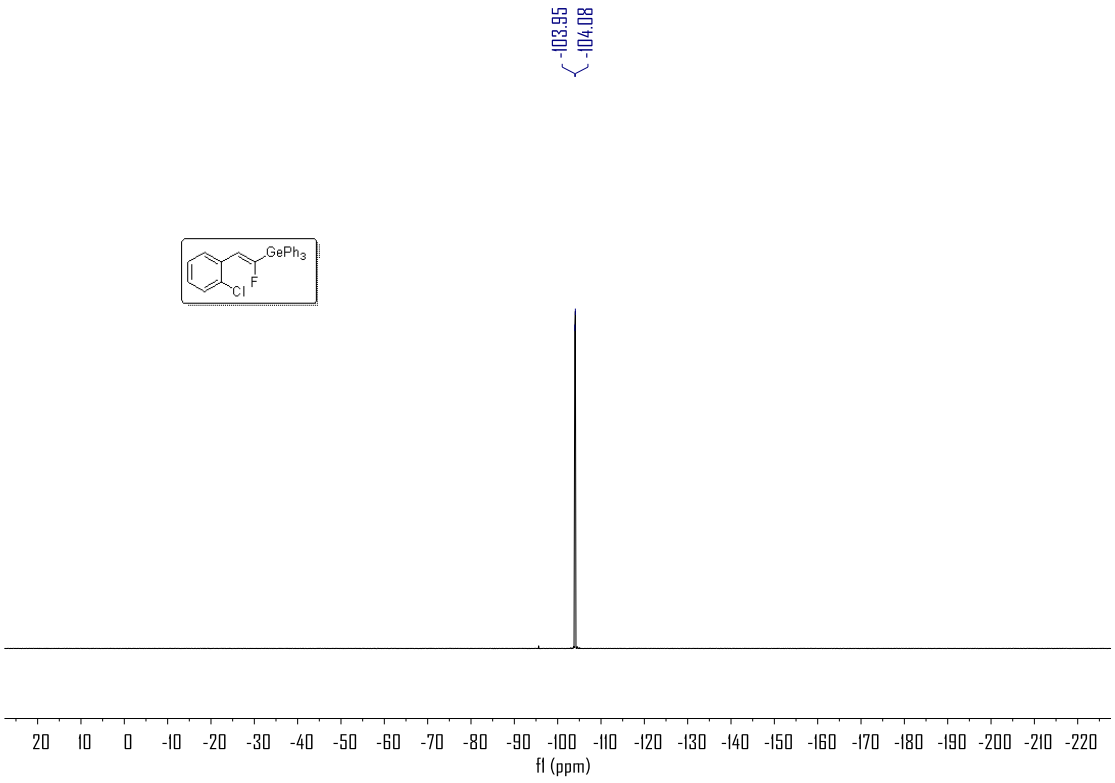
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.52 (d, *J* = 314.2 Hz), 135.30, 133.87 (d, *J* = 2.0 Hz), 132.81, 131.36, 131.10 (d, *J* = 2.5 Hz), 129.88, 129.56, 128.87, 128.69, 126.82, 118.90 (d, *J* = 5.2 Hz).

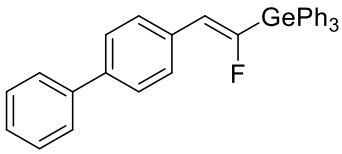
^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.02 (d, *J* = 50.4 Hz).

HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{26}H_{20}ClFGeNa$: 483.0342; found: 483.0346.




170.08
166.96
135.30
133.88
133.86
132.81
131.36
131.24
131.12
131.09
129.88
129.56
128.87
128.69
126.82
118.93
118.88
77.48
77.16
76.84
GePh3
Cl
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-103.95
-104.08
GePh3
Cl
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)triphenylgermane

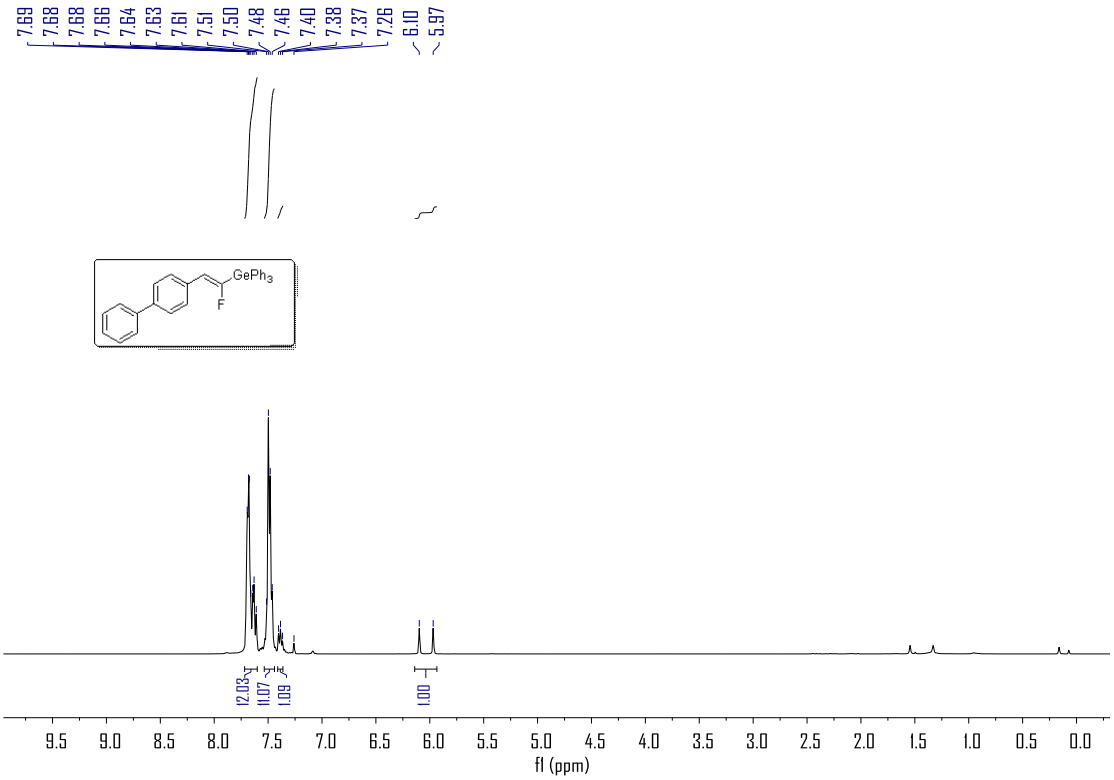
Following the general procedure (**3j**, pale-yellow solid, 31 mg, 63%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

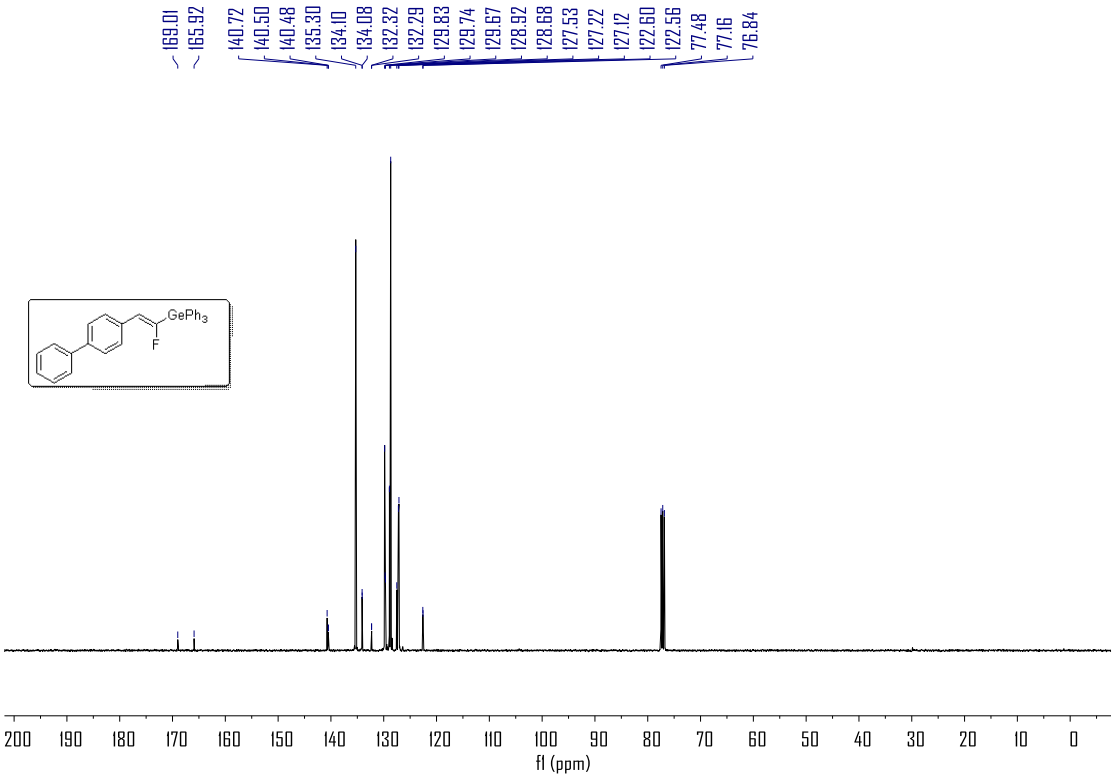
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.60 (m, 12H), 7.53 – 7.45 (m, 11H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.03 (d, *J* = 51.6 Hz, 1H).

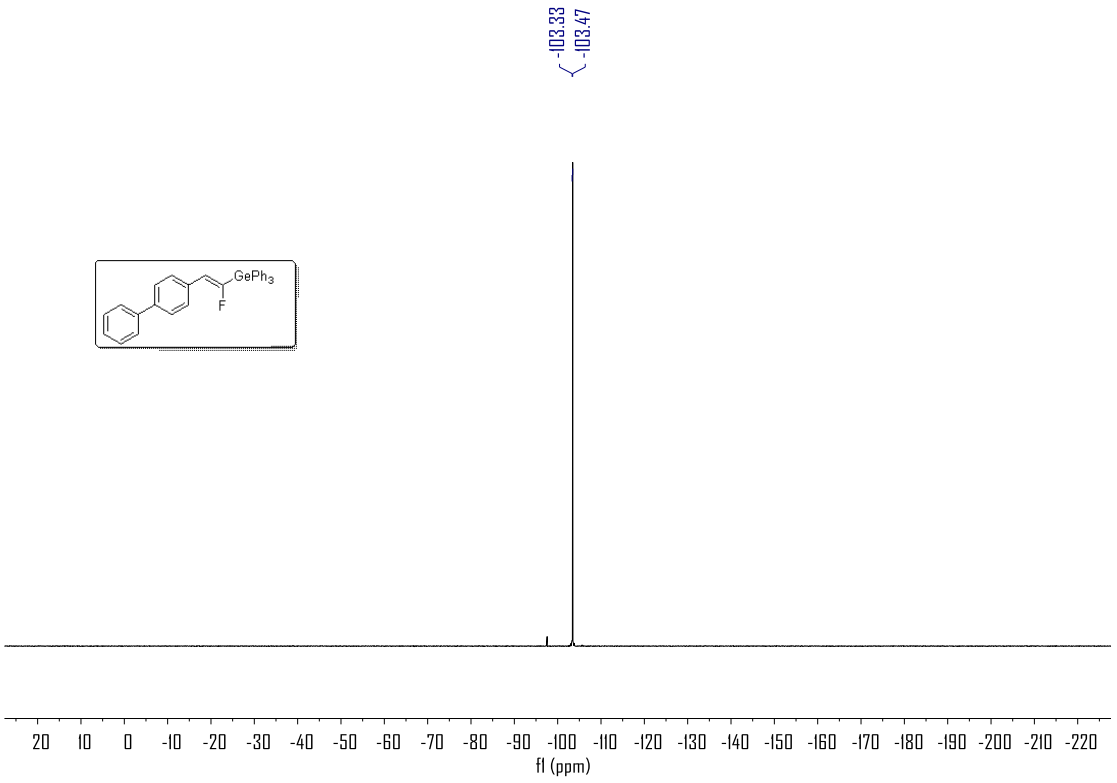
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.46 (d, *J* = 310.9 Hz), 140.72, 140.49 (d, *J* = 2.3 Hz), 135.30, 134.09 (d, *J* = 1.9 Hz), 132.30 (d, *J* = 2.7 Hz), 129.83, 129.71 (d, *J* = 7.4 Hz), 128.92, 128.68, 127.53, 127.22, 127.12, 122.58 (d, *J* = 4.1 Hz).

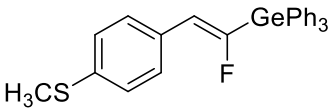
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.40 (d, *J* = 51.3 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}FGeNa$: 525.1044; found: 525.1041.




169.01
165.92
140.72
140.50
140.48
135.30
134.10
134.08
132.32
132.29
129.83
129.74
129.67
128.92
128.68
127.53
127.22
127.12
122.60
122.56
77.48
77.16
76.84
GePh3
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-103.33
-103.47
GePh3
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(1-fluoro-2-(4-(methylthio)phenyl)vinyl)triphenylgermane

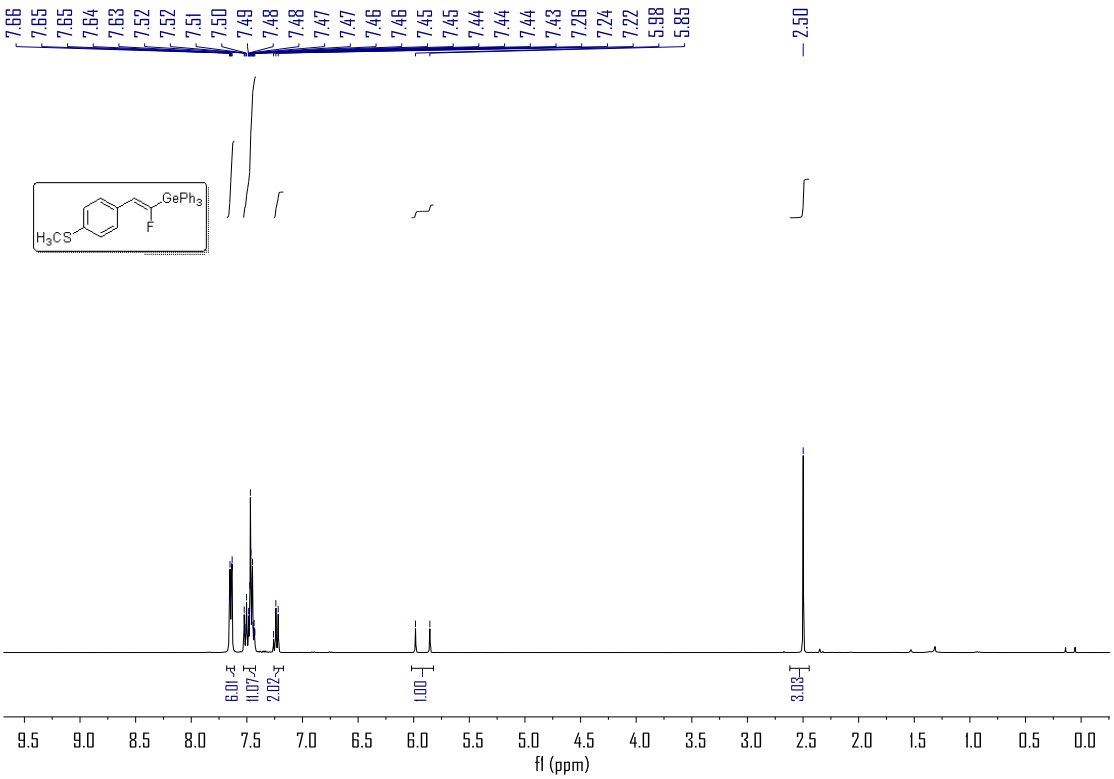
Following the general procedure (**3k**, pale-yellow solid, 24 mg, 51%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (20:1) as an eluent.

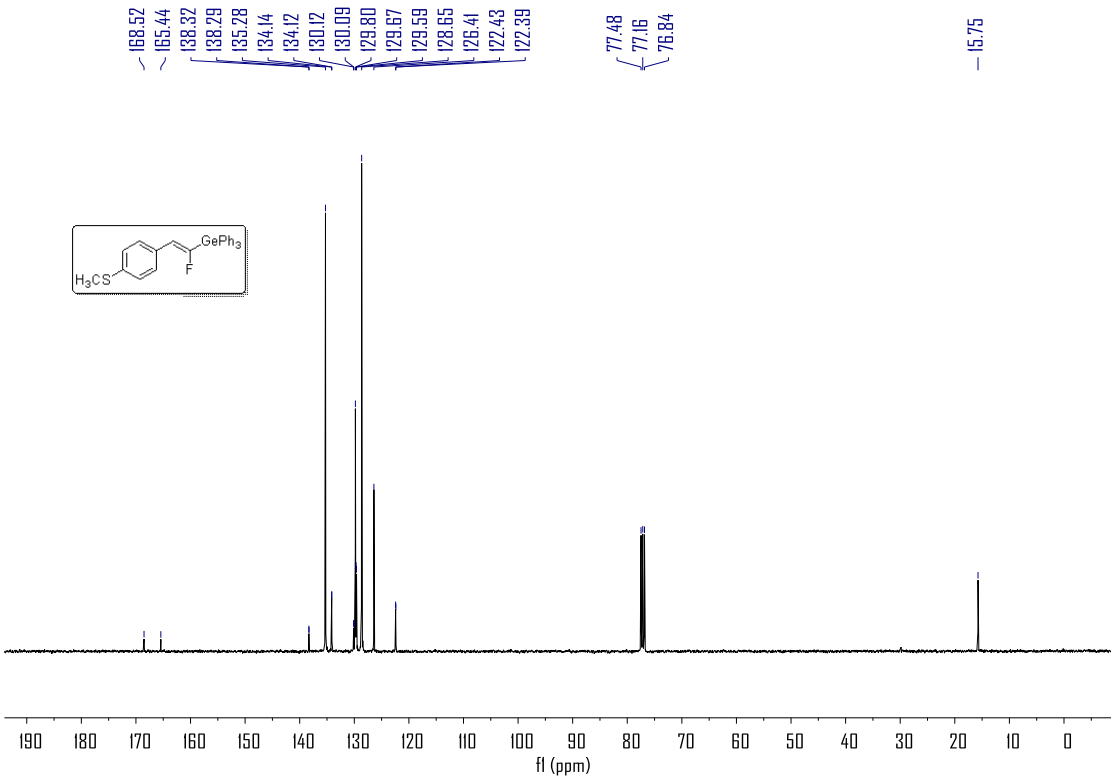
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 6H), 7.53 – 7.42 (m, 11H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.92 (d, *J* = 51.6 Hz, 1H), 2.50 (s, 3H).

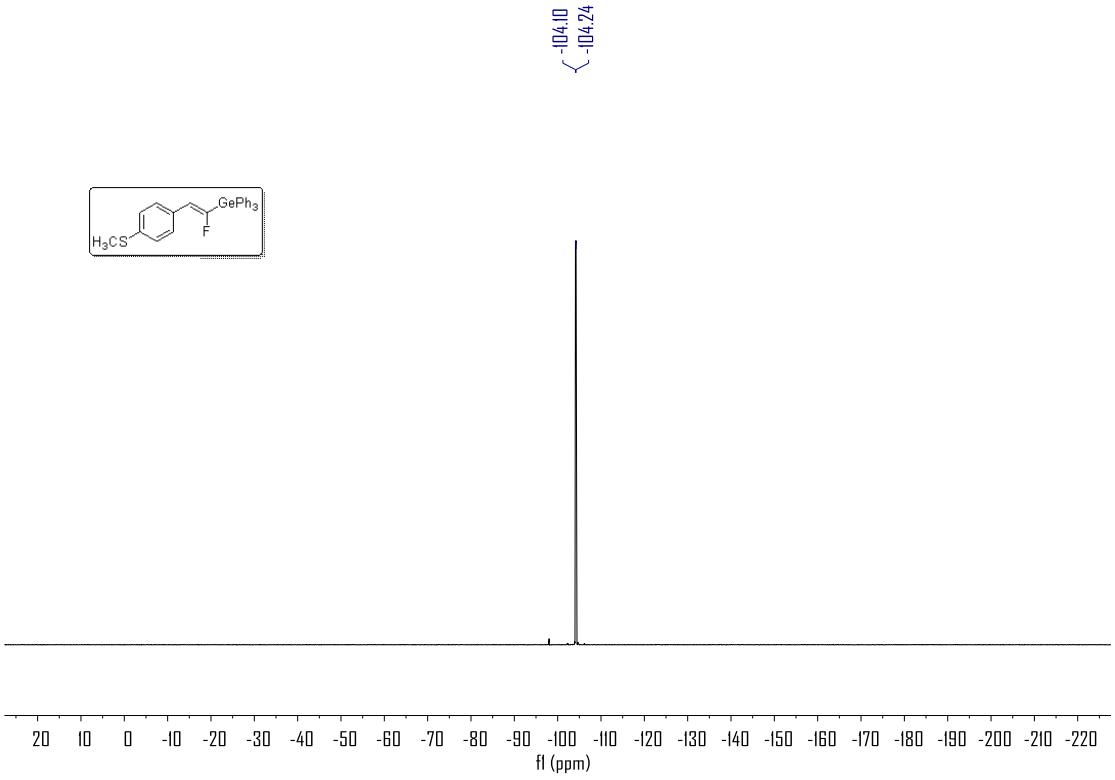
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.98 (d, *J* = 309.8 Hz), 138.31 (d, *J* = 2.9 Hz), 135.28, 134.13 (d, *J* = 1.8 Hz), 130.11 (d, *J* = 2.5 Hz), 129.80, 129.63 (d, *J* = 7.6 Hz), 128.65, 126.41, 122.41 (d, *J* = 4.0 Hz), 15.75.

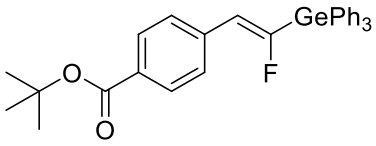
^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.17 (d, *J* = 51.9 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}FGeNaS$: 495.0608; found: 495.0602.




168.52
165.44
138.32
138.29
135.28
134.14
134.12
130.12
130.09
129.80
129.67
129.59
128.65
126.41
122.43
122.39
77.48
77.16
76.84
15.75
GePh3
H3CS
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-104.10
-104.24
GePh3
H3CS
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



Tert-butyl-(E)-4-(2-fluoro-2-(triphenylgermyl)vinyl)benzoate

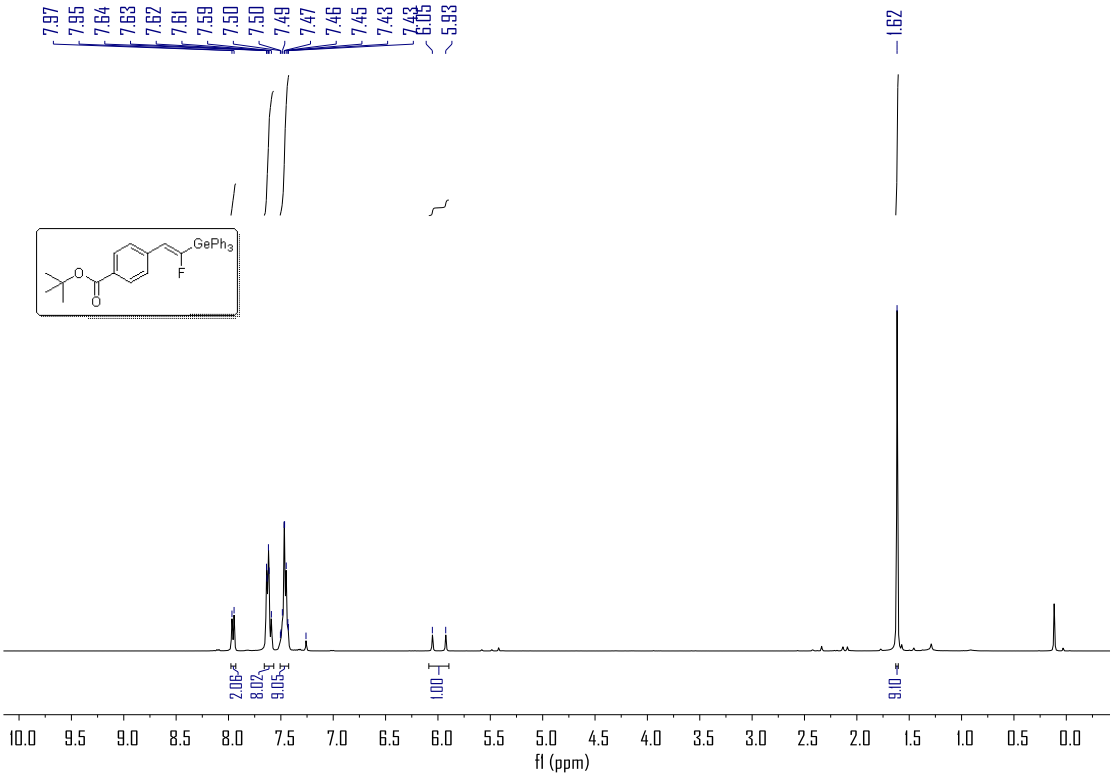
Following the general procedure (**3l**, pale-yellow solid, 35 mg, 67%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (15:1) as an eluent.

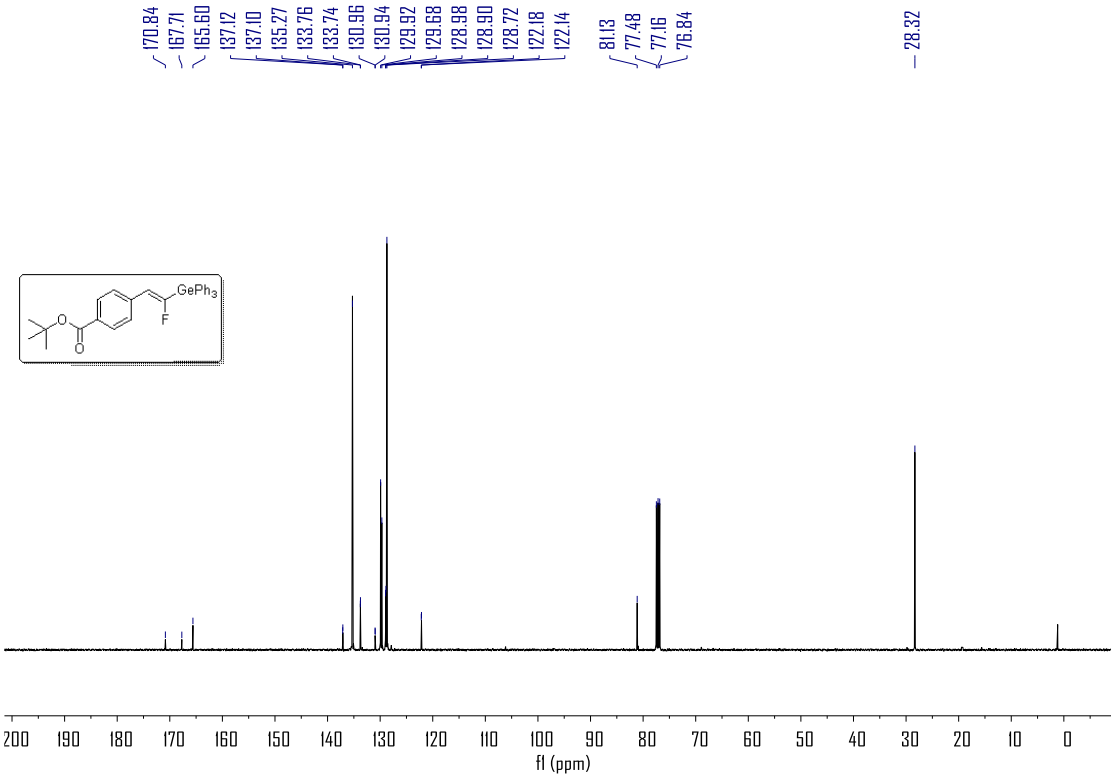
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.61 (dd, *J* = 10.6, 8.0 Hz, 8H), 7.51 – 7.41 (m, 9H), 5.99 (d, *J* = 50.9 Hz, 1H), 1.62 (s, 9H).

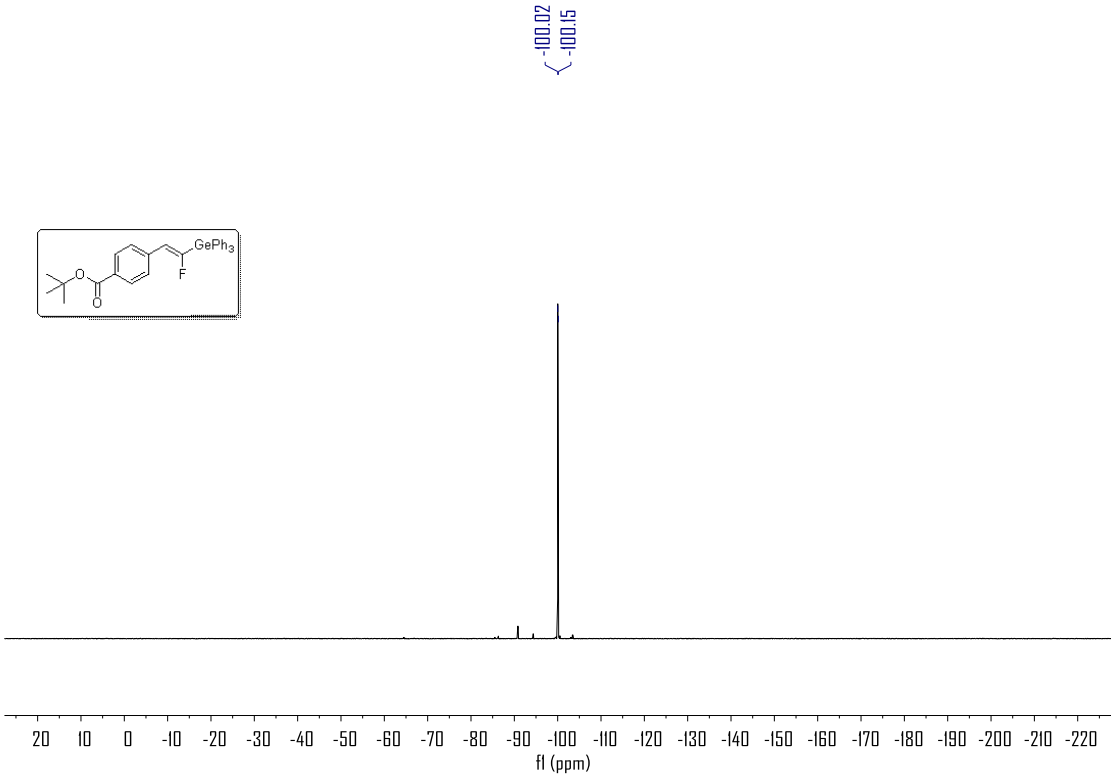
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.28 (d, *J* = 314.5 Hz), 165.60, 137.11 (d, *J* = 2.8 Hz), 135.27, 133.75 (d, *J* = 1.9 Hz), 130.95 (d, *J* = 2.4 Hz), 129.92, 129.68, 128.94 (d, *J* = 7.8 Hz), 128.72, 122.16 (d, *J* = 4.3 Hz), 81.13, 28.32.

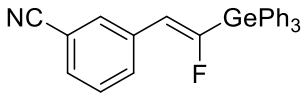
^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.08 (d, *J* = 50.6 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{29}FGeNaO_2$: 549.1256; found: 549.1251.




170.84
167.71
165.60
137.12
137.10
135.27
133.76
133.74
130.96
130.94
129.92
129.68
128.98
128.90
128.72
122.18
122.14
81.13
77.48
77.16
76.84
28.32
GePh3
F
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-100.02
-100.15
GePh3
F
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-3-(2-fluoro-2-(triphenylgermyl)vinyl)benzonitrile

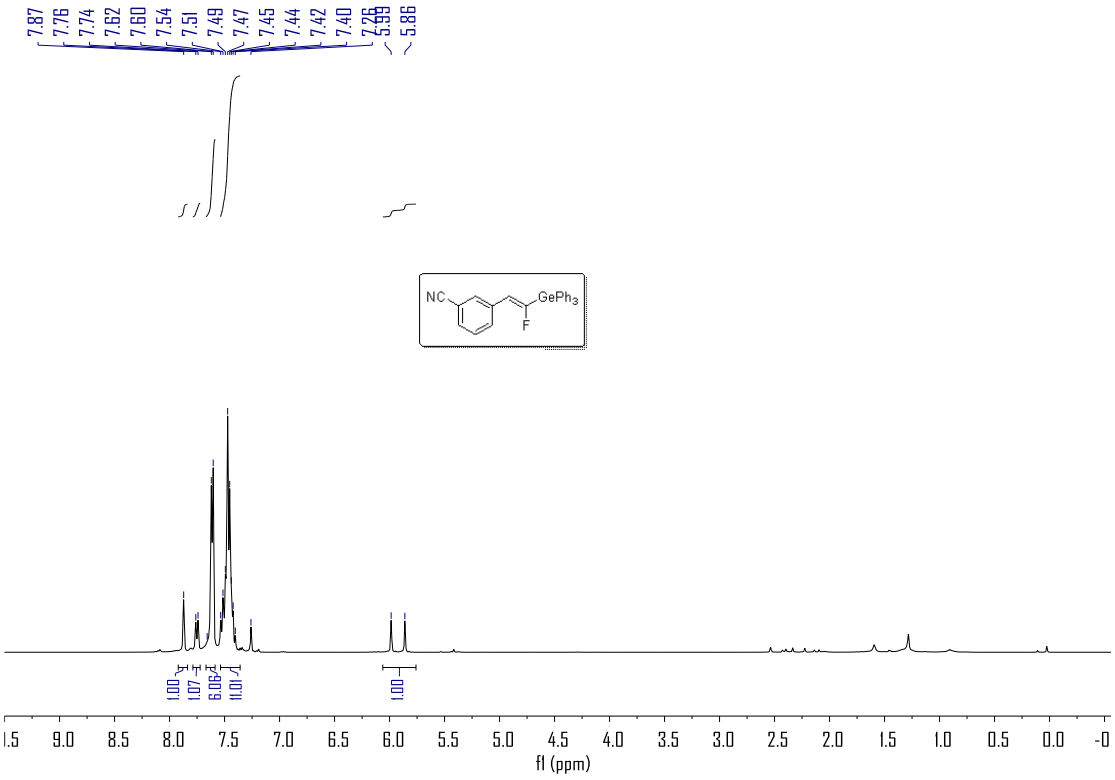
Following the general procedure (**3m**, pale-yellow solid, 27 mg, 61%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (10:1) as an eluent.

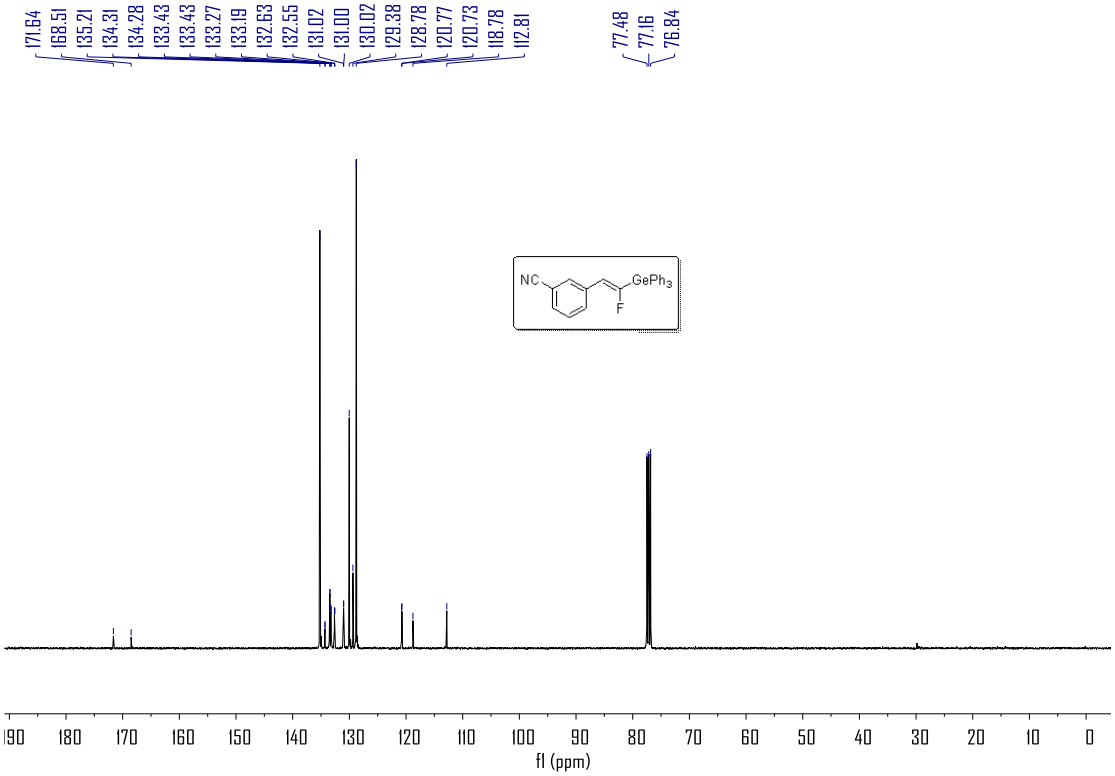
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 6.9 Hz, 6H), 7.54 – 7.40 (m, 11H), 5.92 (d, *J* = 49.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.08 (d, *J* = 314.9 Hz), 135.21, 134.30 (d, *J* = 3.1 Hz), 133.69 – 133.36 (m), 133.23 (d, *J* = 7.4 Hz), 132.59 (d, *J* = 8.3 Hz), 131.01 (d, *J* = 2.2 Hz), 130.02, 129.38, 128.78, 120.75 (d, *J* = 4.3 Hz), 118.78, 112.81.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.98 (d, *J* = 49.7 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{20}FGeNNa$: 474.0684; found: 474.0677.




171.64
168.51
135.21
134.31
134.28
133.43
133.43
133.27
133.19
132.63
132.55
131.02
131.00
130.02
129.38
128.78
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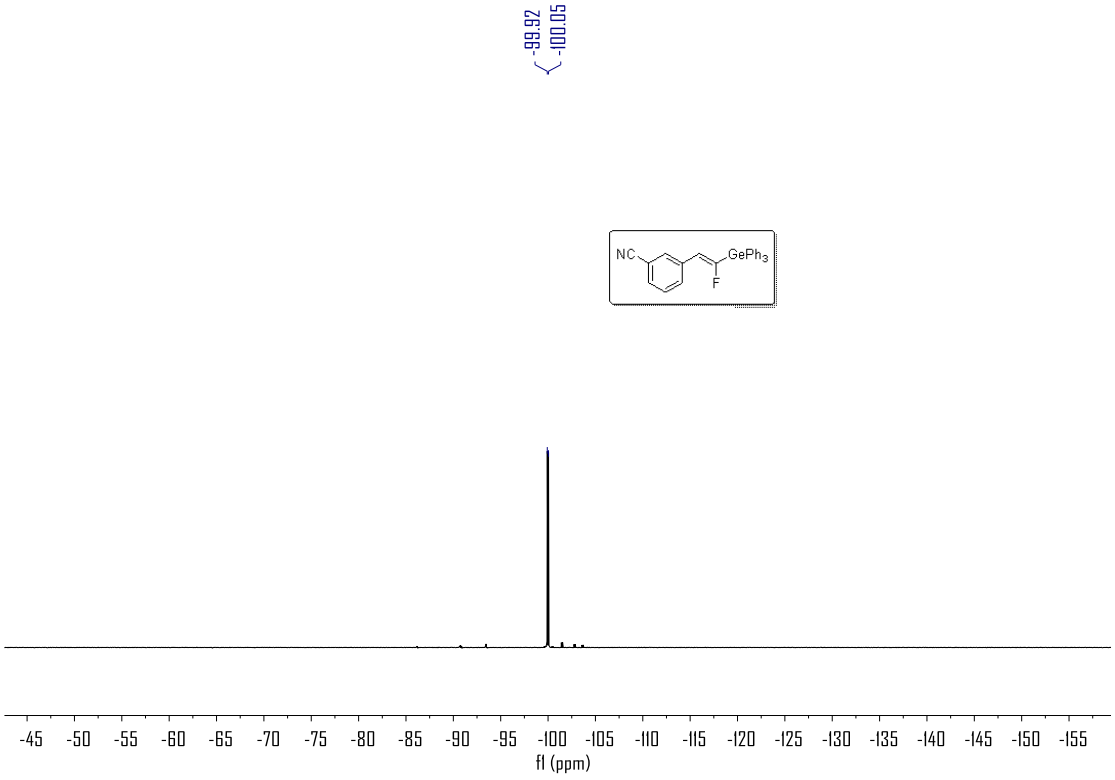
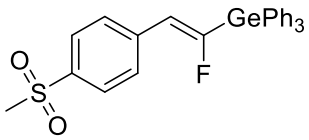
120.73
118.78
112.81
77.48
77.16
76.84
NC
GePh3
F
f1 (ppm)


-99.92
-100.05
NC
GePh3
F
f1 (ppm)



(E)-(1-fluoro-2-(4-(methylsulfonyl)phenyl)vinyl)triphenylgermane

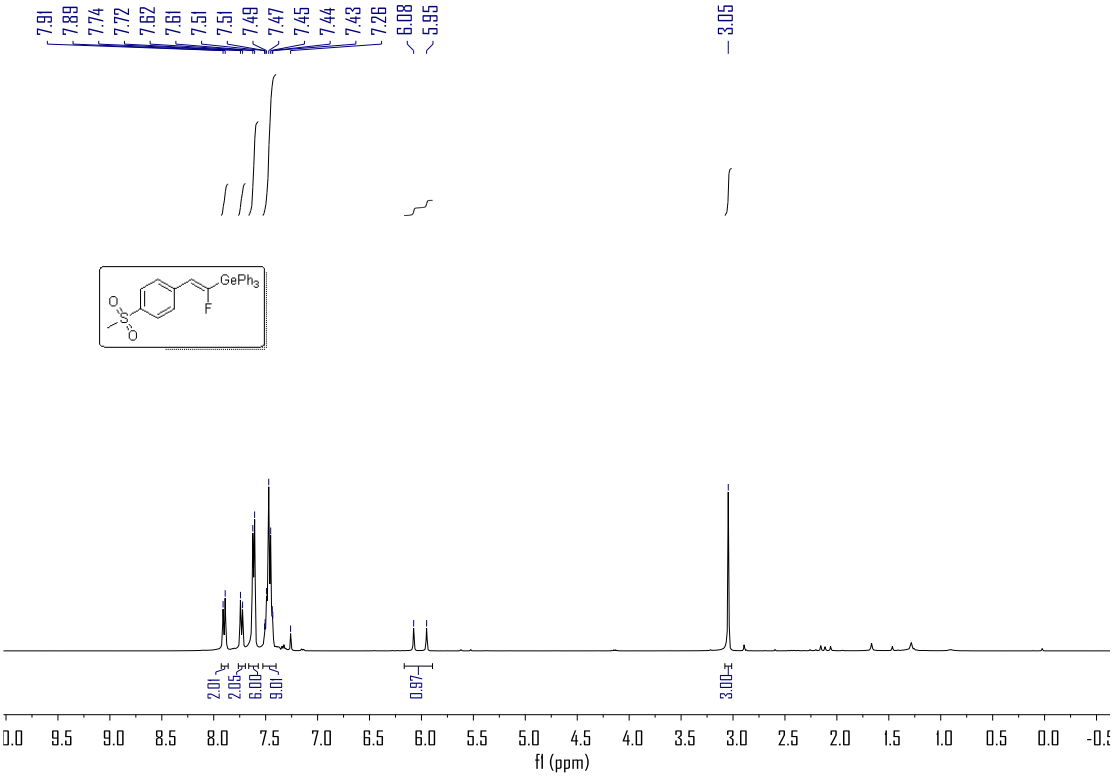
Following the general procedure (**3n**, pale-yellow solid, 33 mg, 65%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (3:1) as an eluent.

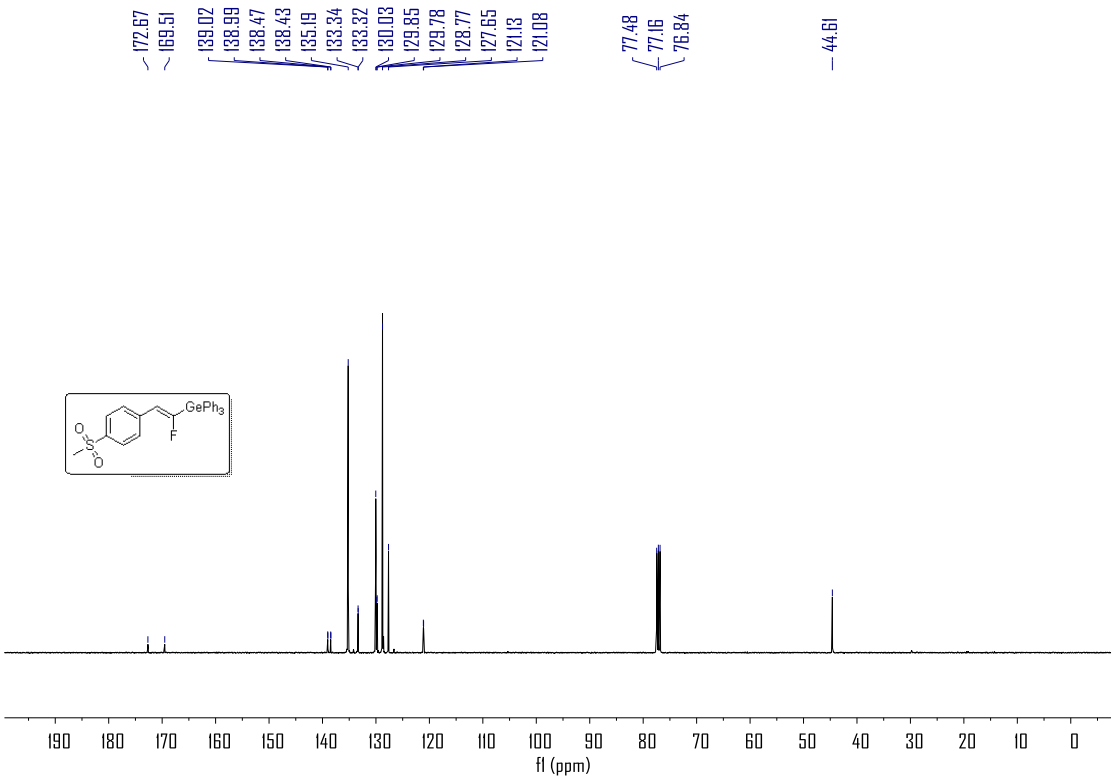
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 6H), 7.46 (q, *J* = 8.2 Hz, 9H), 6.01 (d, *J* = 49.9 Hz, 1H), 3.05 (s, 3H).

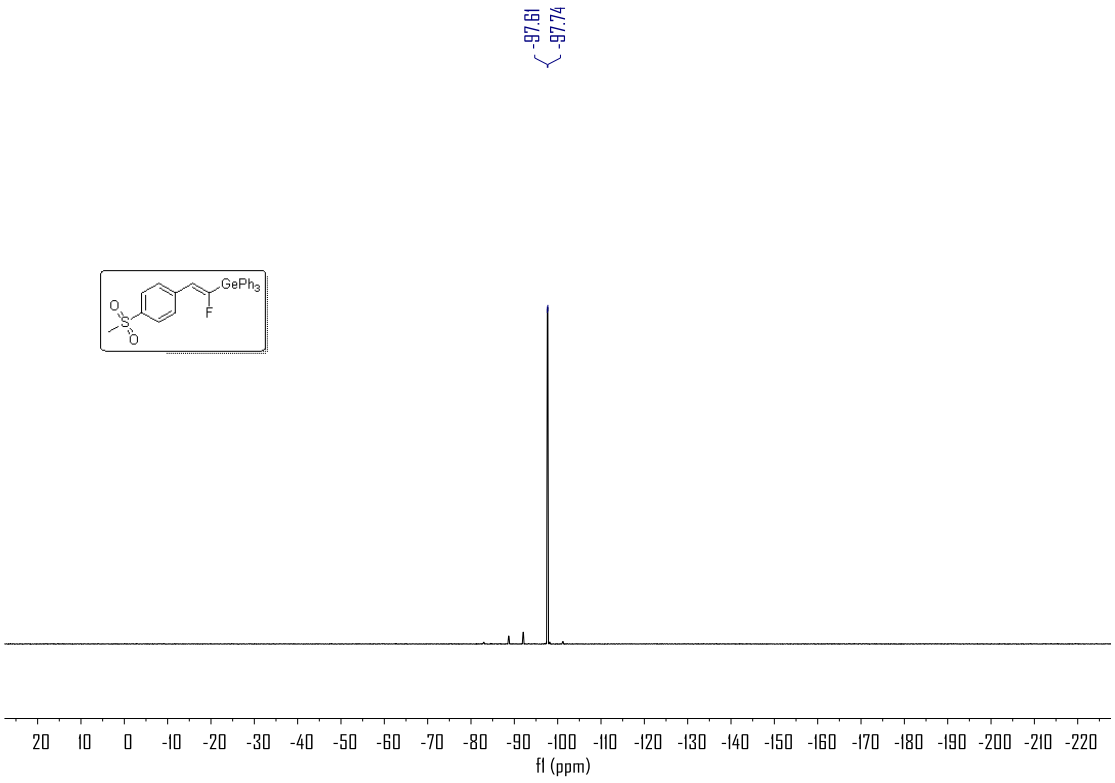
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.09 (d, *J* = 317.3 Hz), 139.01 (d, *J* = 2.8 Hz), 138.45 (d, *J* = 3.1 Hz), 135.19, 133.33 (d, *J* = 1.8 Hz), 130.03, 129.82 (d, *J* = 8.0 Hz), 128.77, 127.65, 121.11 (d, *J* = 4.4 Hz), 44.61.

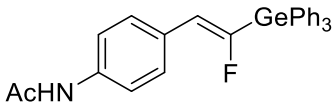
^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.68 (d, *J* = 49.9 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}FGeNaO_2S$: 527.0507; found: 527.0512.




172.67
169.51
139.02
138.99
138.47
138.43
135.19
133.34
133.32
130.03
129.85
129.78
128.77
127.65
121.13
121.08
77.48
77.16
76.84
44.61
GePh3
F
O
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-97.61
-97.74
GePh3
F
O
S
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-N-(4-(2-fluoro-2-(triphenylgermyl)vinyl)phenyl)acetamide

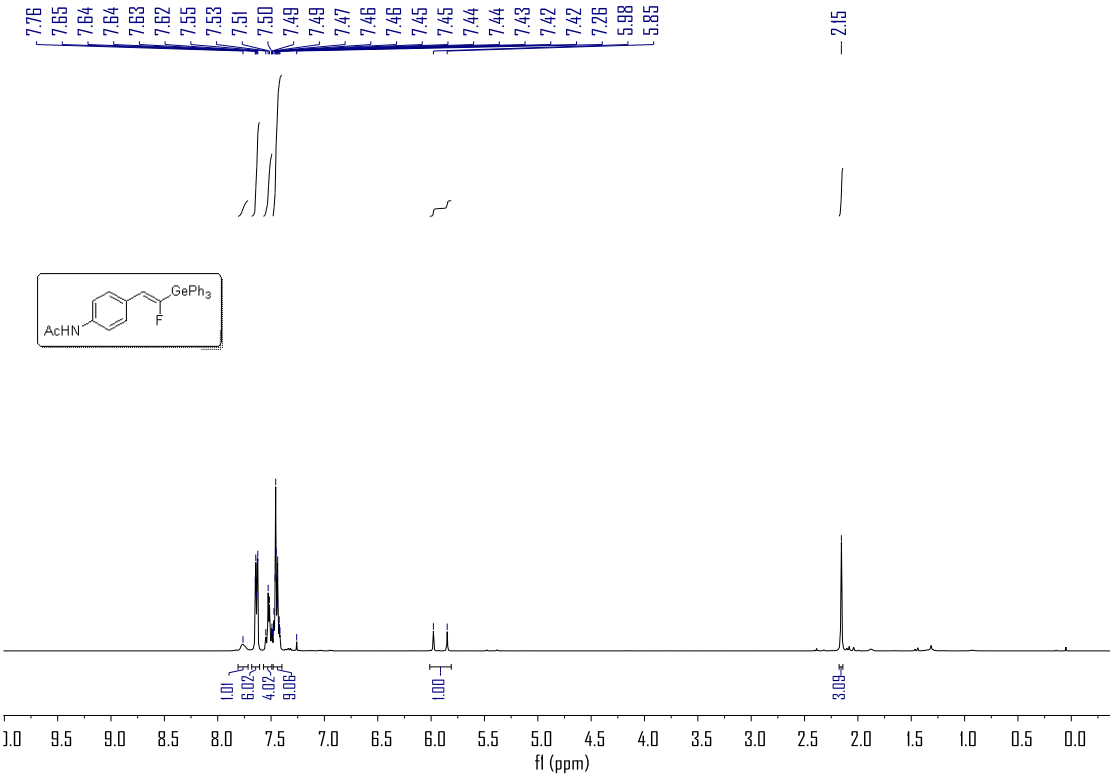
Following the general procedure (**3o**, pale-yellow solid, 28 mg, 58%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (3:1) as an eluent.

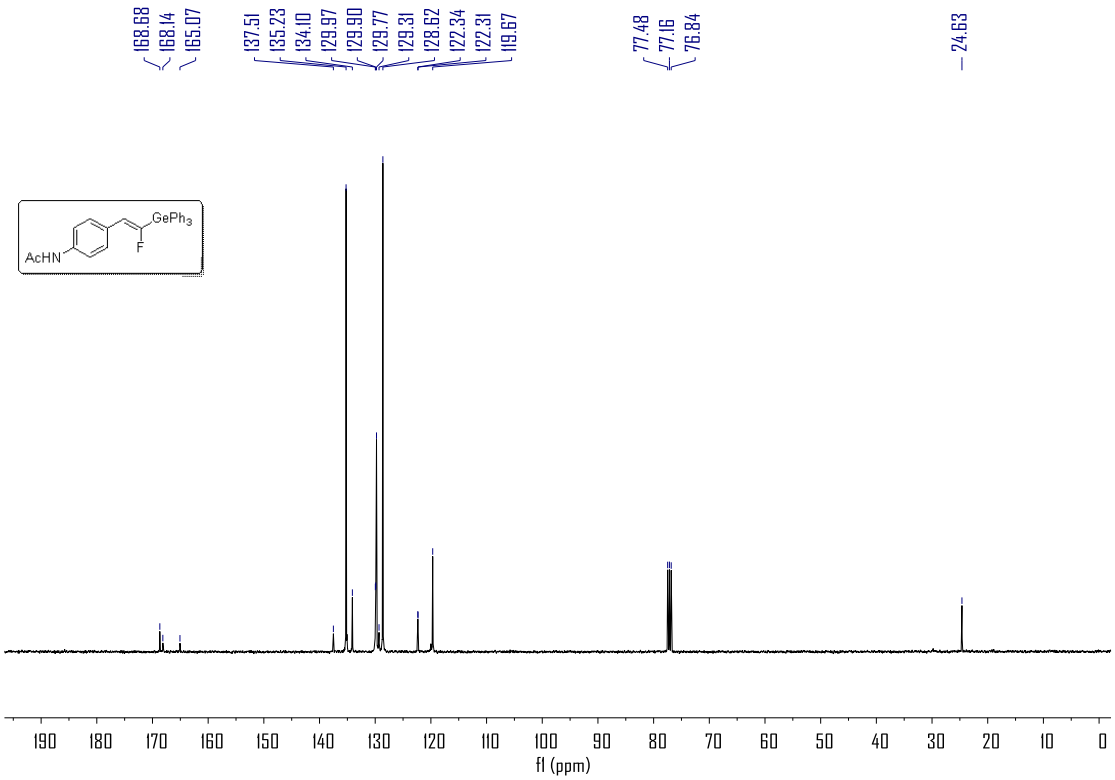
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.64 (dd, *J* = 7.5, 1.9 Hz, 6H), 7.56 – 7.49 (m, 4H), 7.48 – 7.40 (m, 9H), 5.91 (d, *J* = 51.7 Hz, 1H), 2.15 (s, 3H).

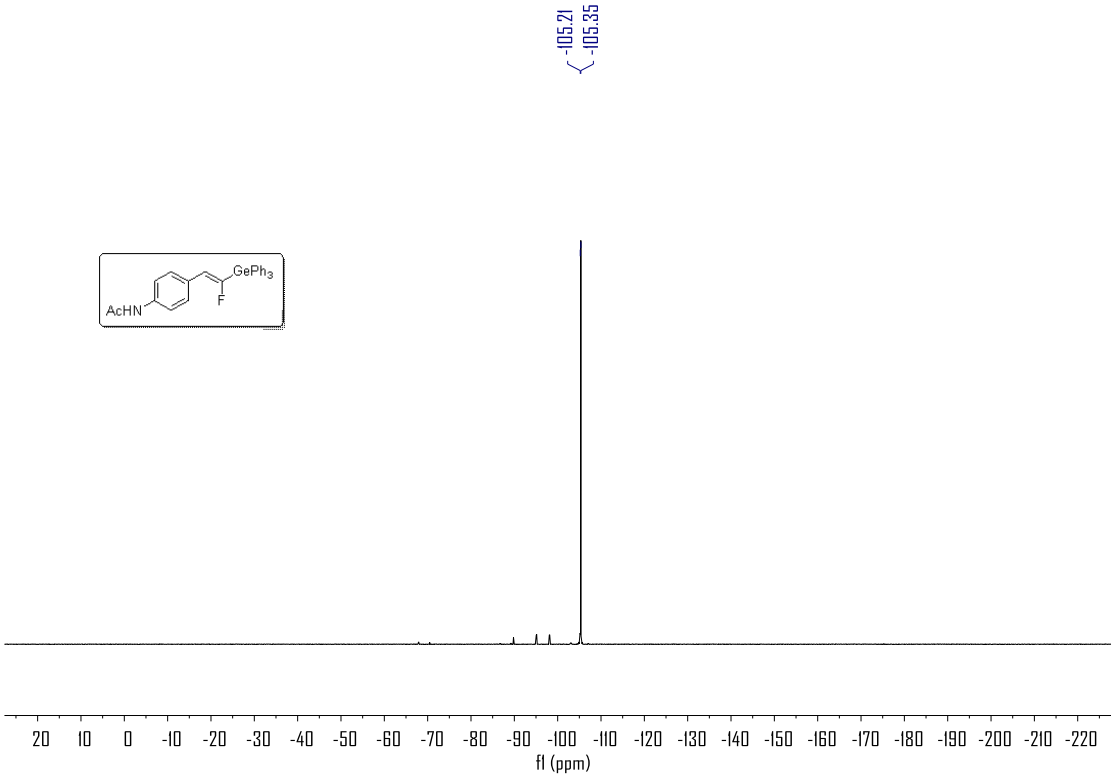
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.68, 166.60 (d, *J* = 309.2 Hz), 137.51, 135.23, 134.10, 129.94 (d, *J* = 7.5 Hz), 129.77, 129.31, 128.62, 122.33 (d, *J* = 2.9 Hz), 119.67, 24.63.

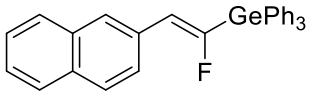
^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.28 (d, *J* = 51.4 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}FGeNNaO$: 506.0946; found: 506.0943.




168.68
168.14
165.07
137.51
135.23
134.10
129.97
129.90
129.77
129.31
128.62
122.34
122.31
119.67
77.48
77.16
76.84
24.63
GePh3
F
AcHN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-105.21
-105.35
GePh3
F
AcHN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(1-fluoro-2-(naphthalen-2-yl)vinyl)triphenylgermane

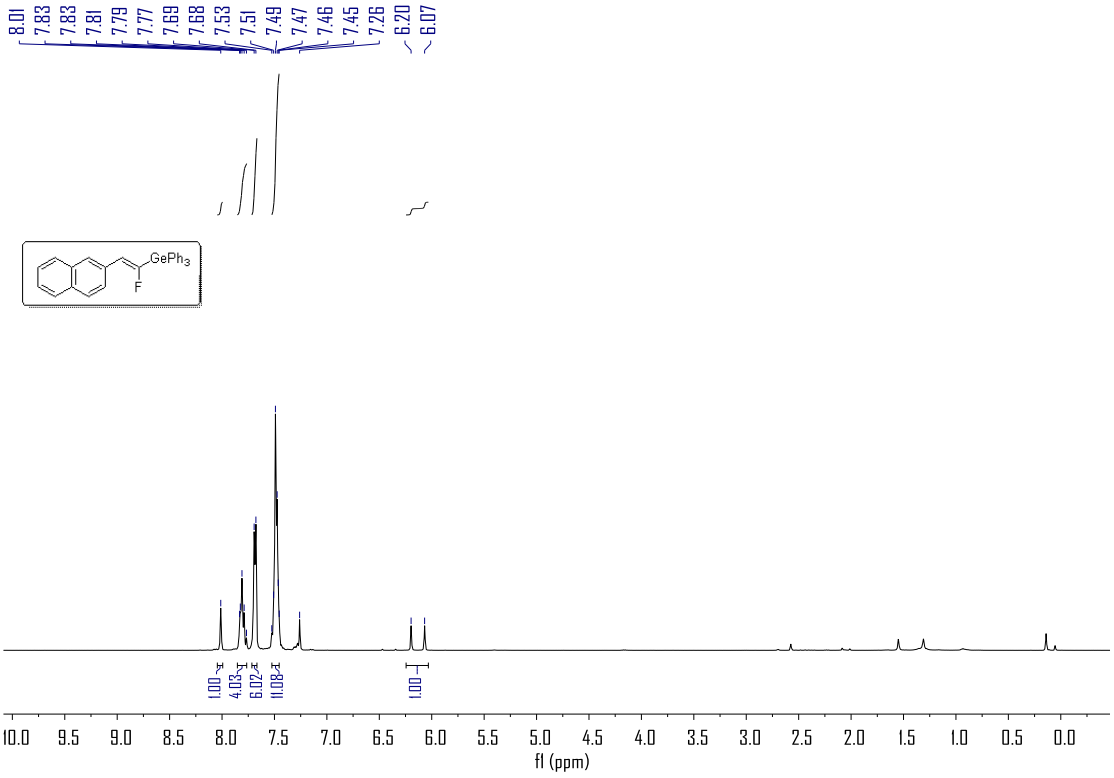
Following the general procedure (**3p**, pale-yellow solid, 28 mg, 60%, E/Z > 30:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

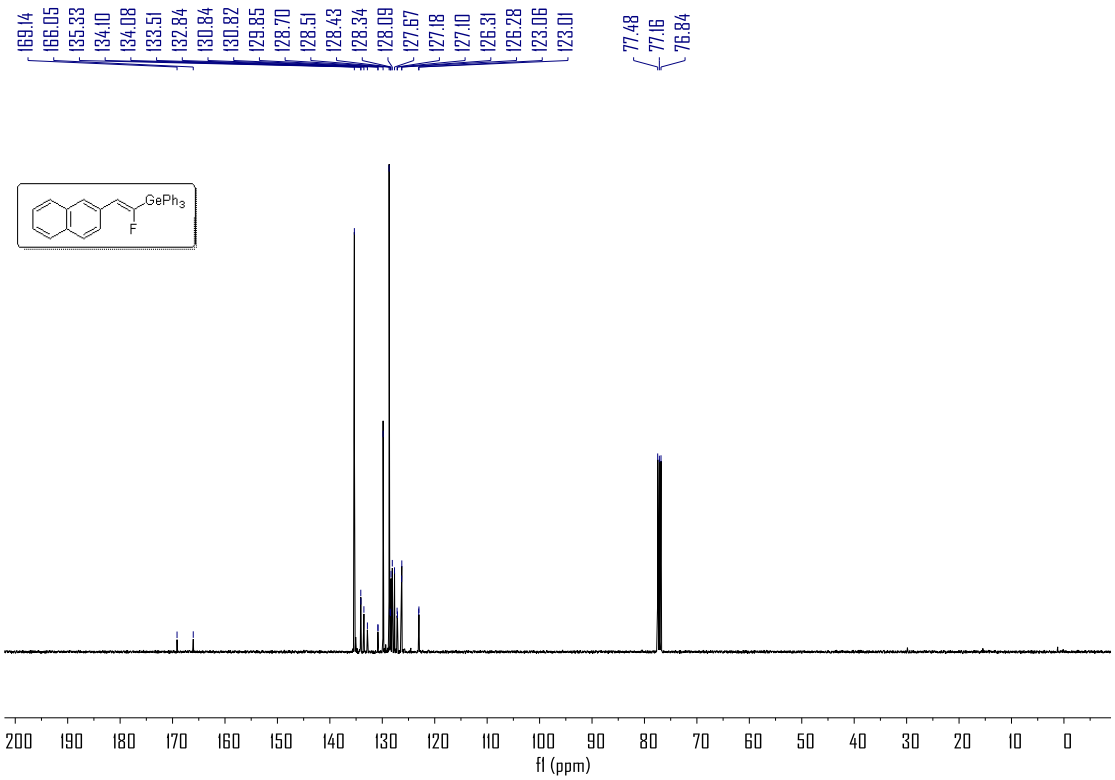
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.86 – 7.77 (m, 4H), 7.69 (d, *J* = 6.7 Hz, 6H), 7.48 (d, *J* = 6.5 Hz, 11H), 6.13 (d, *J* = 51.6 Hz, 1H).

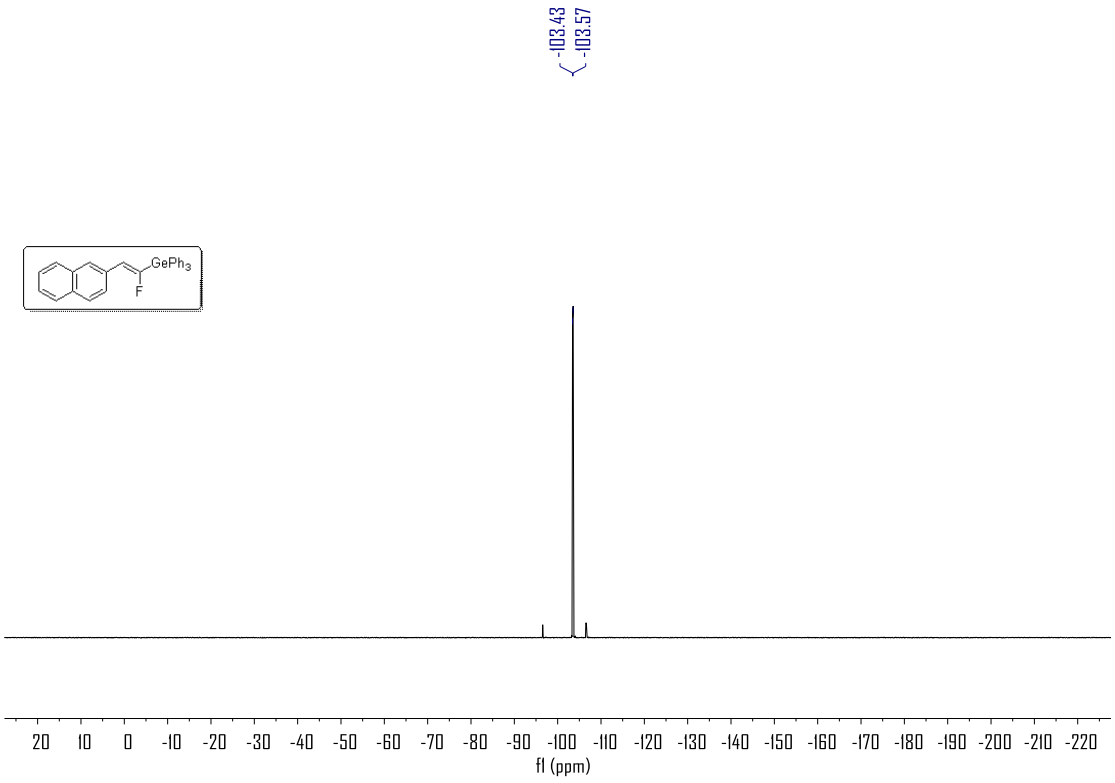
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.60 (d, *J* = 311.0 Hz), 135.33, 134.09 (d, *J* = 1.9 Hz), 133.51, 132.84, 130.83 (d, *J* = 2.6 Hz), 129.85, 128.70, 128.47 (d, *J* = 7.9 Hz), 128.34, 128.09, 127.67, 127.14 (d, *J* = 7.5 Hz), 126.31, 126.28, 123.03 (d, *J* = 4.3 Hz).

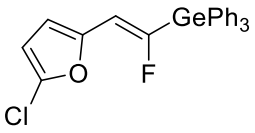
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.50 (d, *J* = 51.6 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{23}FGeNa$: 499.0888; found: 499.0885.




169.14
166.05
135.33
134.10
134.08
133.51
132.84
130.84
130.82
129.85
128.70
128.51
128.43
128.34
128.09
127.67
127.18
127.10
126.31
126.28
123.06
123.01
77.48
77.16
76.84
GePh3
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-103.43
-103.57
GePh3
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(2-(5-chlorofuran-2-yl)-1-fluorovinyl)triphenylgermane

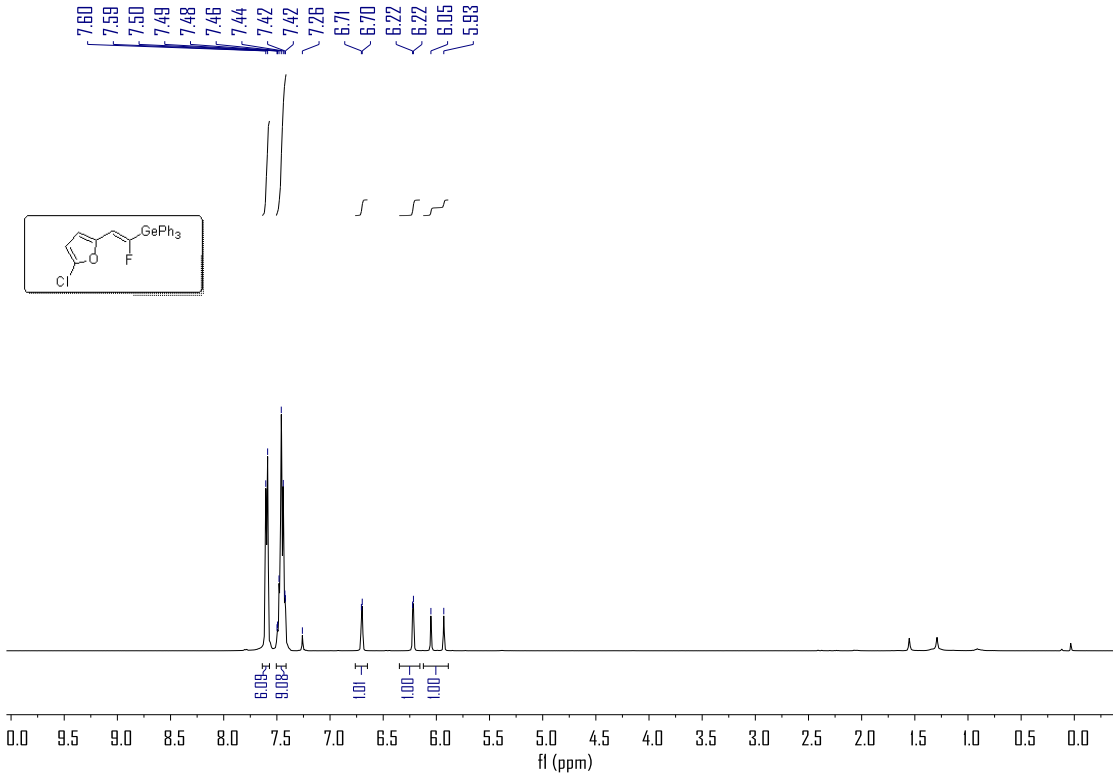
Following the general procedure (**3q**, pale-yellow solid, 30 mg, 68%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

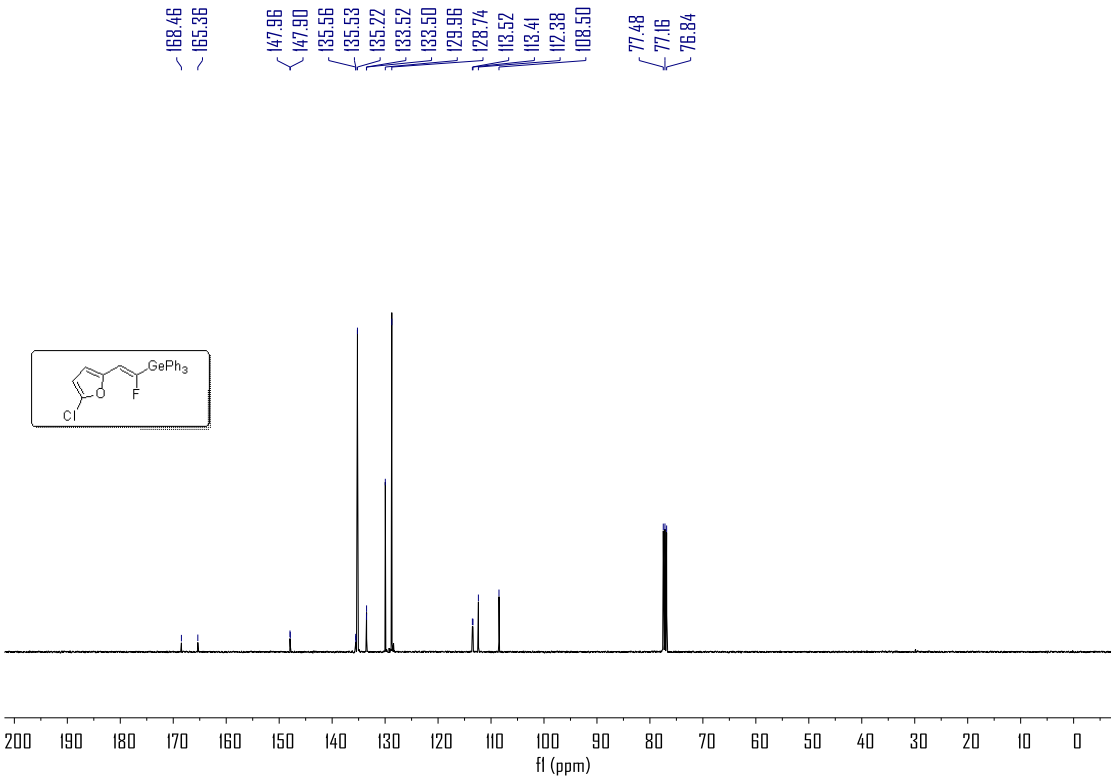
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.0 Hz, 6H), 7.45 (q, *J* = 8.3 Hz, 9H), 6.70 (d, *J* = 3.2 Hz, 1H), 6.22 (d, *J* = 3.3 Hz, 1H), 5.99 (d, *J* = 48.5 Hz, 1H).

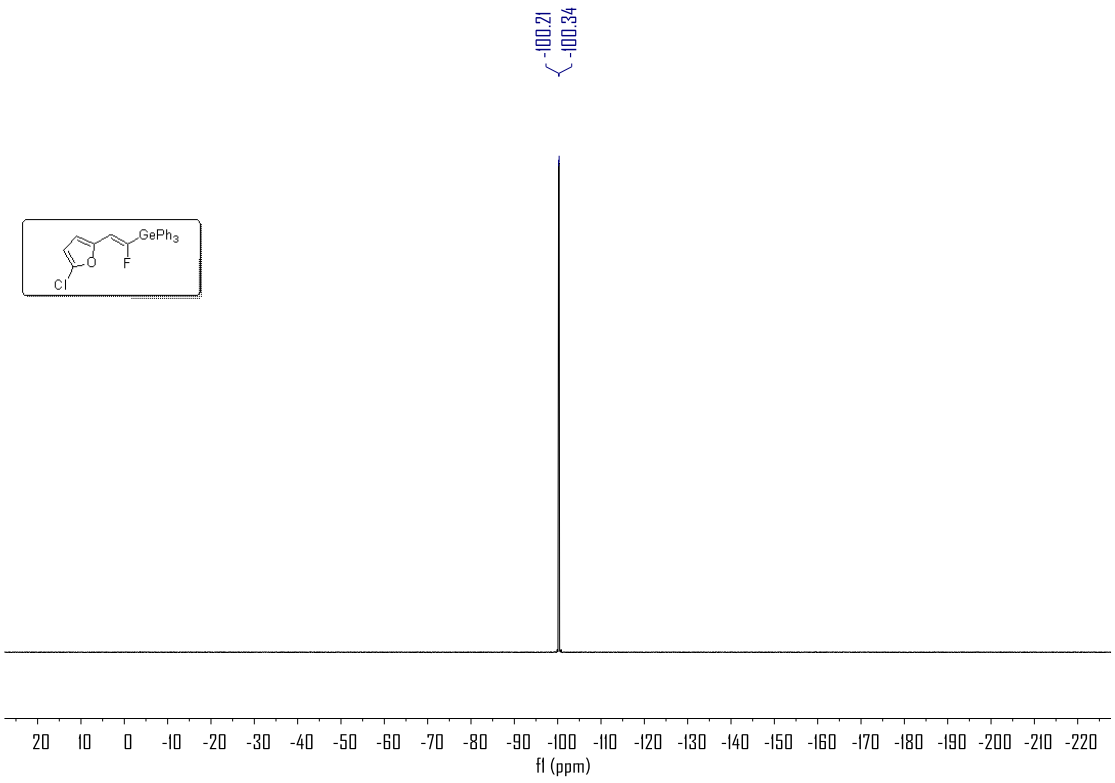
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.91 (d, *J* = 311.8 Hz), 147.93 (d, *J* = 5.5 Hz), 135.58 (d, *J* = 4.3 Hz), 135.22, 133.51 (d, *J* = 2.0 Hz), 129.96, 128.74, 113.47 (d, *J* = 11.3 Hz), 112.38, 108.50.

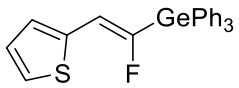
^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.27 (d, *J* = 48.5 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{18}ClFGeNaO$: 473.0134; found: 473.0141.




168.46
165.36
147.96
147.90
135.56
135.53
135.22
133.52
133.50
129.96
128.74
113.52
113.41
112.38
108.50
77.48
77.16
76.84
GePh3
O
F
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-100.21
-100.34
GePh3
O
F
Cl
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(1-fluoro-2-(thiophen-2-yl)vinyl)triphenylgermane

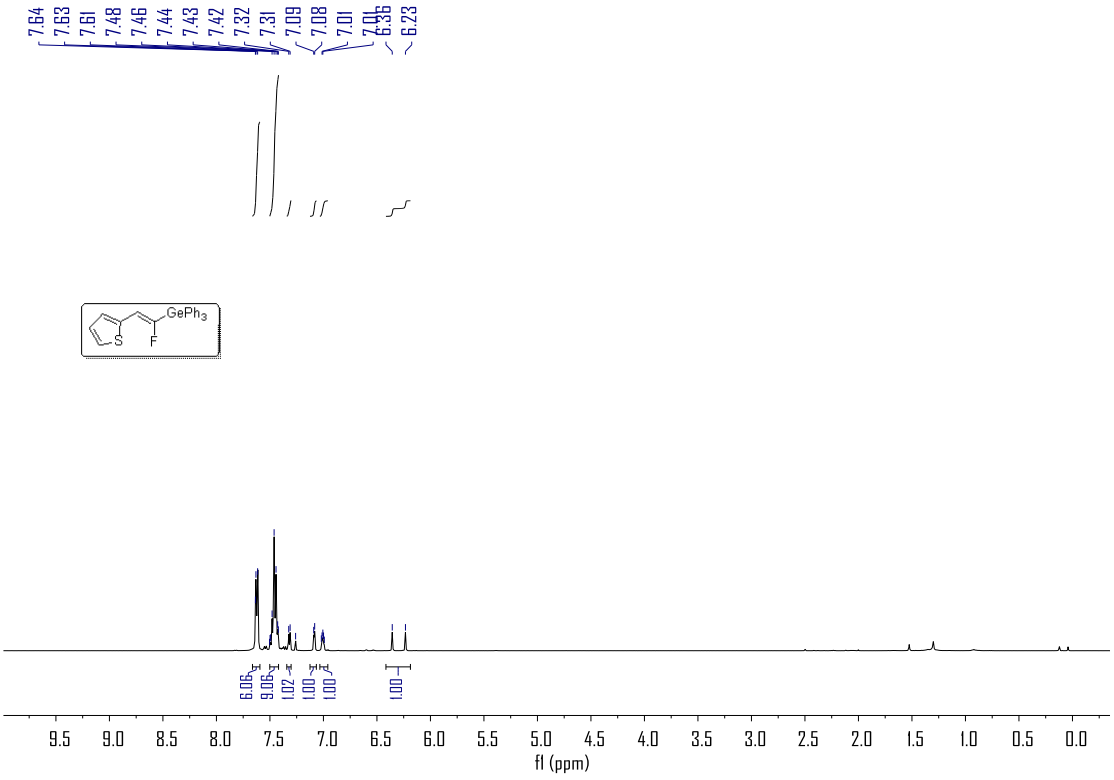
Following the general procedure (**3r**, pale-yellow solid, 27 mg, 63%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (3:1) as an eluent.

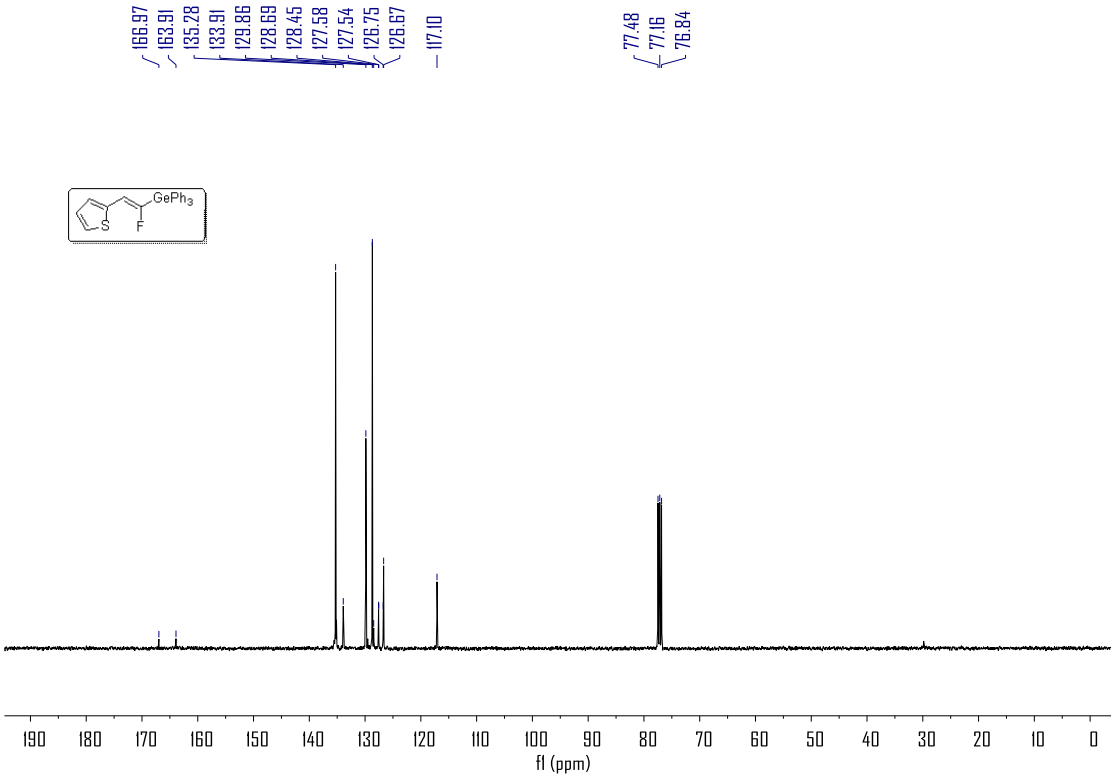
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 6.3 Hz, 6H), 7.45 (q, *J* = 6.8, 6.1 Hz, 9H), 7.32 (d, *J* = 5.2 Hz, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 7.01 (p, *J* = 2.8 Hz, 1H), 6.30 (d, *J* = 49.4 Hz, 1H).

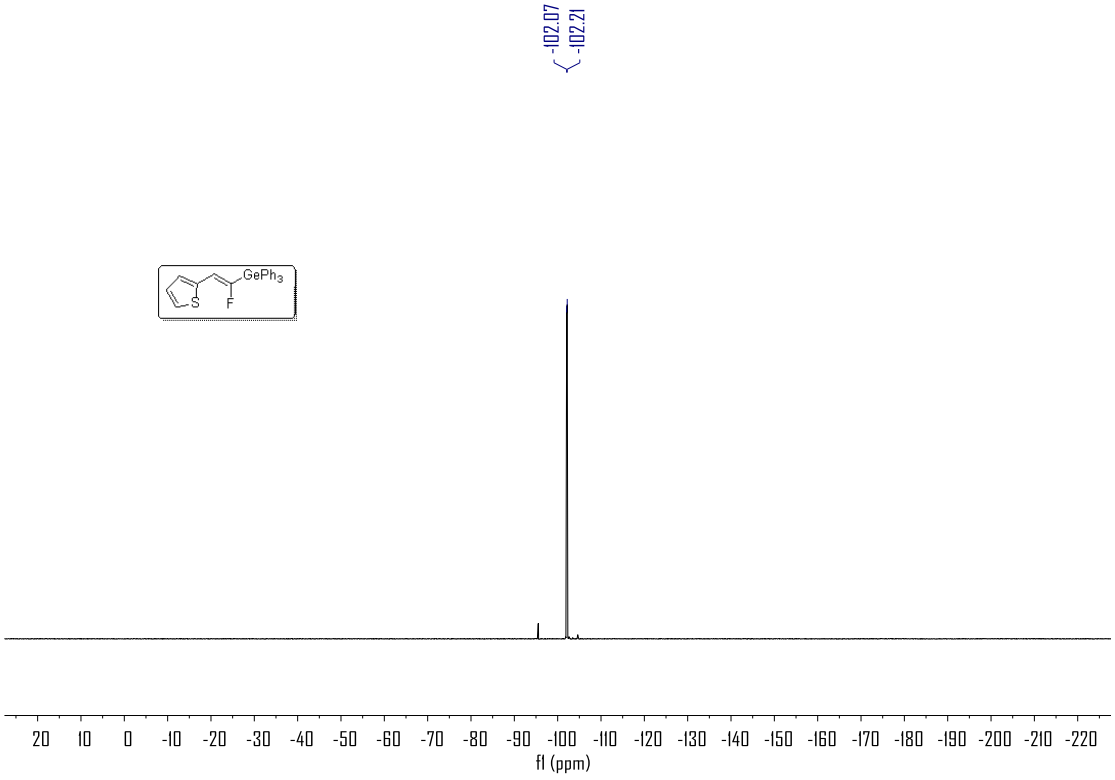
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.44 (d, *J* = 308.6 Hz), 135.28, 133.91, 129.86, 128.69, 128.45, 127.56 (d, *J* = 3.8 Hz), 126.75, 126.67, 117.10.

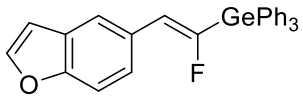
^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.14 (d, *J* = 49.5 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}FGeNaS$: 455.0295; found: 455.0290.




166.97
163.91
135.28
133.91
129.86
128.69
128.45
127.58
127.54
126.75
126.67
117.10
77.48
77.16
76.84
GePh3
S
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-102.07
-102.21
GePh3
S
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(2-(benzofuran-5-yl)-1-fluorovinyl)triphenylgermane

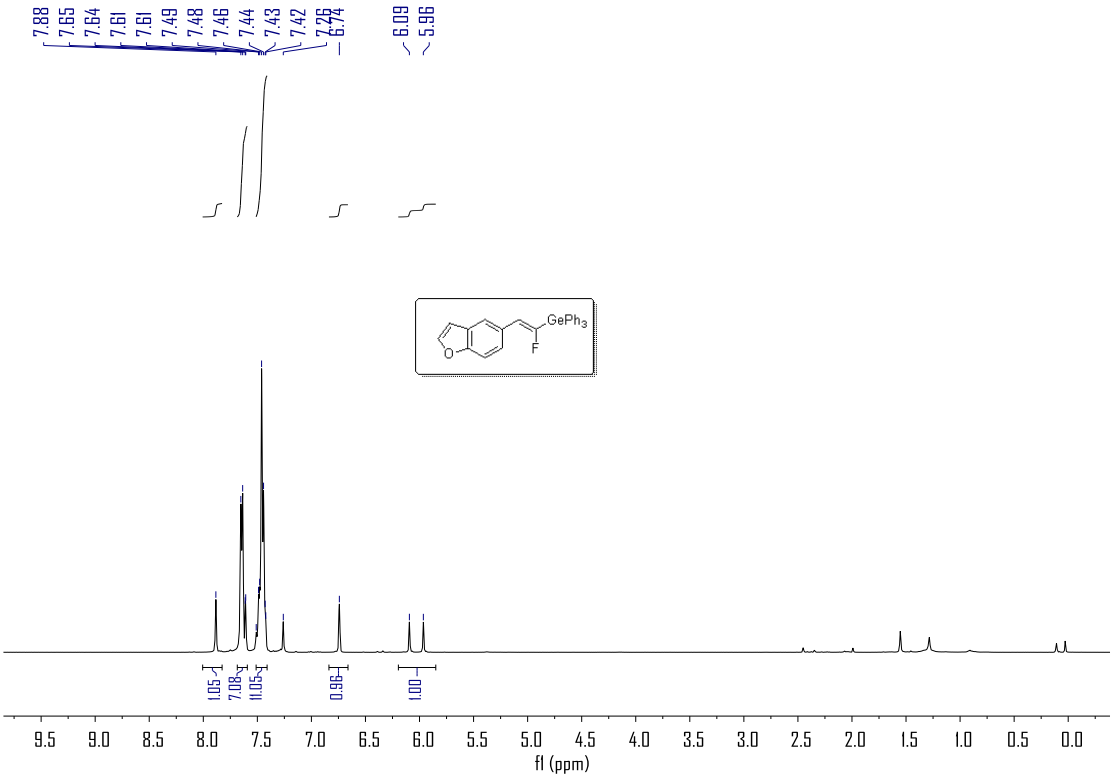
Following the general procedure (**3s**, pale-yellow solid, 30 mg, 65%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

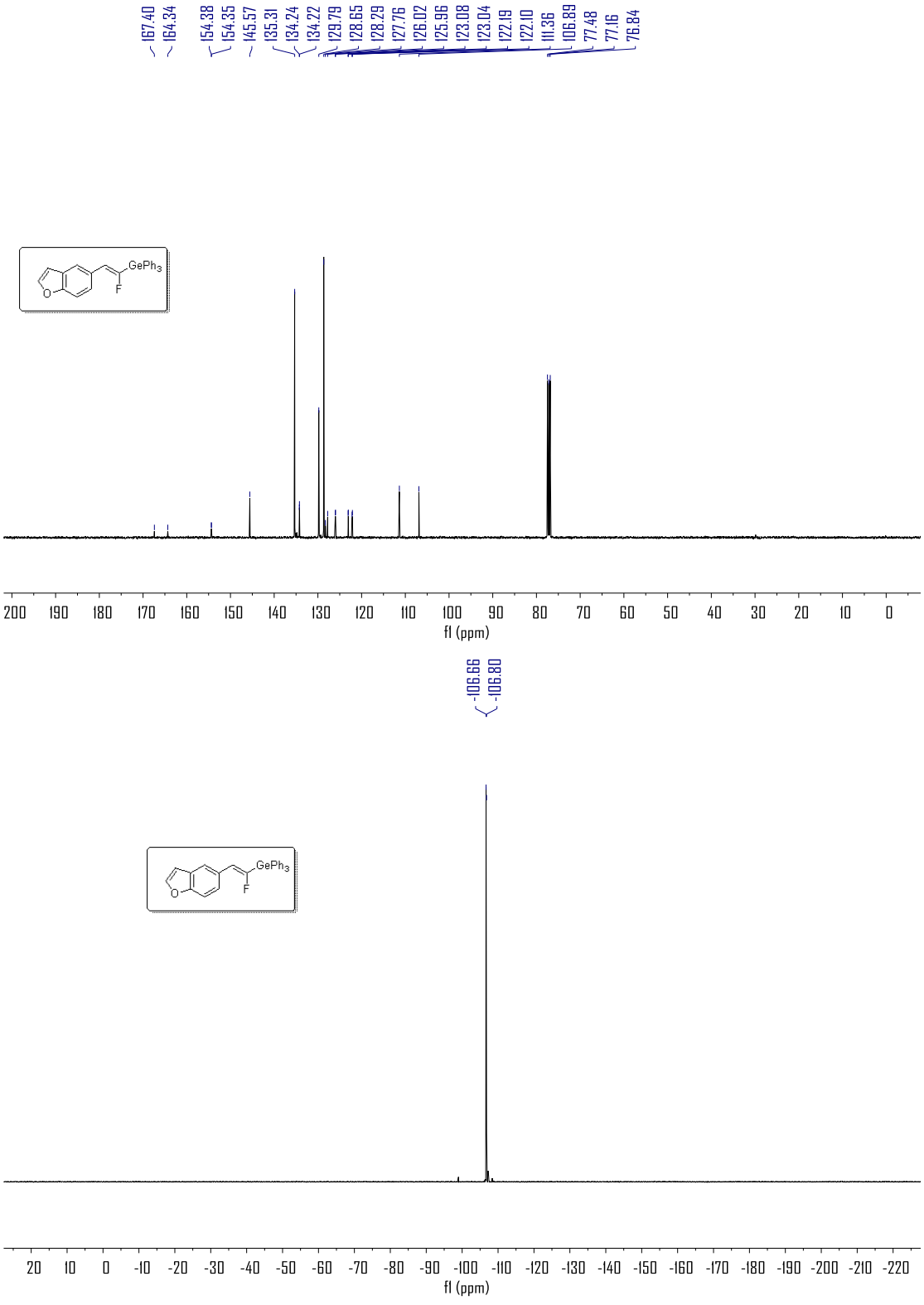
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.63 (dd, *J* = 13.7, 4.4 Hz, 7H), 7.53 – 7.41 (m, 11H), 6.74 (s, 1H), 6.03 (d, *J* = 51.7 Hz, 1H).

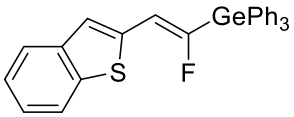
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.87 (d, *J* = 308.2 Hz), 154.36 (d, *J* = 2.9 Hz), 145.57, 135.31, 134.23 (d, *J* = 2.0 Hz), 129.79, 128.65, 128.29, 127.76, 125.99 (d, *J* = 6.7 Hz), 123.06 (d, *J* = 4.3 Hz), 122.14 (d, *J* = 8.7 Hz), 111.36, 106.89.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.73 (d, *J* = 51.5 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}FGeNaO$: 489.0680; found: 489.0687.




167.40
164.34
154.38
154.35
145.57
135.31
134.24
134.22
129.79
128.65
128.29
127.76
126.02
125.96
123.08
123.04
122.19
122.10
111.36
106.89
77.48
77.16
76.84
GePh3
F
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
-106.66
-106.80
GePh3
F
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(2-(benzo[b]thiophen-2-yl)-1-fluorovinyl)triphenylgermane

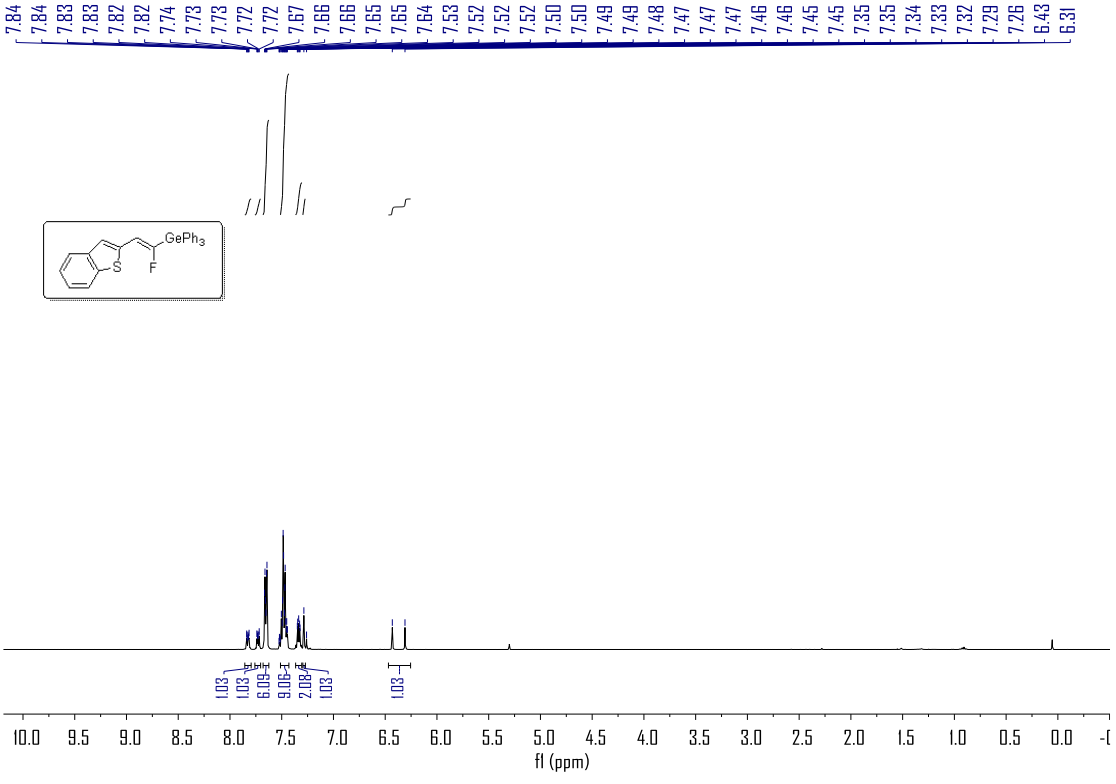
Following the general procedure (**3t**, pale-yellow solid, 27 mg, 56%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

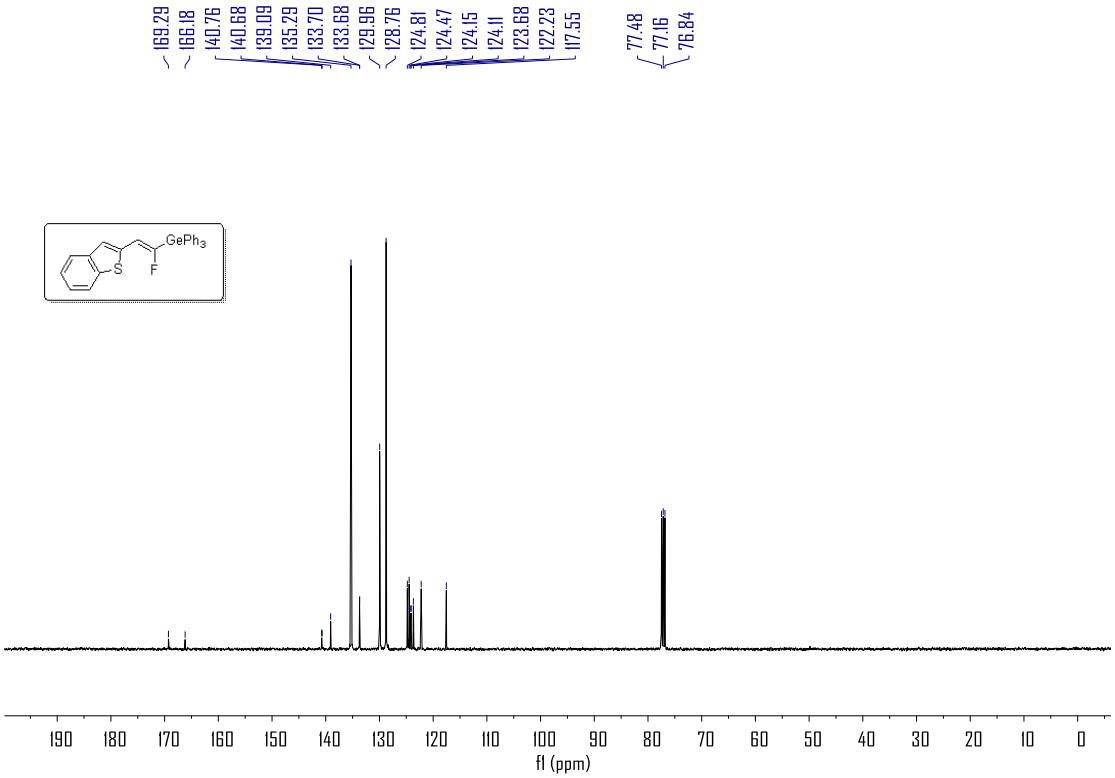
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.80 (m, 1H), 7.75 – 7.71 (m, 1H), 7.69 – 7.62 (m, 6H), 7.54 – 7.42 (m, 9H), 7.38 – 7.31 (m, 2H), 7.29 (s, 1H), 6.37 (d, *J* = 49.0 Hz, 1H).

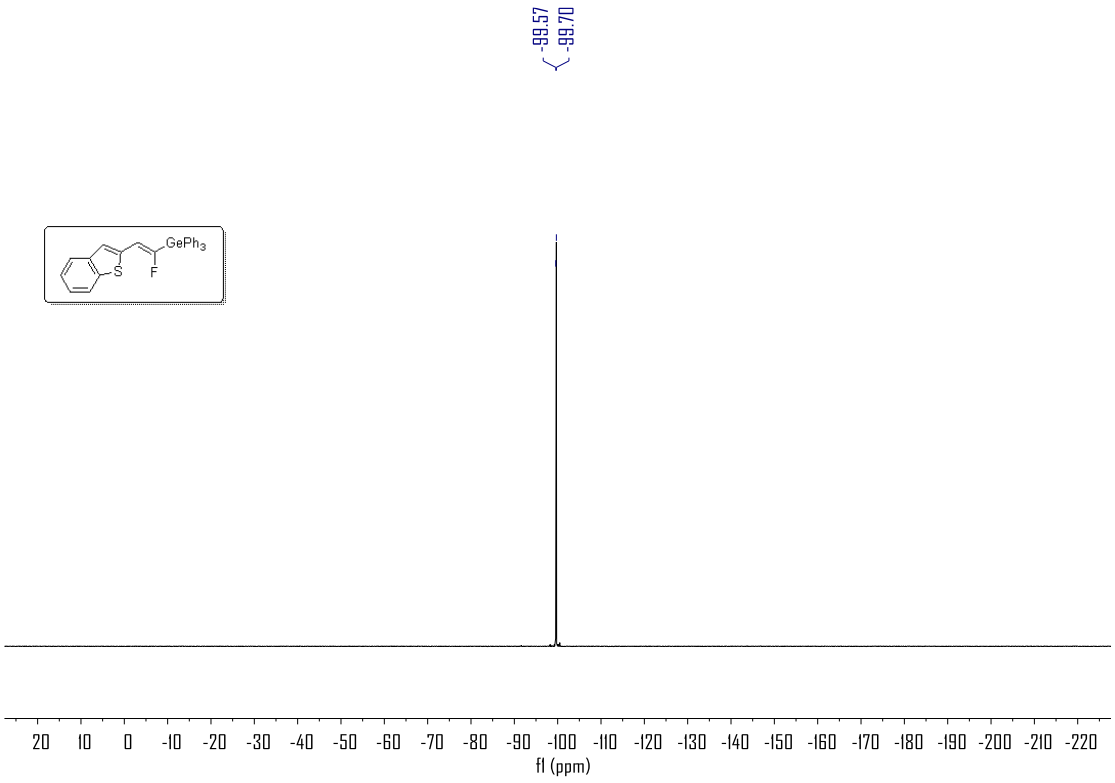
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.73 (d, *J* = 312.4 Hz), 140.72 (d, *J* = 7.9 Hz), 139.09, 135.29, 133.69 (d, *J* = 1.9 Hz), 129.96, 128.76, 124.81, 124.47, 124.13 (d, *J* = 4.5 Hz), 123.68, 123.67, 122.23, 117.55.

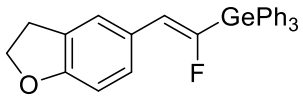
^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.63 (d, *J* = 49.6 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}FGeNaS$: 505.0452; found: 505.0455.




169.29
166.18
140.76
140.68
139.09
135.29
133.70
133.68
129.96
128.76
124.81
124.47
124.15
124.11
123.68
122.23
117.55
77.48
77.16
76.84
GePh3
S
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-99.57
-99.70
GePh3
S
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(2-(2,3-dihydrobenzofuran-5-yl)-1-fluorovinyl)triphenylgermane

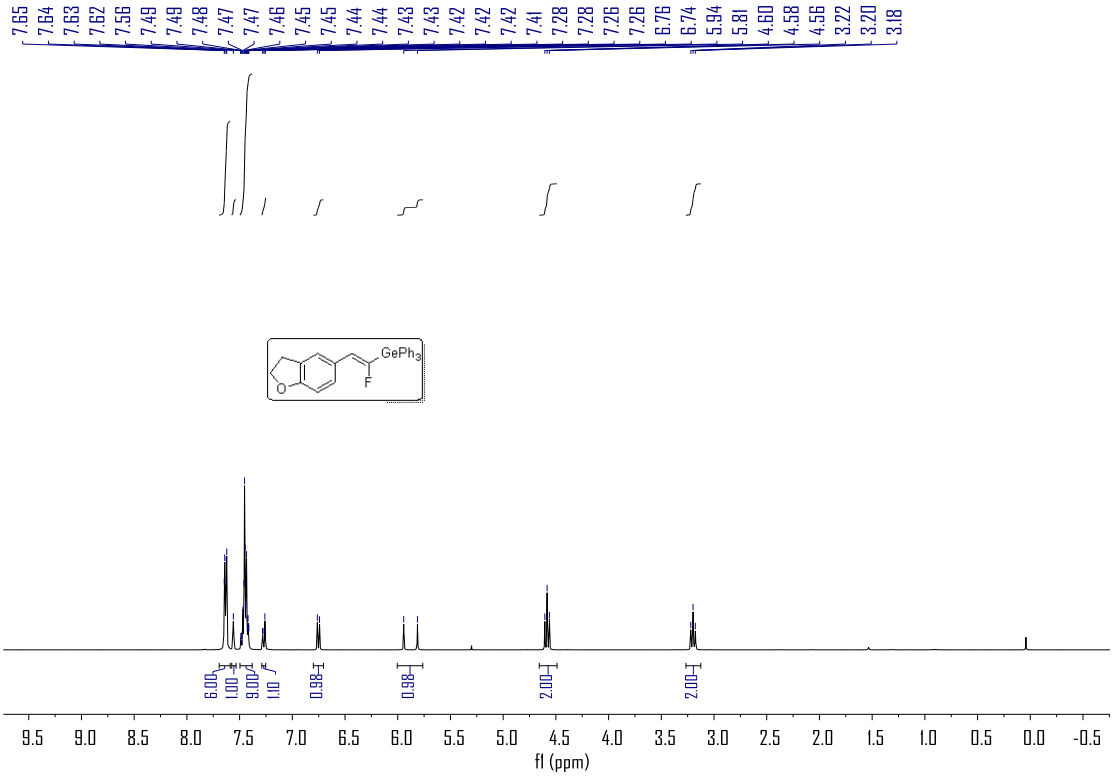
Following the general procedure (**3u**, pale-yellow solid, 27 mg, 58%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (15:1) as an eluent.

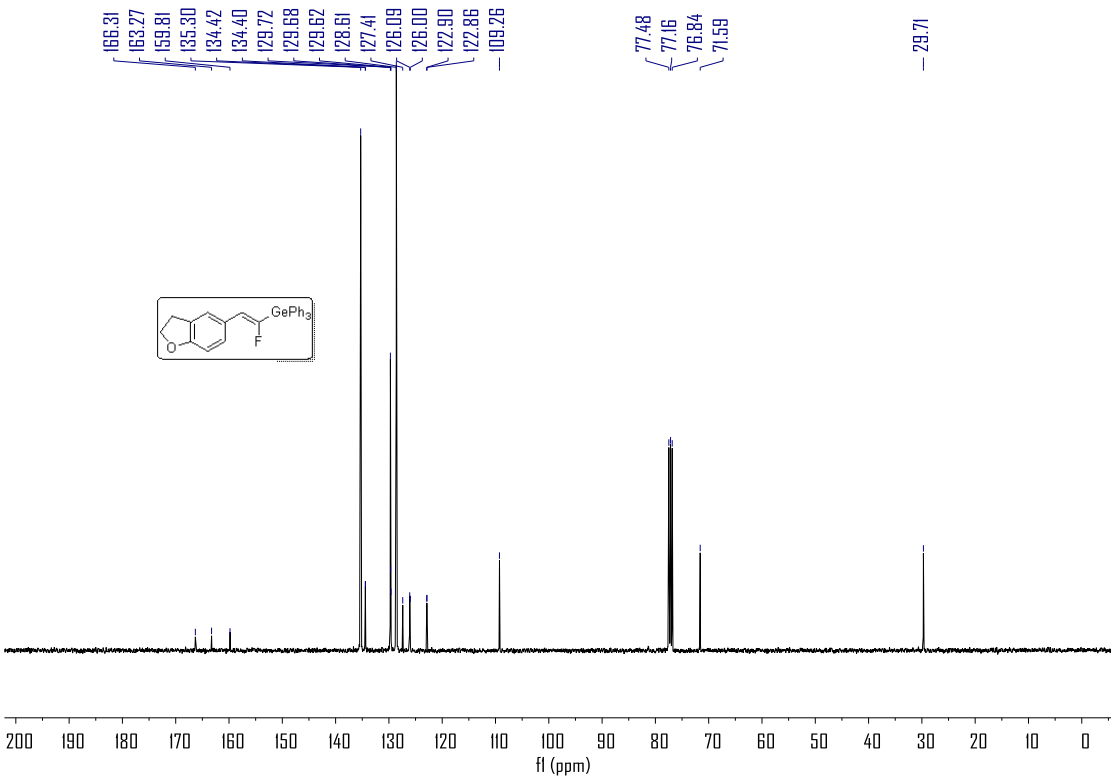
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 7.5, 1.9 Hz, 6H), 7.56 (s, 1H), 7.50 – 7.40 (m, 9H), 7.29 – 7.24 (m, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.88 (d, *J* = 52.2 Hz, 1H), 4.58 (t, *J* = 8.7 Hz, 2H), 3.20 (t, *J* = 8.6 Hz, 2H).

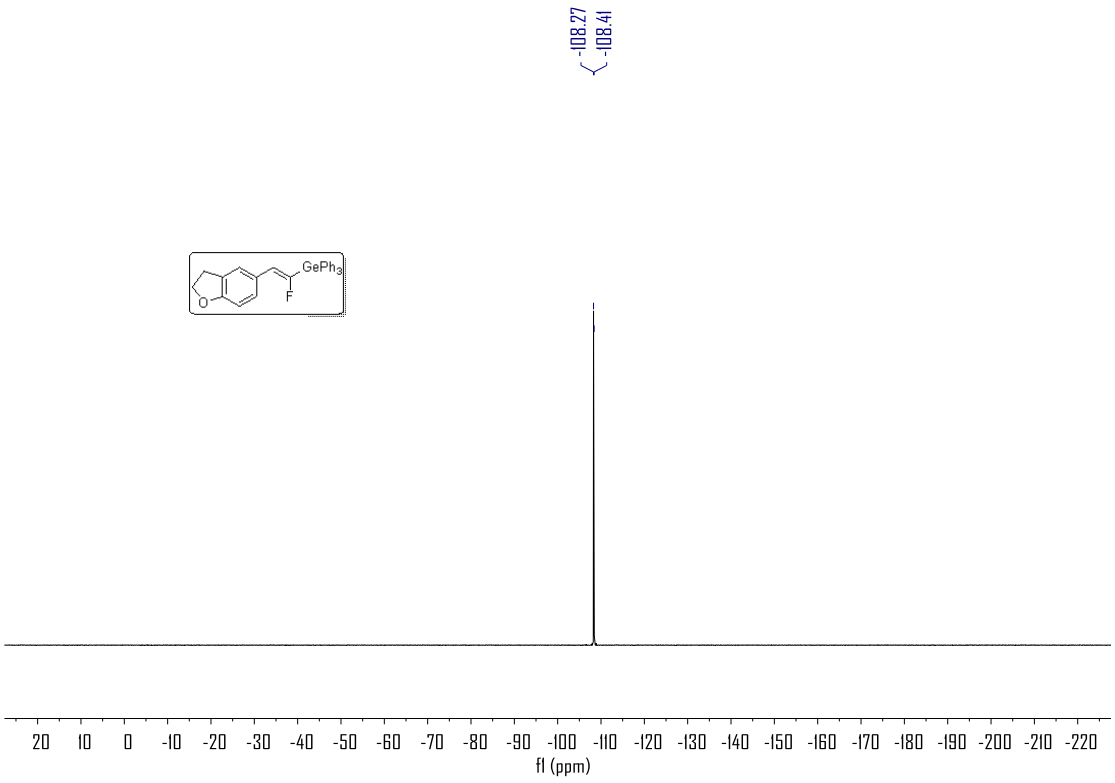
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.79 (d, *J* = 306.0 Hz), 159.81 (d, *J* = 2.9 Hz), 135.30, 134.41 (d, *J* = 2.0 Hz), 129.72, 129.68, 129.62, 128.61, 127.41, 126.04 (d, *J* = 9.9 Hz), 122.88 (d, *J* = 4.1 Hz), 109.26, 71.59, 29.71.

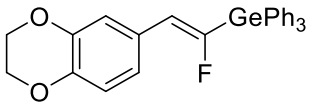
^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.34 (d, *J* = 52.4 Hz).

HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{28}H_{23}FGeNaO$: 491.0837; found: 491.0831.




166.31
163.27
159.81
135.30
134.42
134.40
129.72
129.68
129.62
128.61
127.41
126.09
126.00
122.90
122.86
109.26
77.48
77.16
76.84
71.59
29.71
GePh3
F
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-108.27
-108.41
GePh3
F
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1-fluorovinyl)triphenylgermane

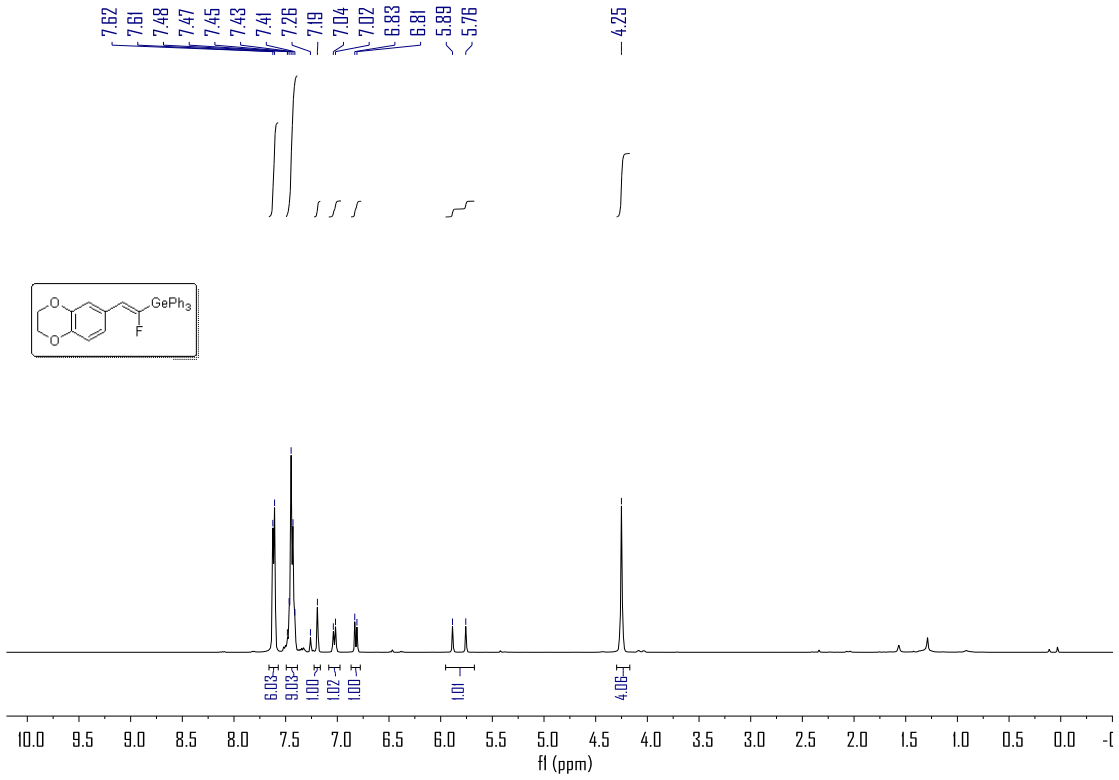
Following the general procedure (**3v**, pale-yellow solid, 32 mg, 66%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (10:1) as an eluent.

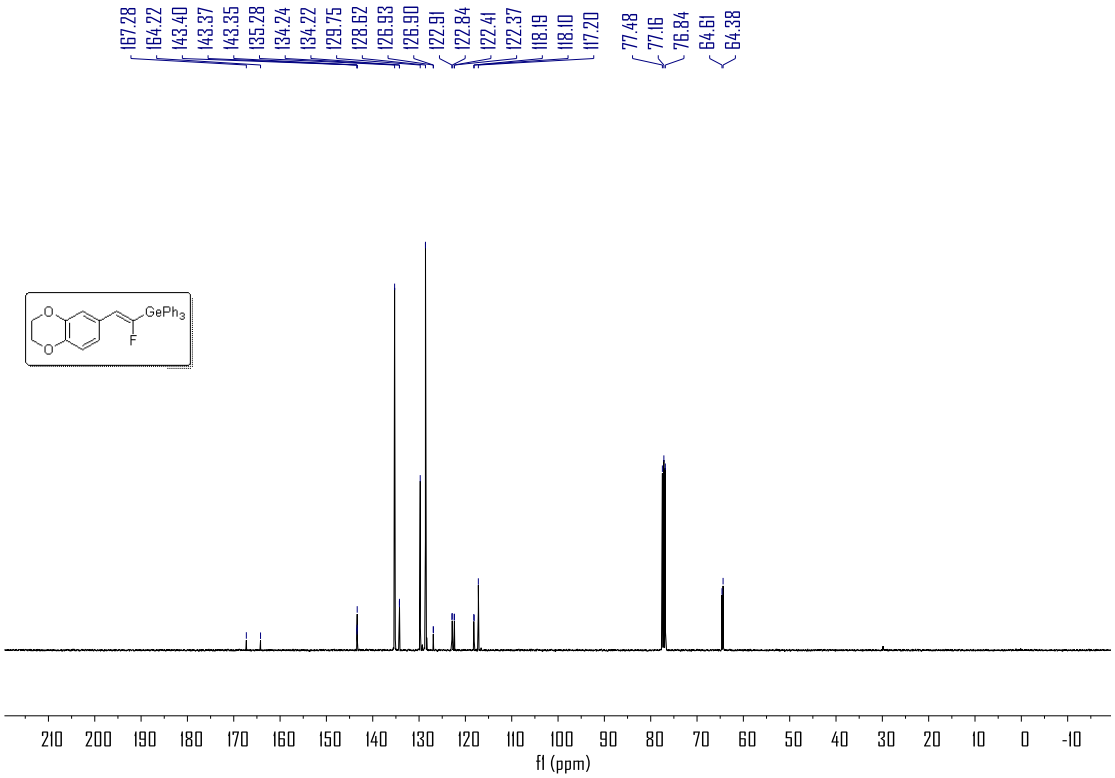
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 6.7 Hz, 6H), 7.49 – 7.38 (m, 9H), 7.19 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.82 (d, *J* = 51.3 Hz, 1H), 4.25 (s, 4H).

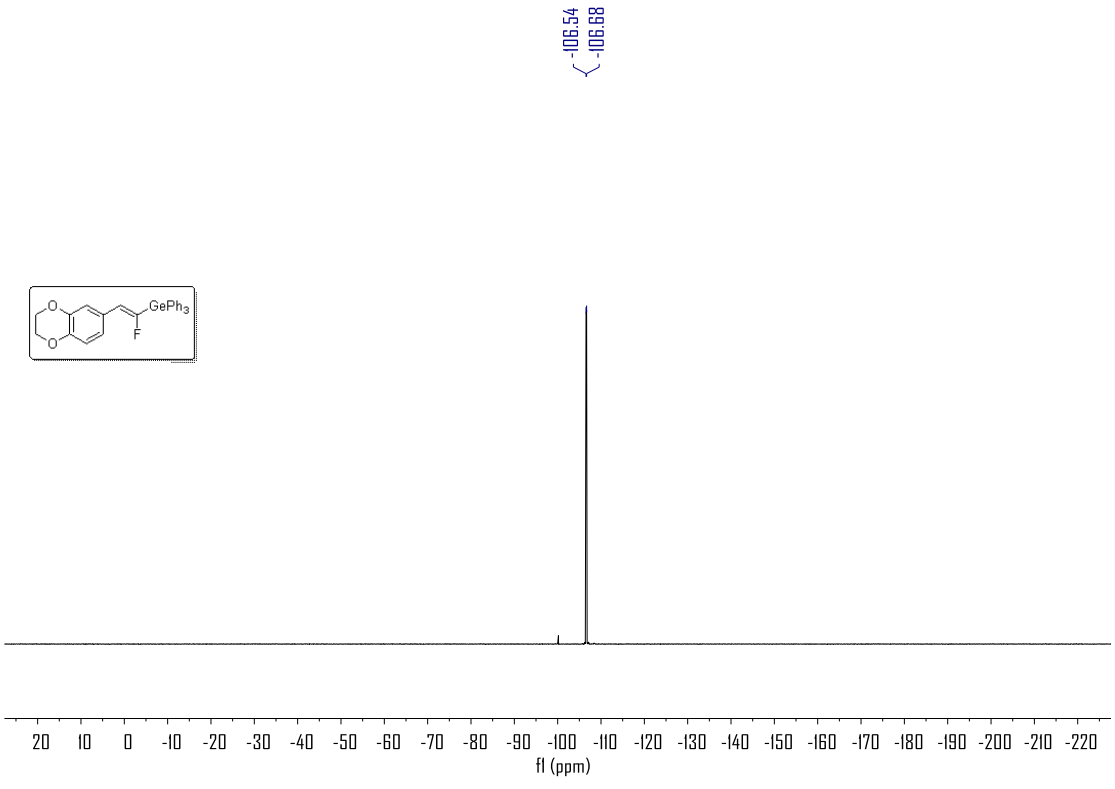
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.75 (d, *J* = 308.1 Hz), 143.39 (d, *J* = 2.7 Hz), 143.35, 135.28, 134.23 (d, *J* = 1.9 Hz), 129.75, 128.62, 126.92 (d, *J* = 2.7 Hz), 122.87 (d, *J* = 6.7 Hz), 122.39 (d, *J* = 4.1 Hz), 118.15 (d, *J* = 8.5 Hz), 117.20, 64.61, 64.38.

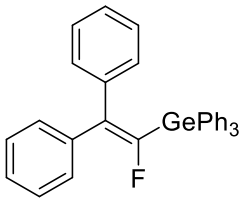
^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.61 (d, *J* = 51.4 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{23}FGeNaO_2$: 507.0786; found: 507.0778.




167.28
164.22
143.40
143.37
143.35
135.28
134.24
134.22
129.75
128.62
126.93
126.90
122.91
122.84
122.41
122.37
118.19
118.10
117.20
77.48
77.16
76.84
64.61
64.38
GePh3
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-106.54
-106.68
GePh3
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(1-fluoro-2,2-diphenylvinyl)triphenylgermane

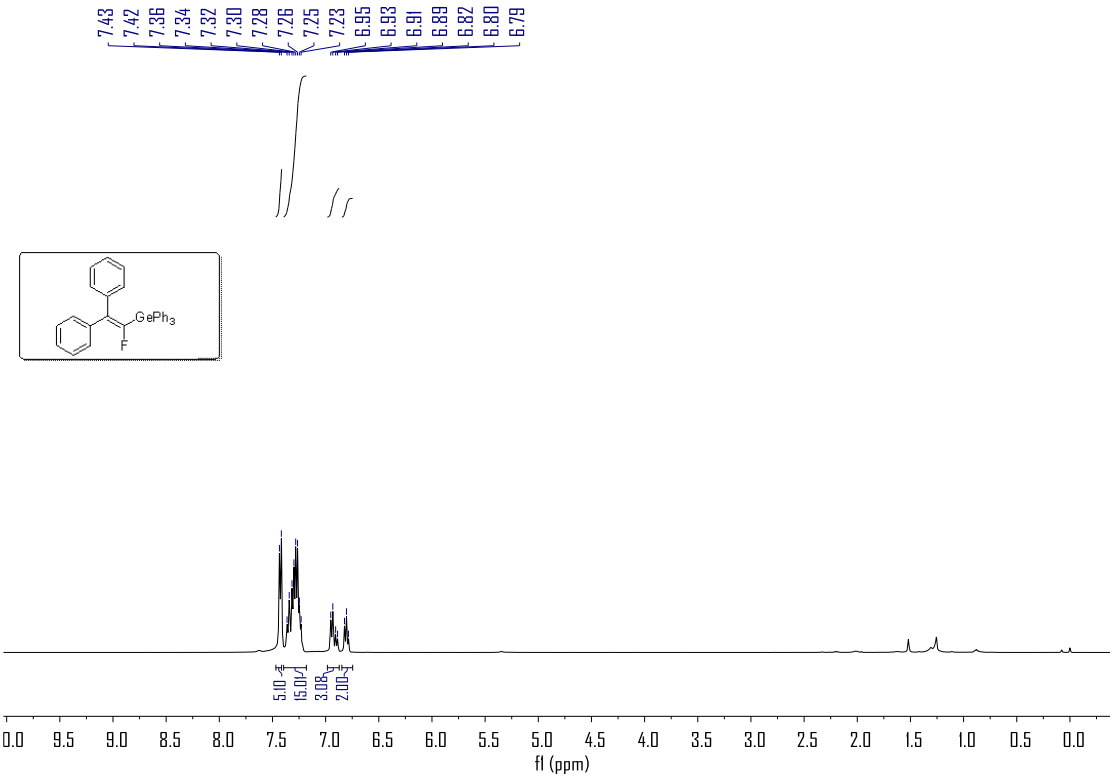
Following the general procedure (**3w**, pale-yellow solid, 19 mg, 39%). The residue was purified by silica gel-columun chromatography using PE/DCM (20:1) as an eluent.

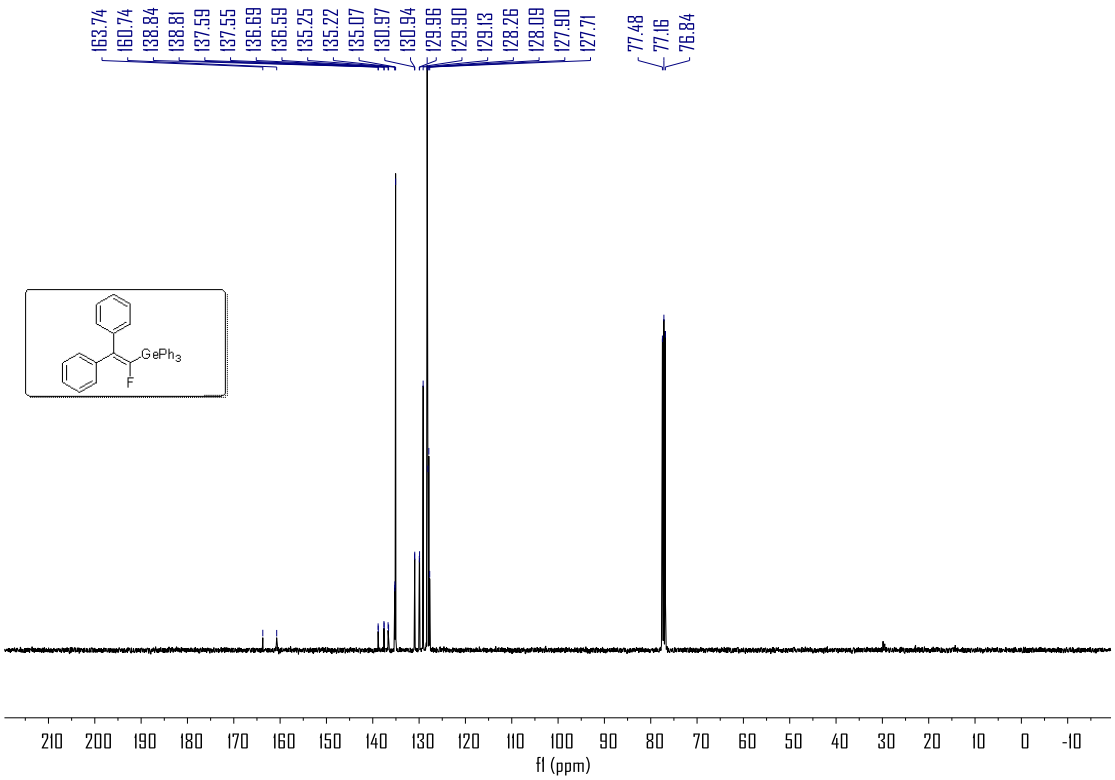
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.2 Hz, 5H), 7.38 – 7.22 (m, 15H), 6.92 (dd, *J* = 18.1, 7.5 Hz, 3H), 6.80 (t, *J* = 7.5 Hz, 2H).

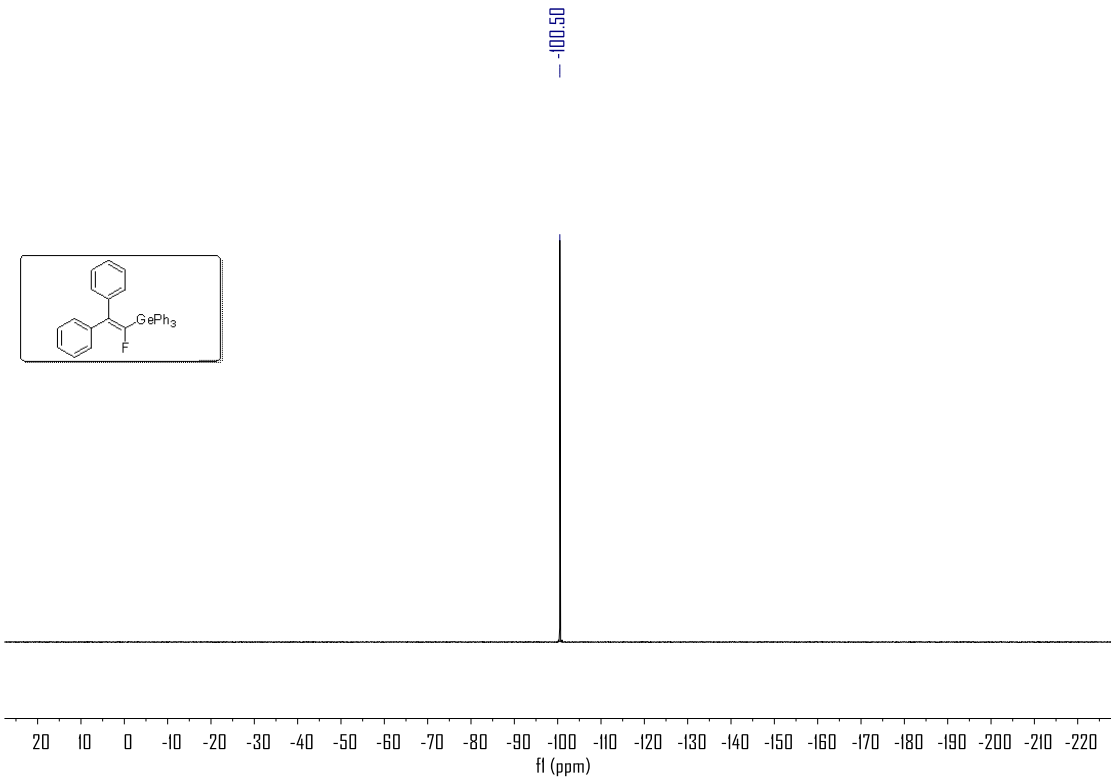
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.24 (d, *J* = 301.7 Hz), 138.83 (d, *J* = 3.6 Hz), 137.57 (d, *J* = 3.7 Hz), 136.64 (d, *J* = 10.7 Hz), 135.24 (d, *J* = 2.7 Hz), 135.07, 130.96 (d, *J* = 3.0 Hz), 129.96, 129.90, 129.13, 128.26, 128.09, 127.90, 127.71.

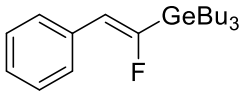
^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.50.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}FGeNa$: 525.1044; found: 525.1040.




163.74
160.74
138.84
138.81
137.59
137.55
136.69
136.59
135.25
135.22
135.07
130.97
130.94
129.96
129.90
129.13
128.26
128.09
127.90
127.71
77.48
77.16
76.84
GePh3
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-100.50
GePh3
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(E)-tributyl(1-fluoro-2-phenylvinyl)germane

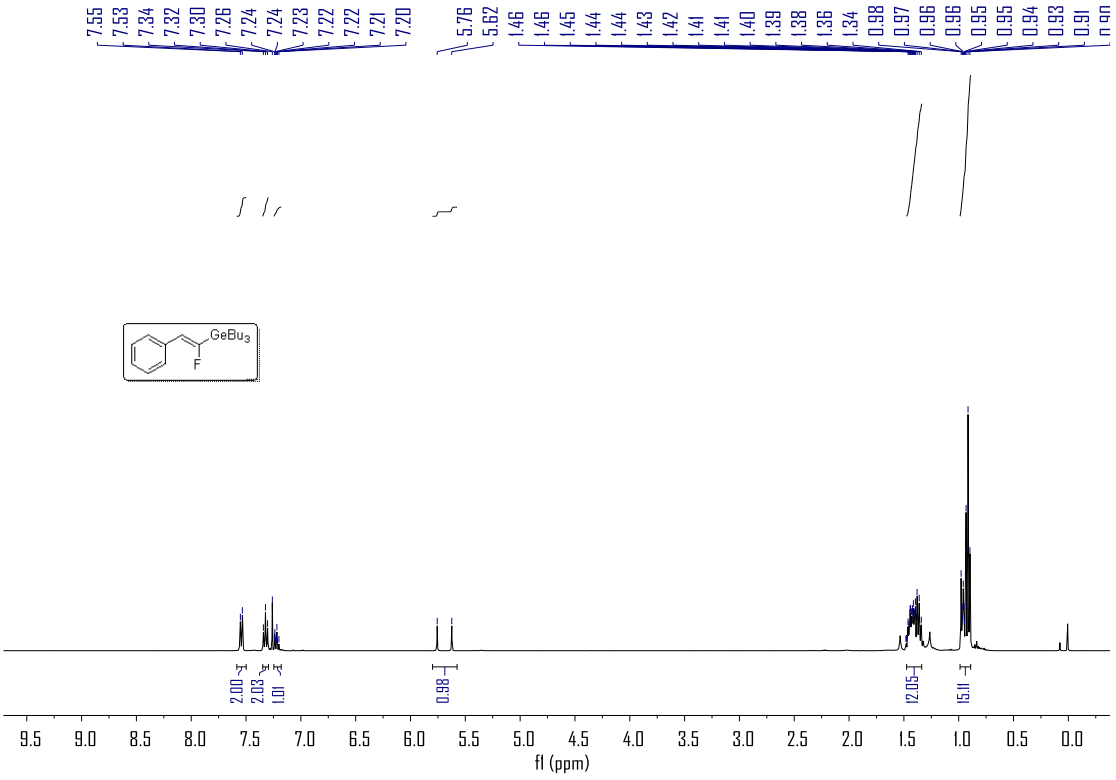
Following the general procedure (**3x**, pale-yellow liquid, 9 mg, 26%, E/Z > 30:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

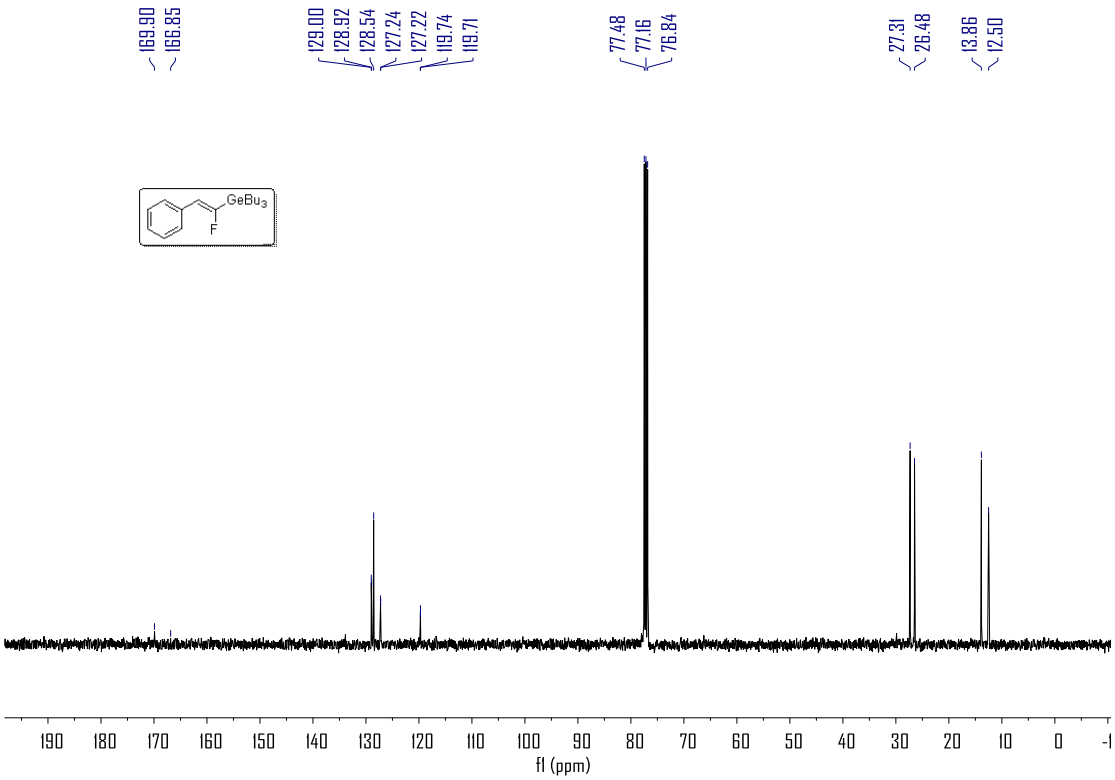
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.19 (m, 1H), 5.69 (d, *J* = 53.2 Hz, 1H), 1.48 – 1.32 (m, 12H), 1.00 – 0.87 (m, 15H).

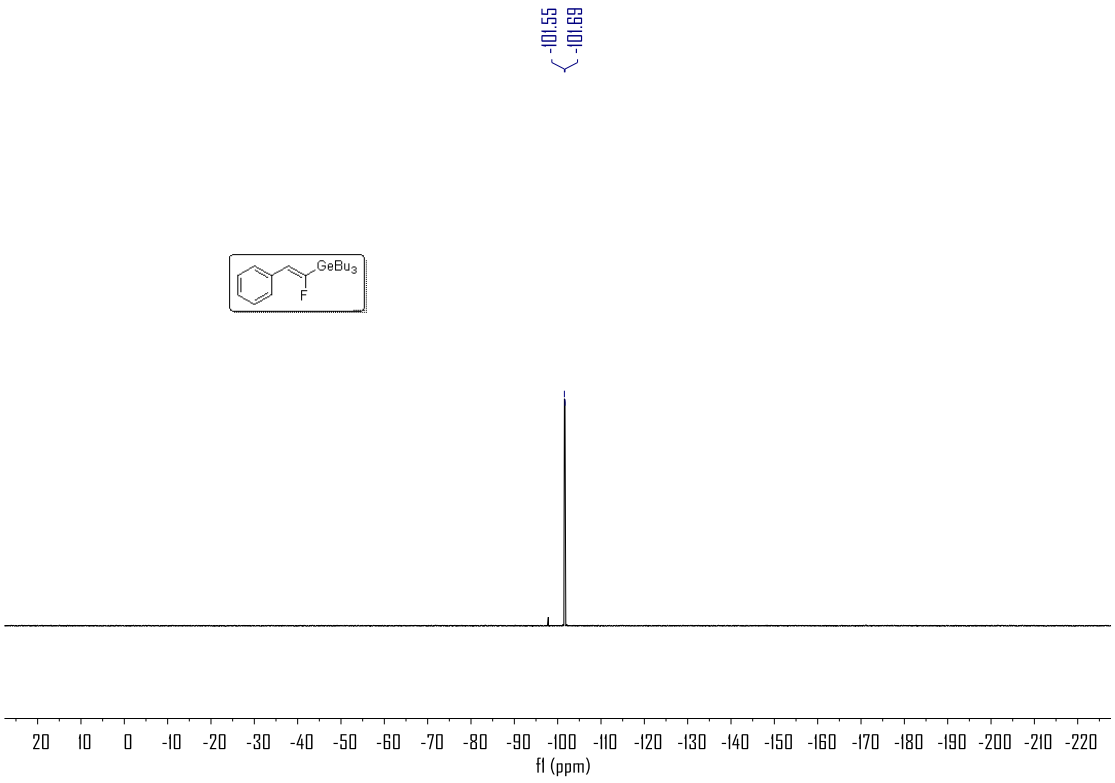
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.38 (d, *J* = 306.6 Hz), 129.00, 128.92, 128.54, 127.23 (d, *J* = 2.3 Hz), 119.72 (d, *J* = 3.7 Hz), 27.31, 26.48, 13.86, 12.50.

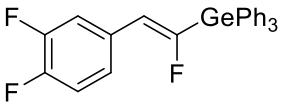
^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.62 (d, *J* = 53.0 Hz).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{33}FGe$: 366.1778; found: 366.1781.




169.90
166.85
129.00
128.92
128.54
127.24
127.22
119.74
119.71
77.48
77.16
76.84
27.31
26.48
13.86
12.50
GeBu3
F
f1 (ppm)


-101.55
-101.69
GeBu3
F
f1 (ppm)



(E)-(2-(3,4-difluorophenyl)-1-fluorovinyl)triphenylgermane

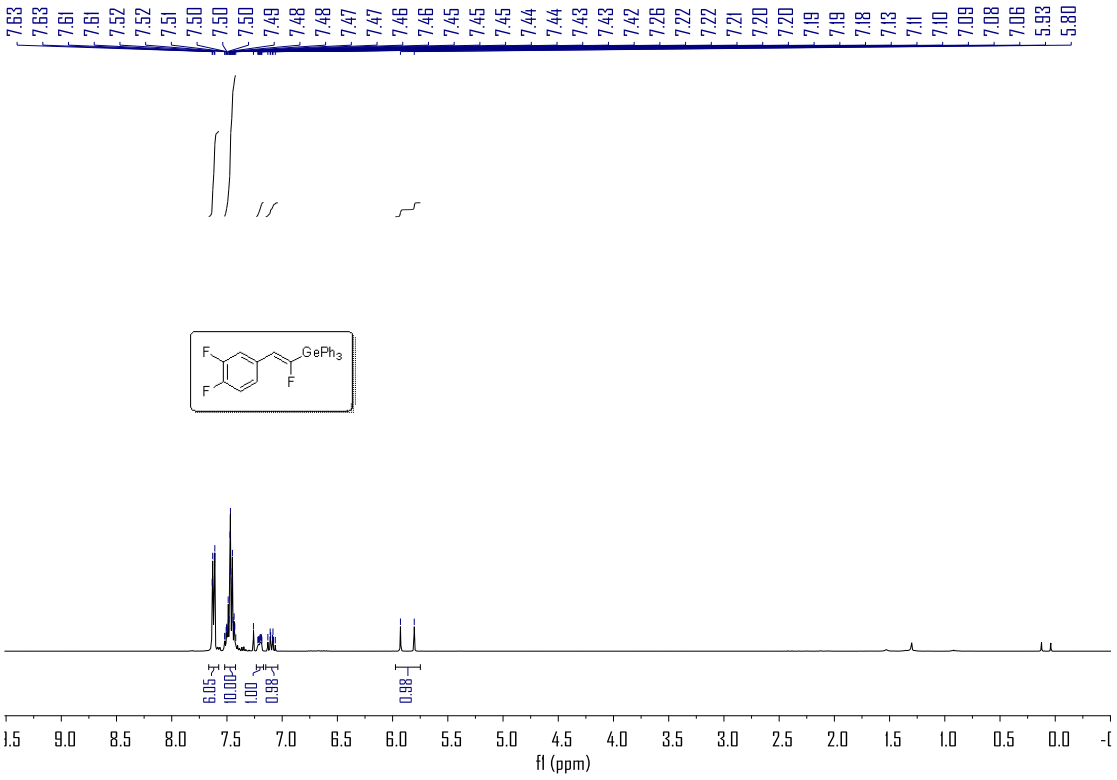
Following the general procedure (**3y**, pale-yellow solid, 28 mg, 60%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

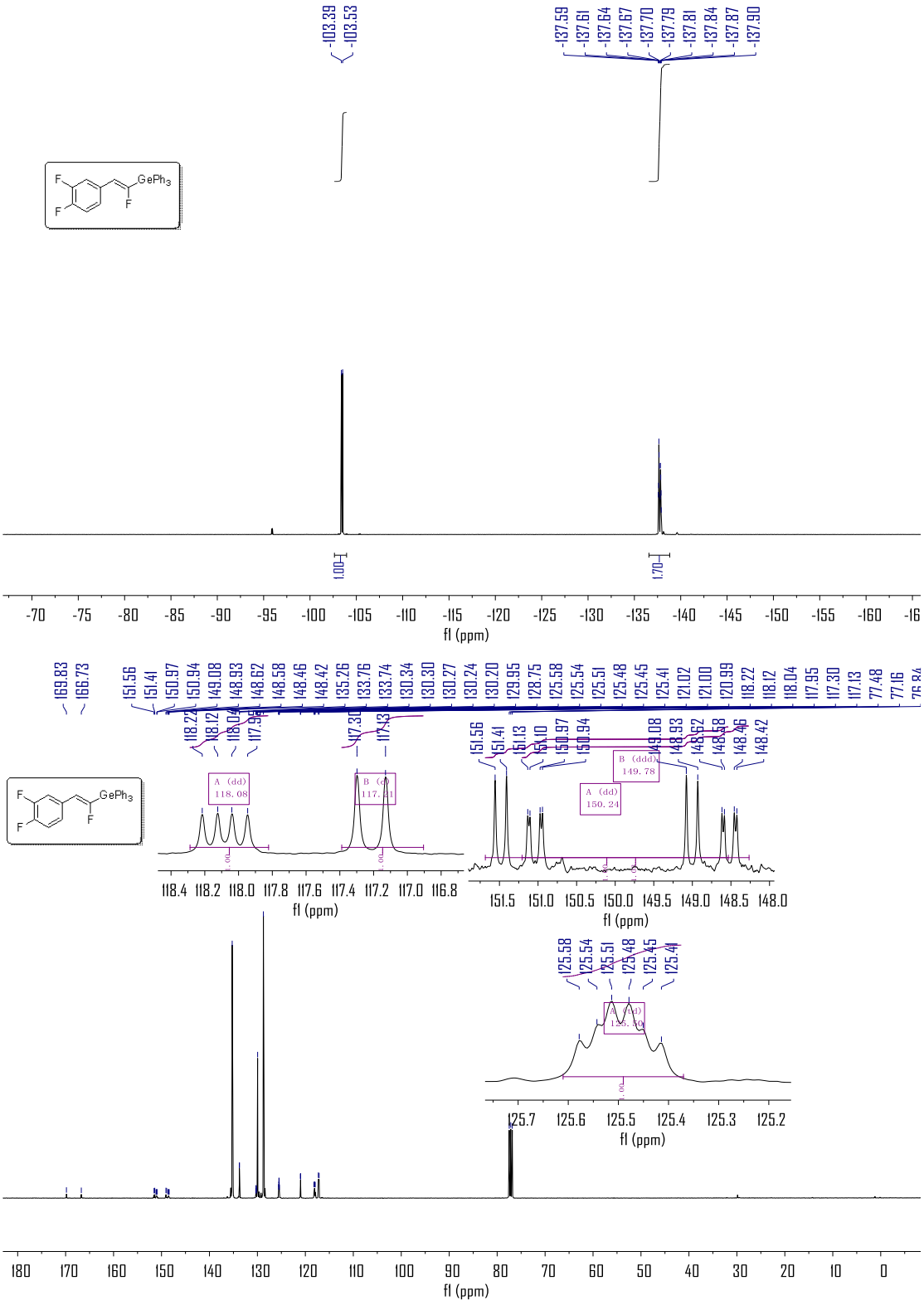
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 7.6, 1.8 Hz, 6H), 7.53 – 7.41 (m, 10H), 7.20 (ddd, *J* = 7.9, 4.0, 1.8 Hz, 1H), 7.10 (dt, *J* = 10.1, 8.4 Hz, 1H), 5.87 (d, *J* = 50.0 Hz, 1H).

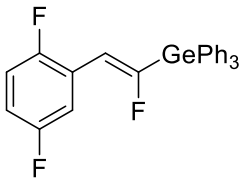
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.46 (d, *J* = 49.9 Hz, 1F), -137.74 (ddt, *J* = 75.5, 20.2, 9.5 Hz, 2F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.28 (d, *J* = 312.1 Hz), 150.24 (dd, *J* = 249.3, 14.9 Hz), 149.78 (ddd, *J* = 253.4, 16.2, 3.1 Hz), 135.26, 133.75 (d, *J* = 2.0 Hz), 130.27 (dt, *J* = 7.1, 3.8 Hz), 129.95, 128.75, 125.50 (td, *J* = 6.5, 3.6 Hz), 121.00 (t, *J* = 2.0 Hz), 118.08 (dd, *J* = 17.7, 9.3 Hz), 117.21 (d, *J* = 17.0 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{19}F_3GeNa$: 485.0543; found: 485.0540.




-103.39
-103.53
-137.59
-137.61
-137.64
-137.67
-137.70
-137.79
-137.81
-137.84
-137.87
-137.90
F
F
GePh3
F
1.00
1.70
f1 (ppm)
169.83
166.73
151.56
151.41
150.97
150.94
149.08
148.93
148.62
148.58
148.46
148.42
135.26
133.76
133.74
130.34
130.30
130.27
130.24
130.20
129.95
128.75
125.58
125.54
125.51
125.48
125.45
125.41
121.02
121.00
120.99
118.22
118.12
118.04
117.95
117.30
117.13
77.48
77.16
118.27
118.12
118.04
117.98
117.30
117.13
A (dd)
118.08
B (dd)
117.21
151.56
151.41
151.13
151.10
150.97
150.94
149.08
148.93
148.62
148.58
148.46
148.42
B (ddd)
149.78
A (dd)
150.24
125.58
125.54
125.51
125.48
125.45
125.41
A (dd)
125.50
f1 (ppm)



(E)-(2-(2,5-difluorophenyl)-1-fluorovinyl)triphenylgermane

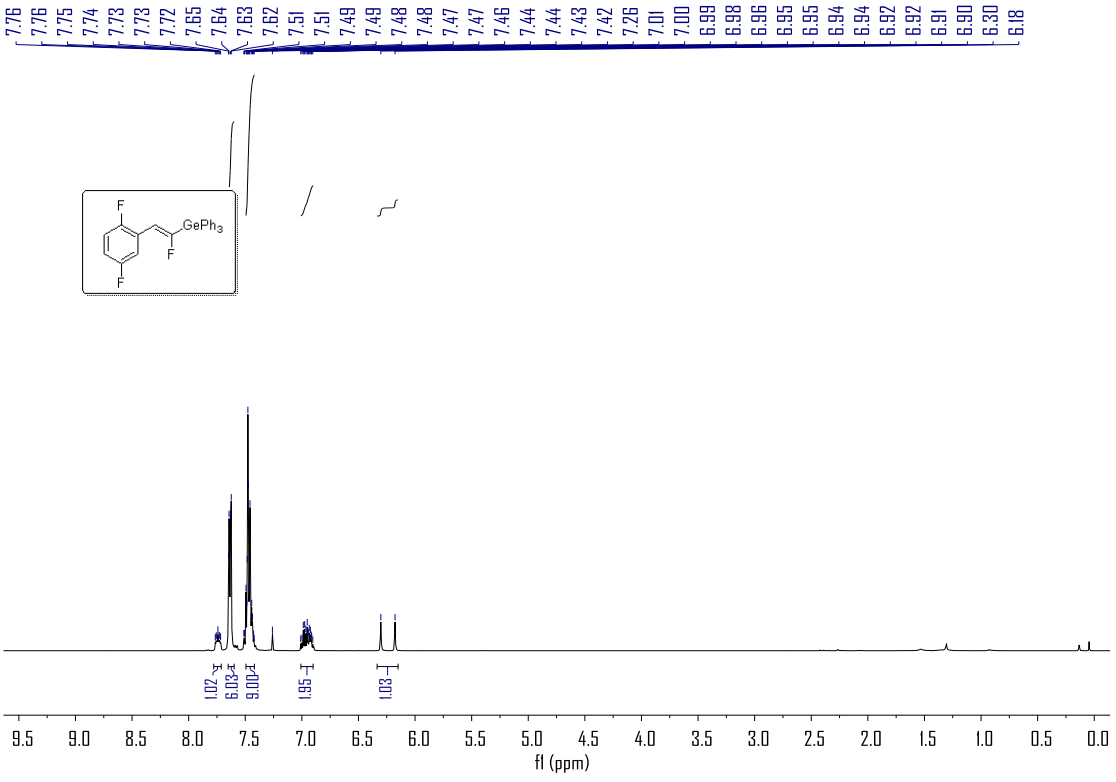
Following the general procedure (**3z**, pale-yellow solid, 23 mg, 51%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

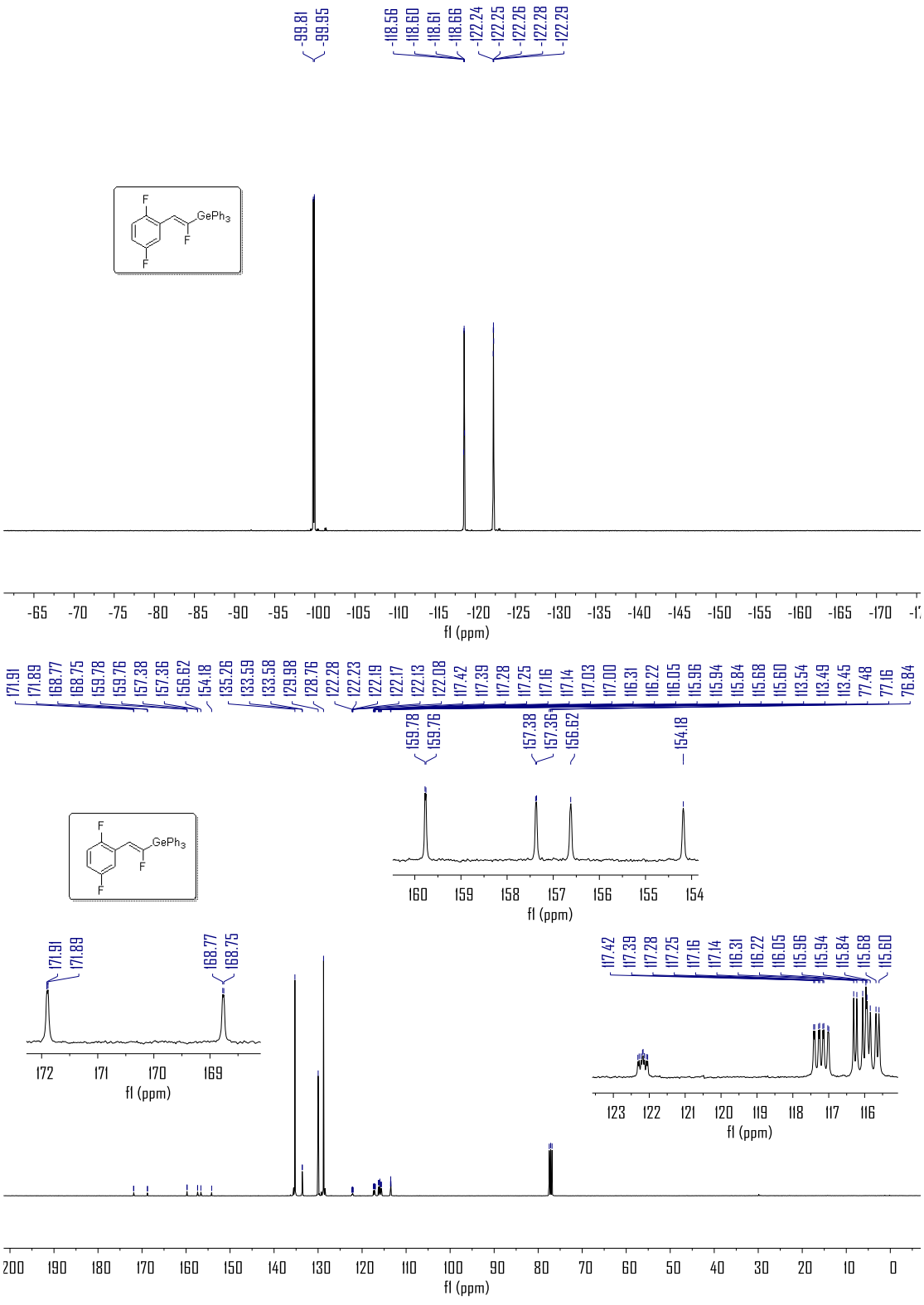
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (ddd, *J* = 9.5, 5.9, 3.0 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.9 Hz, 6H), 7.52 – 7.40 (m, 9H), 7.01 – 6.89 (m, 2H), 6.24 (d, *J* = 50.2 Hz, 1H).

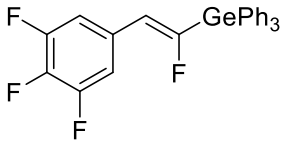
^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.88 (d, *J* = 50.0 Hz), -118.61 (q, *J* = 16.1 Hz), -122.26 (dt, *J* = 10.6, 4.7 Hz).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.33 (dd, *J* = 317.1, 2.0 Hz), 158.57 (dd, *J* = 242.4, 2.0 Hz), 155.40 (d, *J* = 245.6 Hz), 135.26 , 133.59 (d, *J* = 1.0 Hz), 129.98, 128.76, 122.18 (ddd, *J* = 14.4, 9.1, 3.5 Hz), 117.21 (ddd, *J* = 25.6, 13.8, 2.7 Hz), 116.14 (dd, *J* = 25.3, 8.9 Hz), 115.77 (dd, *J* = 24.9, 8.9 Hz), 113.49 (t, *J* = 5.0).

HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{26}H_{19}F_3GeNa$: 485.0543; found: 485.0538.




-99.81
-99.95
-118.56
-118.60
-118.61
-118.66
-122.24
-122.25
-122.26
-122.28
-122.29
F
GePh3
F
F
f1 (ppm)
171.91
171.89
168.77
168.75
159.78
159.76
157.38
157.36
156.62
154.18
135.26
133.59
133.58
129.98
128.76
122.28
122.23
122.19
122.17
122.13
122.08
117.42
117.39
117.28
117.25
117.16
117.14
117.03
117.00
116.31
116.22
116.05
115.96
115.94
115.84
115.68
115.60
113.54
113.49
113.45
77.48
77.16
76.84
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)



(E)-(1-fluoro-2-(3,4,5-trifluorophenyl)vinyl)triphenylgermane

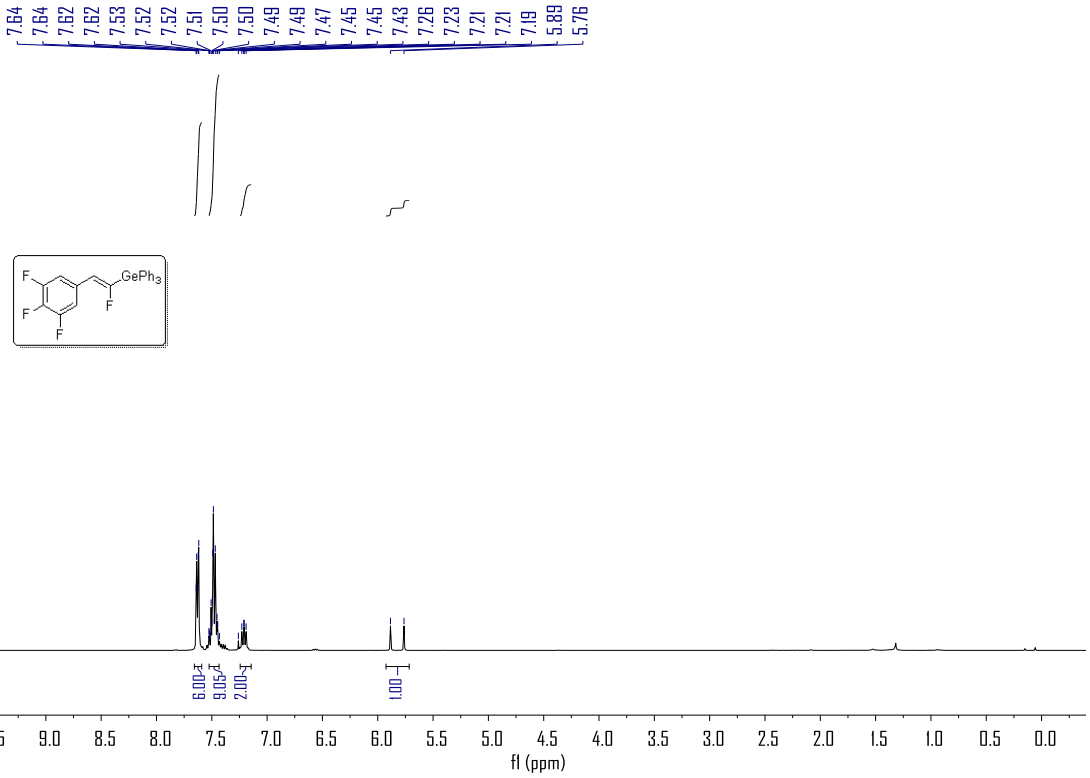
Following the general procedure (**3aa**, pale-yellow solid, 23 mg, 48%, E/Z > 50:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

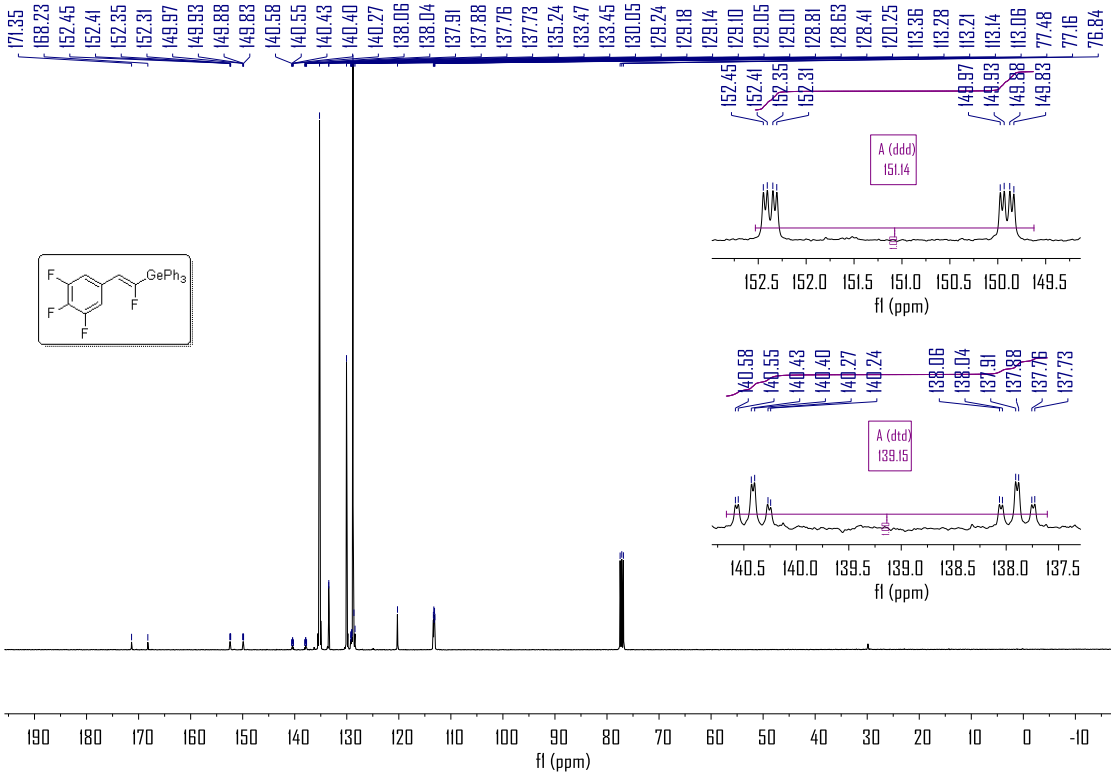
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.57 (m, 6H), 7.53 – 7.42 (m, 9H), 7.21 (dd, *J* = 8.7, 6.7 Hz, 2H), 5.82 (d, *J* = 48.9 Hz, 1H).

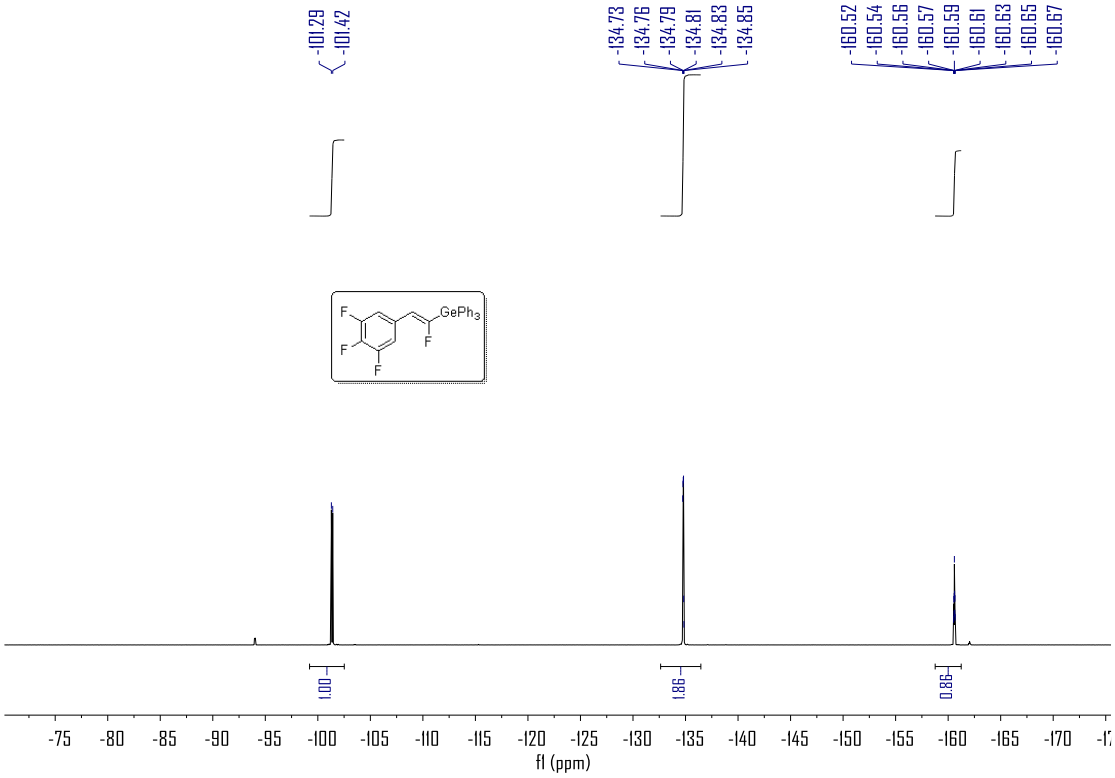
^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.35 (d, *J* = 48.9 Hz, 1F), -134.77 (dd, *J* = 20.6, 9.0 Hz, 2F), -160.59 (tt, *J* = 20.4, 7.0 Hz, 1F).

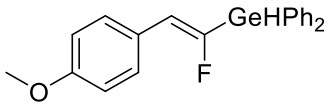
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.79 (d, *J* = 316.1 Hz), 151.14 (ddd, *J* = 249.0, 10.1, 4.2 Hz), 139.15 (dtd, *J* = 253.2, 15.4, 2.8 Hz), 135.24, 133.46 (d, *J* = 2.0 Hz), 130.05, 129.33 – 128.56 (m), 128.81, 120.25, 113.63 – 112.97 (m).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{18}F_4GeNa$: 503.0449; found: 503.0445.




171.35
168.23
152.45
152.41
152.35
152.31
149.97
149.93
149.88
149.83
140.58
140.55
140.43
140.40
140.27
138.06
138.04
137.91
137.88
137.76
137.73
135.24
133.47
133.45
130.05
129.24
129.18
129.14
129.10
129.05
129.01
128.81
128.63
128.41
120.25
113.36
113.28
113.21
113.14
113.06
77.48
77.16
76.84
A (ddd)
151.14
152.5 152.0 151.5 151.0 150.5 150.0 149.5
f1 (ppm)
A (dtd)
139.15
140.5 140.0 139.5 139.0 138.5 138.0 137.5
f1 (ppm)
GePh3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-101.29
-101.42
-134.73
-134.76
-134.79
-134.81
-134.83
-134.85
-160.52
-160.54
-160.56
-160.57
-160.59
-160.61
-160.63
-160.65
-160.67
GePh3
1.00
1.86
0.86
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)



(E)-(1-fluoro-2-(4-methoxyphenyl)vinyl)diphenylgermane

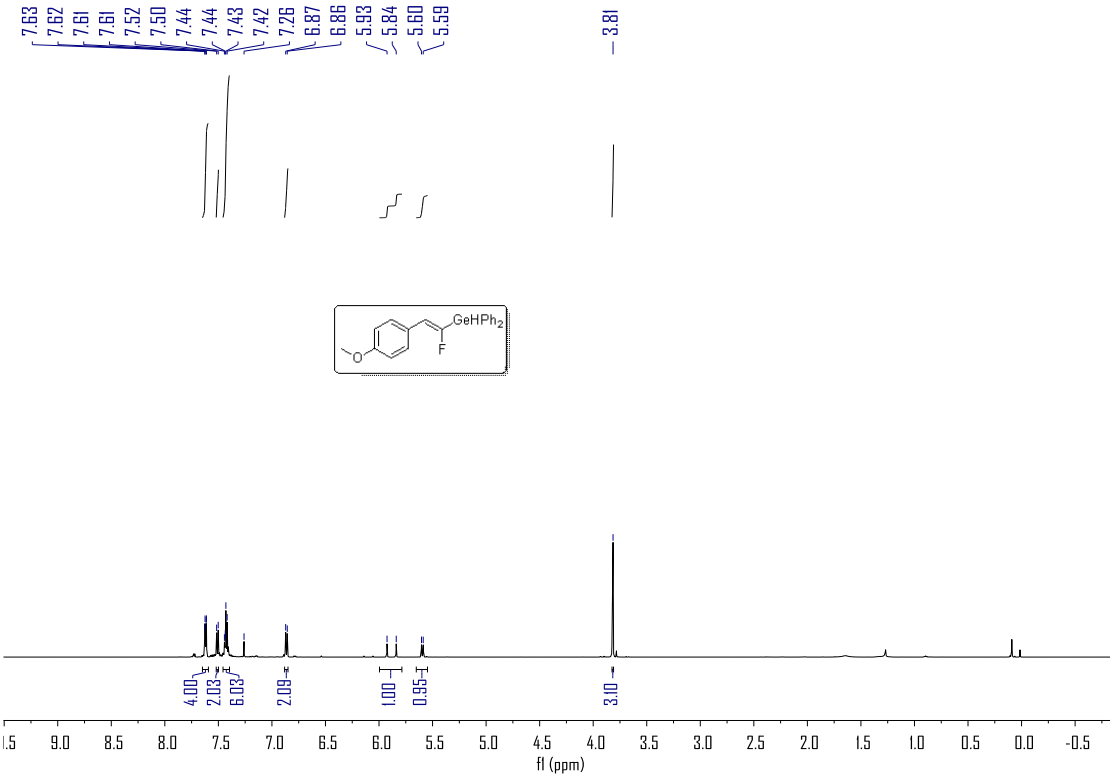
Following the general procedure (**3ab**, pale-yellow liquid, 4 mg, 10%, E/Z > 20:1). The residue was purified by silica gel-columun chromatography using PE/DCM (25:1) as an eluent.

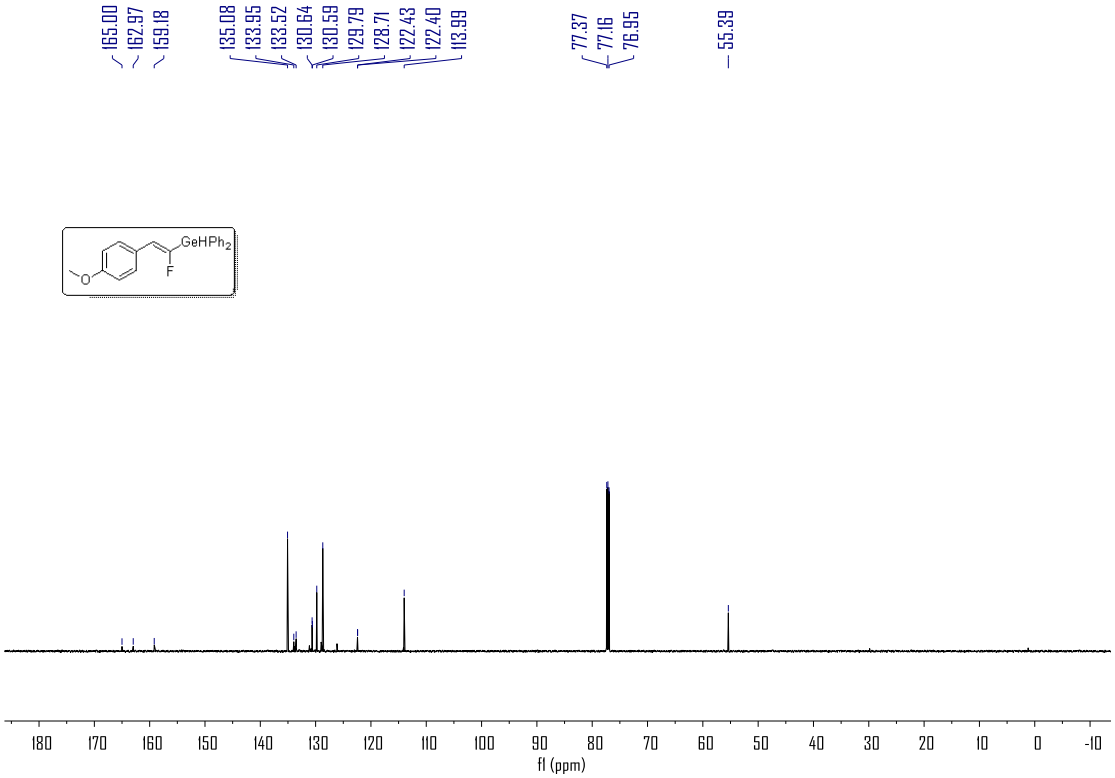
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 7.5, 1.6 Hz, 4H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.43 (dd, *J* = 9.2, 6.1 Hz, 6H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.88 (d, *J* = 51.5 Hz, 1H), 5.60 (d, *J* = 9.6 Hz, 1H), 3.81 (s, 3H).

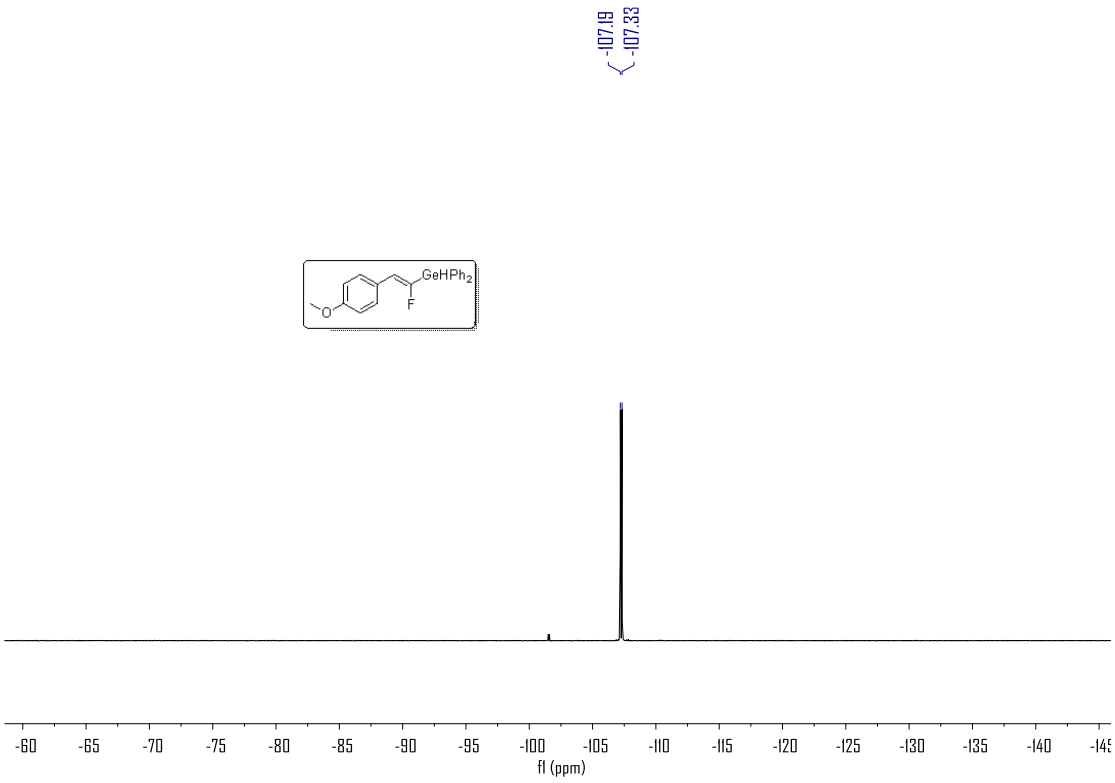
^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.99 (d, *J* = 306.4 Hz), 159.18, 135.08, 133.95, 133.52, 130.61 (d, *J* = 7.4 Hz), 129.79, 128.71, 122.42 (d, *J* = 3.7 Hz), 113.99, 55.39.

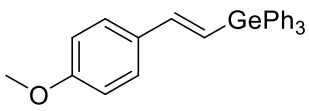
^{19}F NMR (564 MHz, Chloroform-*d*) δ -107.26 (d, *J* = 51.4 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}FGeNaO$: 403.0524; found: 403.0530.




165.00
162.97
159.18
135.08
133.95
133.52
130.64
130.59
129.79
128.71
122.43
122.40
113.99
77.37
77.16
76.95
55.39
GeHPh2
F
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-107.19
-107.33
GeHPh2
F
O
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)



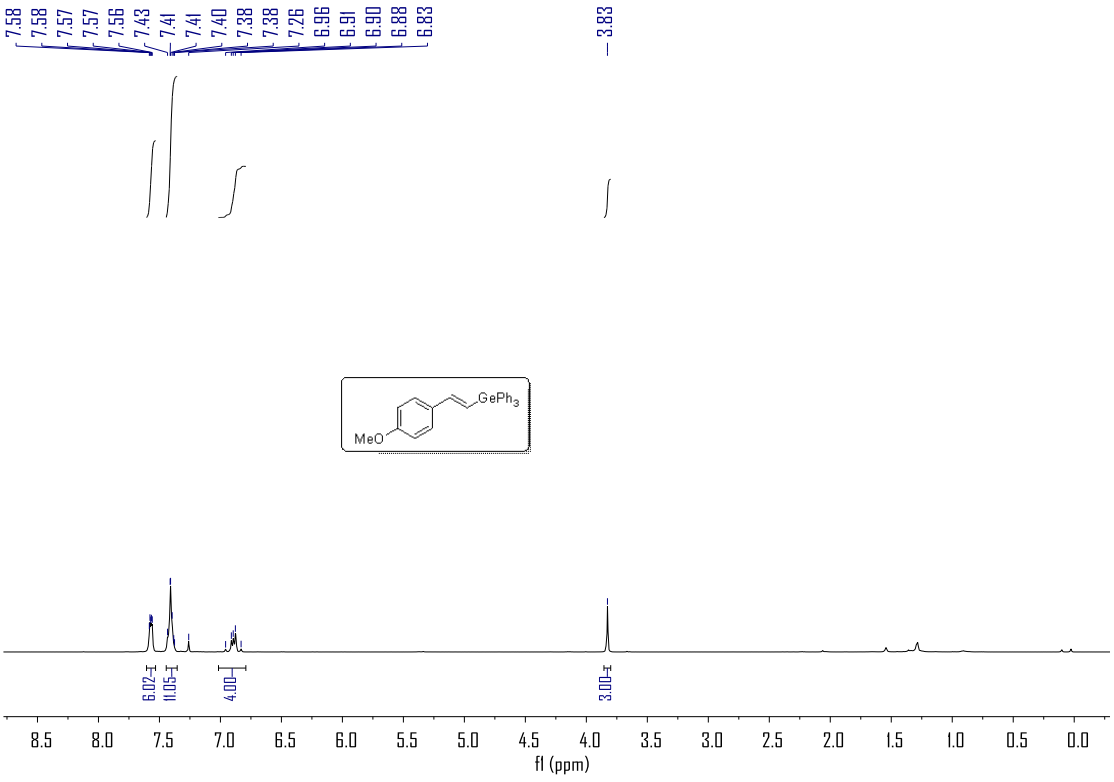
(E)-(4-methoxystyryl)triphenylgermane

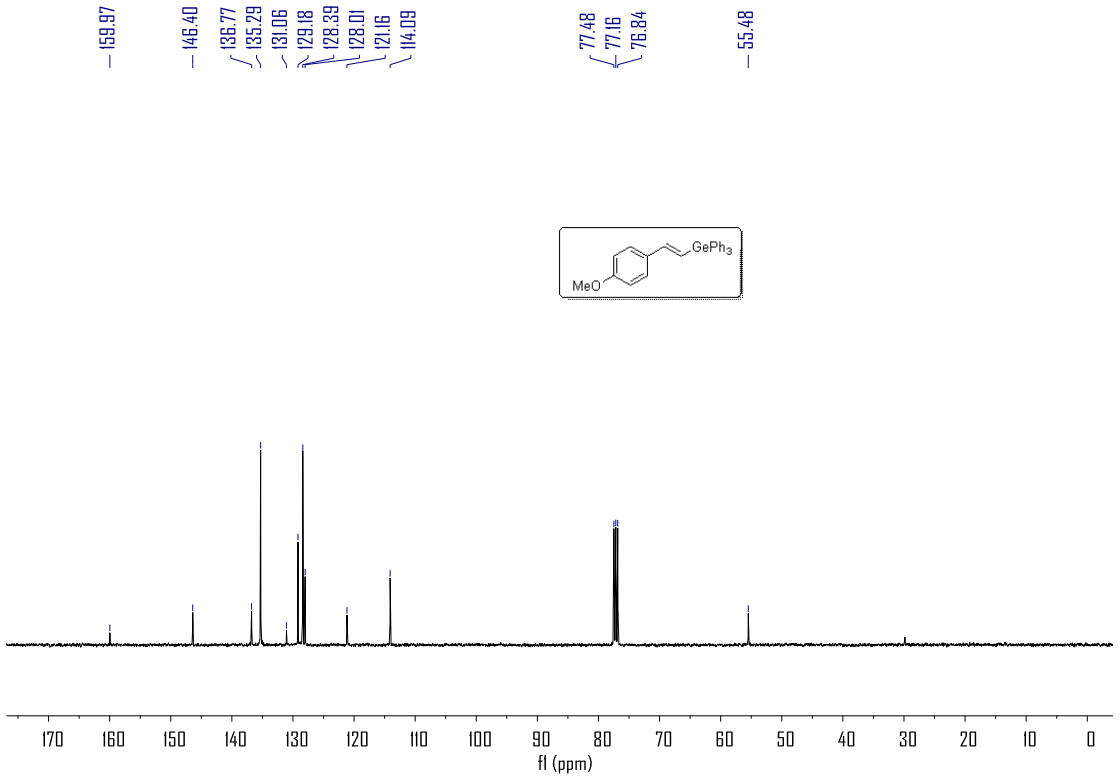
Following the general procedure (1 mL CH_3CN as solvent, **3ac**, pale-yellow liquid, 13 mg, 29%, E/Z > 30:1). The residue was purified by silica gel-columun chromatography using PE/DCM (20:1) as an eluent.

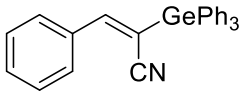
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.52 (m, 6H), 7.48 – 7.35 (m, 11H), 7.01 – 6.77 (m, 4H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.97, 146.40, 136.77, 135.29, 131.06, 129.18, 128.39, 128.01, 121.16, 114.09, 55.48.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{24}GeNaO$: 461.0931; found: 461.0938.




159.97
146.40
136.77
135.29
131.06
129.18
128.39
128.01
121.16
114.09
77.48
77.16
76.84
55.48
GePh3
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



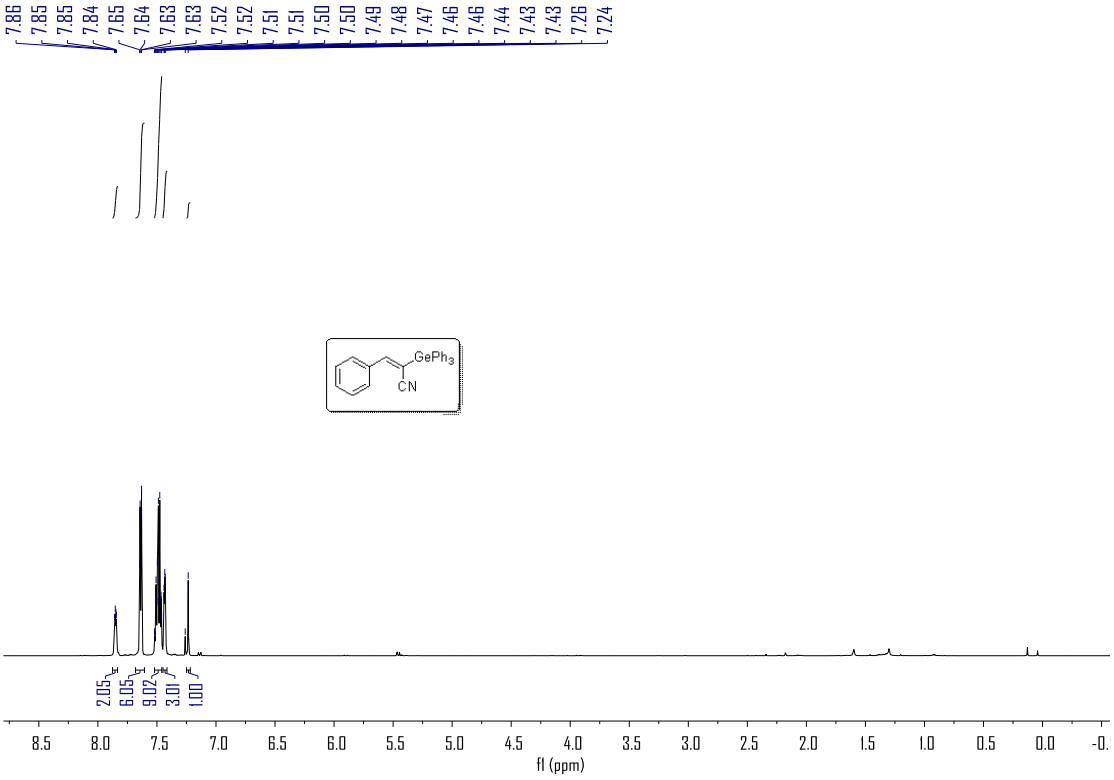
(E)-3-phenyl-2-(triphenylgermyl)acrylonitrile

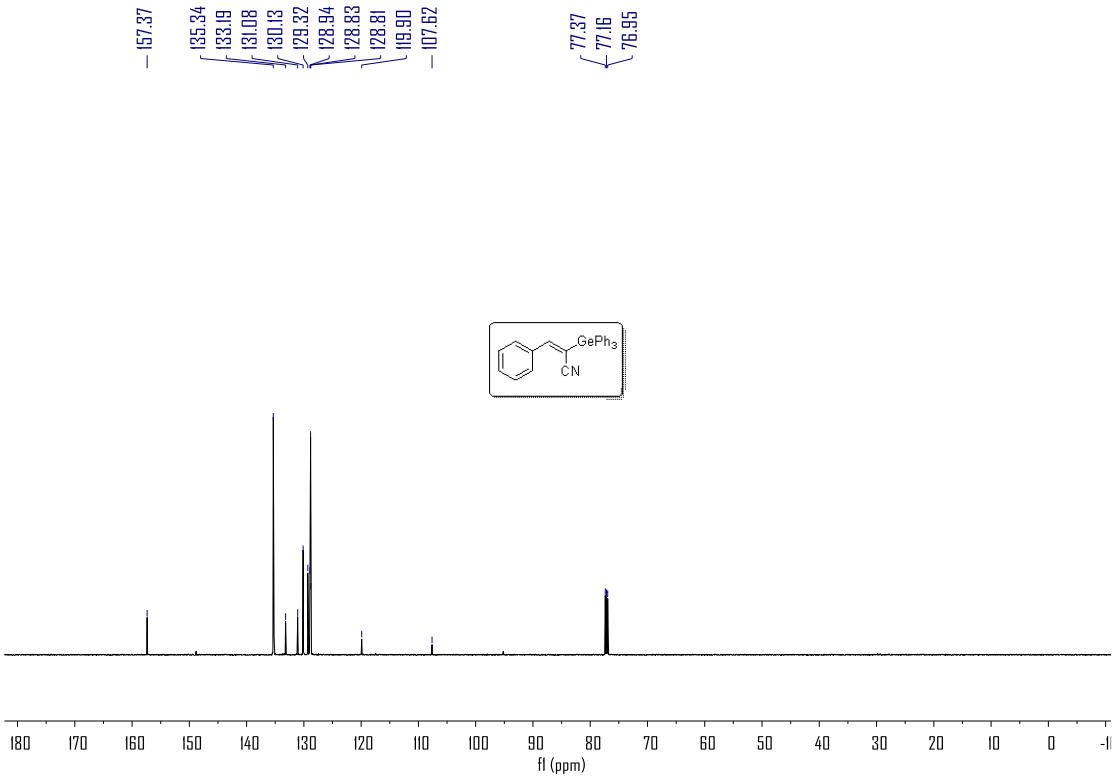
Following the general procedure (0.5 mL CH_3CN and 0.5 mL DMSO as solvent, **3ad**, pale-yellow solid, 15 mg, 35%, E/Z > 30:1). The residue was purified by silica gel-columun chromatography using PE/DCM (5:1) as an eluent.

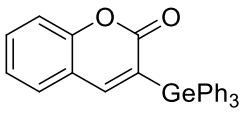
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.8 Hz, 6H), 7.52 – 7.46 (m, 9H), 7.46 – 7.41 (m, 3H), 7.24 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.37, 135.34, 133.19, 131.08, 130.13, 129.32, 128.94, 128.83, 128.81, 119.90, 107.62.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{21}GeNNa$: 456.0778; found: 456.0786.




157.37
135.34
133.19
131.08
130.13
129.32
128.94
128.83
128.81
119.90
107.62
77.37
77.16
76.95
GePh3
CN
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



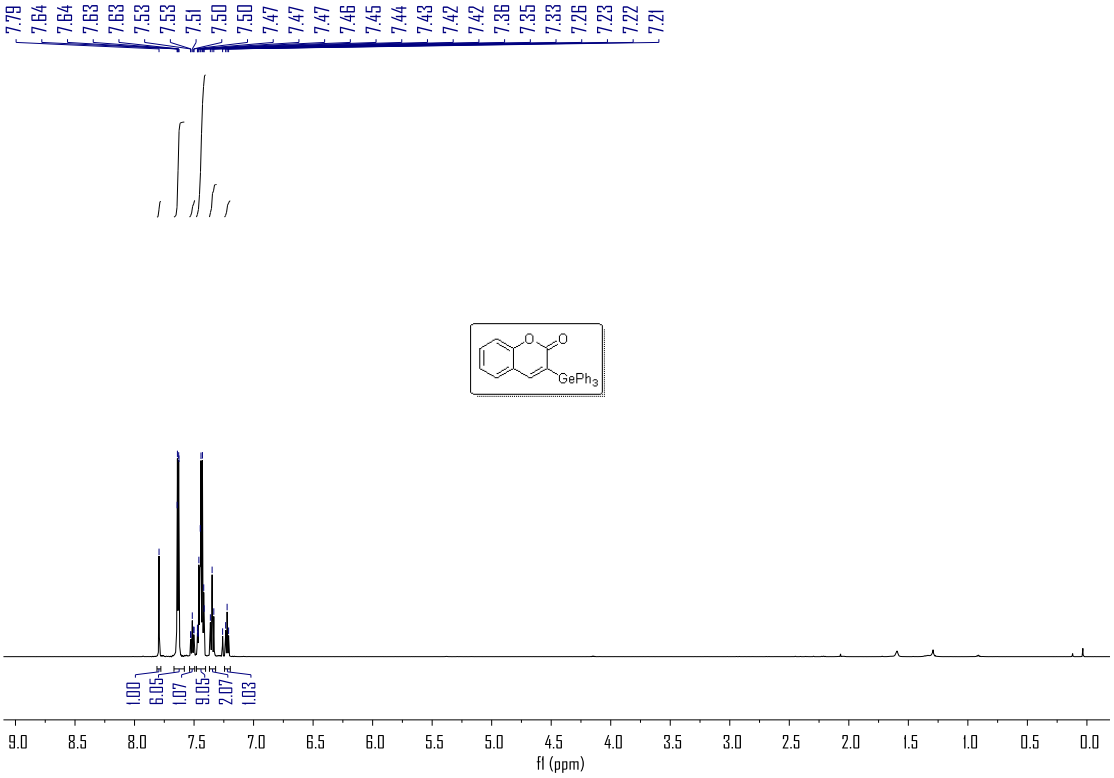
3-(triphenylgermyl)-2H-chromen-2-one

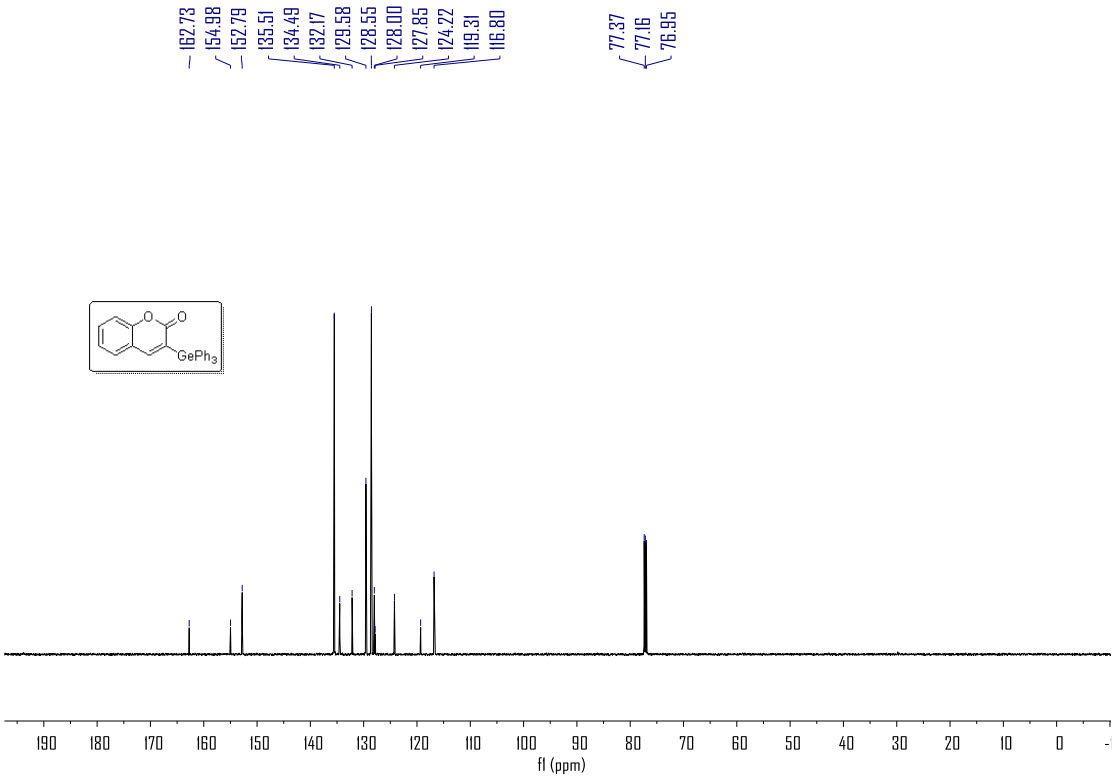
Following the general procedure (0.5 mL CH_3CN and 0.5 mL DMSO as solvent, **3ae**, pale-yellow solid, 18 mg, 41%). The residue was purified by silica gel-columun chromatography using PE/DCM (5:1) as an eluent.

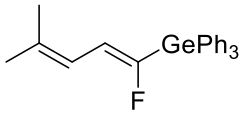
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.63 (dd, *J* = 7.7, 1.4 Hz, 6H), 7.54 – 7.49 (m, 1H), 7.48 – 7.39 (m, 9H), 7.35 (t, *J* = 8.7 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.73, 154.98, 152.79, 135.51, 134.49, 132.17, 129.58, 128.55, 128.00, 127.85, 124.22, 119.31, 116.80.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{20}GeNaO_2$: 473.0567; found: 473.0575.




162.73
154.98
152.79
135.51
134.49
132.17
129.58
128.55
128.00
127.85
124.22
119.31
116.80
77.37
77.16
76.95
GePh3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(E)-(1-fluoro-4-methylpenta-1,3-dien-1-yl)triphenylgermane

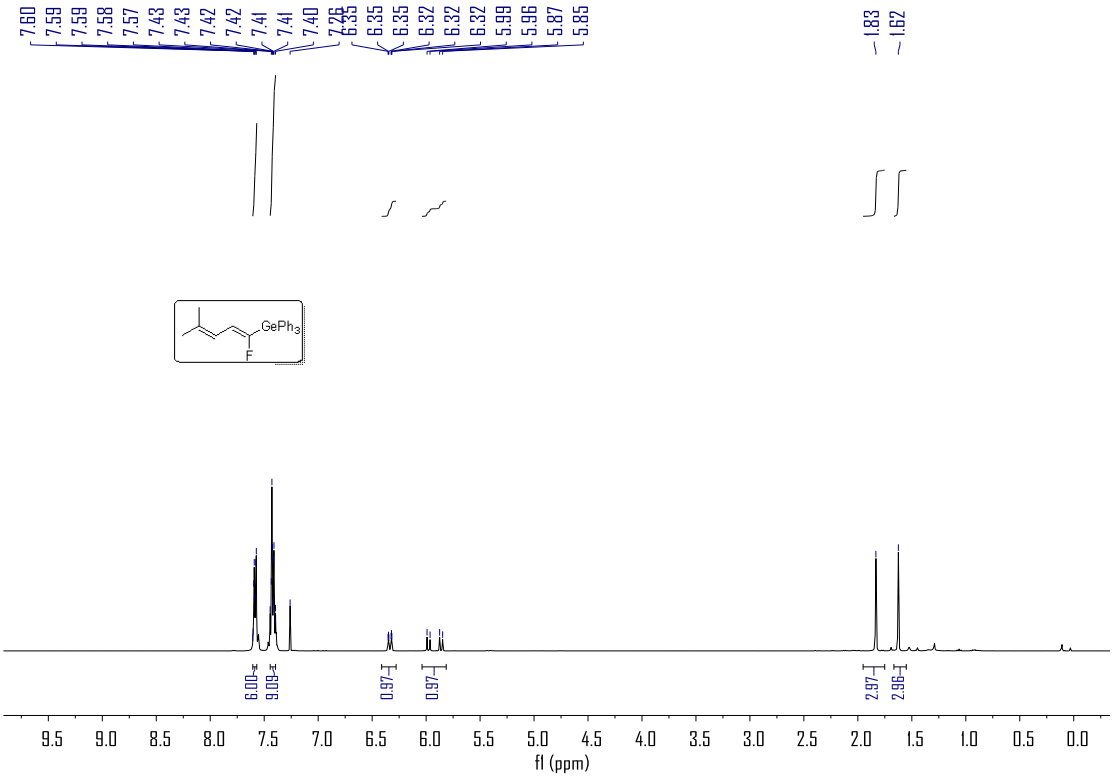
Following the general procedure (**4a**, pale-yellow liquid, 15 mg, 38%, E/Z > 30:1). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

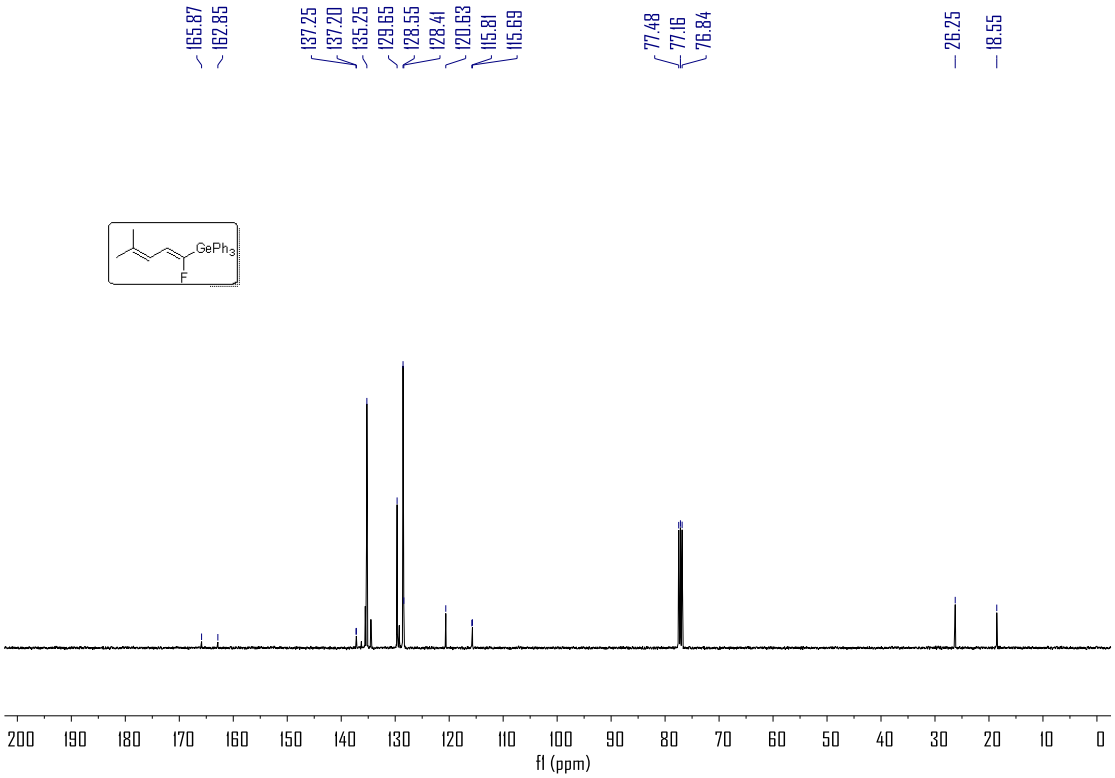
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.52 (m, 6H), 7.46 – 7.38 (m, 9H), 6.33 (dt, *J* = 11.2, 1.5 Hz, 1H), 5.92 (dd, *J* = 46.7, 11.2 Hz, 1H), 1.83 (s, 3H), 1.62 (s, 3H).

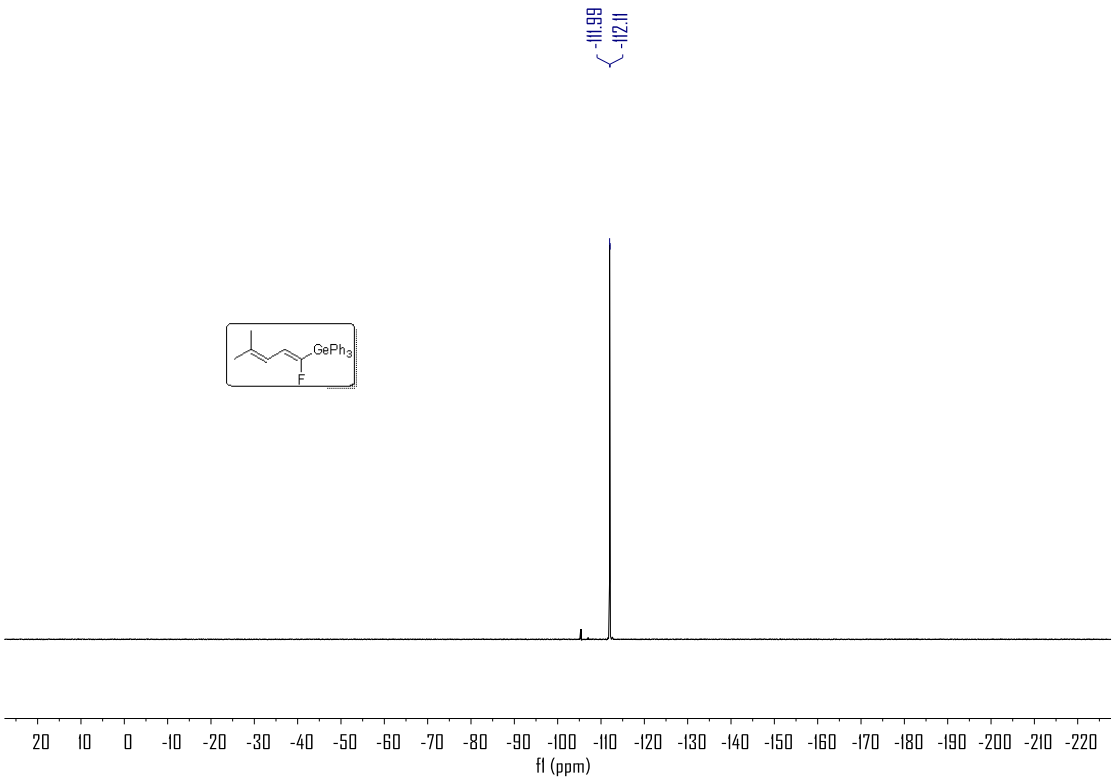
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.36 (d, *J* = 303.7 Hz), 137.22 (d, *J* = 4.9 Hz), 135.25, 129.65, 128.55, 128.41, 120.63, 115.75 (d, *J* = 11.7 Hz), 26.25, 18.55.

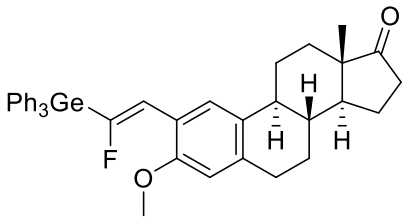
^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.05 (d, *J* = 46.7 Hz).

HRMS (EI) m/z: [M] $^{+}$ Calcd for $C_{24}H_{23}FGe$: 404.0996; found: 404.0991.




165.87
162.85
137.25
137.20
135.25
129.65
128.55
128.41
120.63
115.81
115.69
77.48
77.16
76.84
26.25
18.55
GePh3
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-111.99
-112.11
GePh3
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



(8R,9S,13S,14S)-2-((E)-2-fluoro-2-(triphenylgermyl)vinyl)-3-methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one

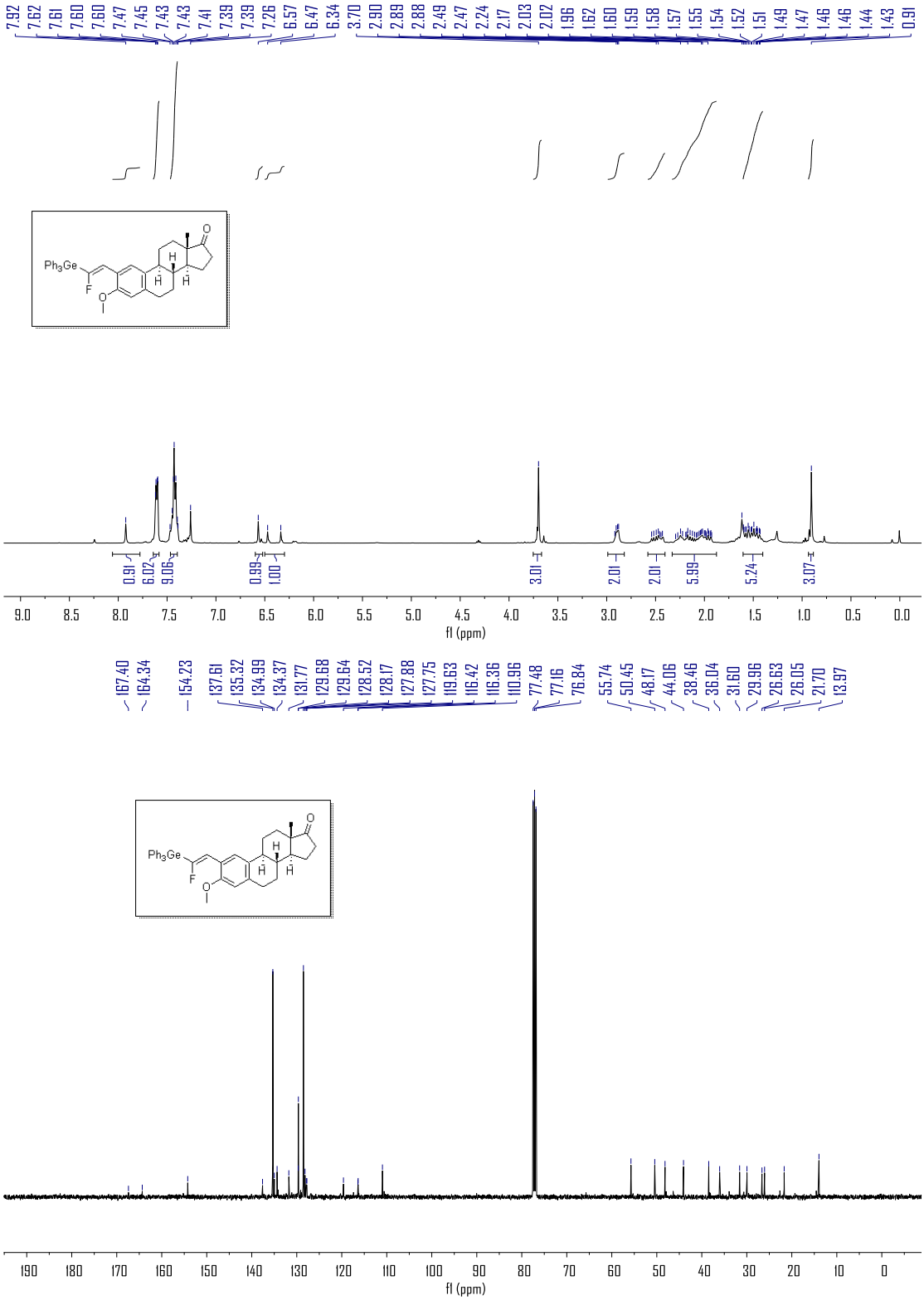
Following the general procedure (**5a**, pale-yellow solid, 23 mg, 36%, E/Z = 10:1). The residue was purified by silica gel-columun chromatography using PE/DCM (5:1) as an eluent.

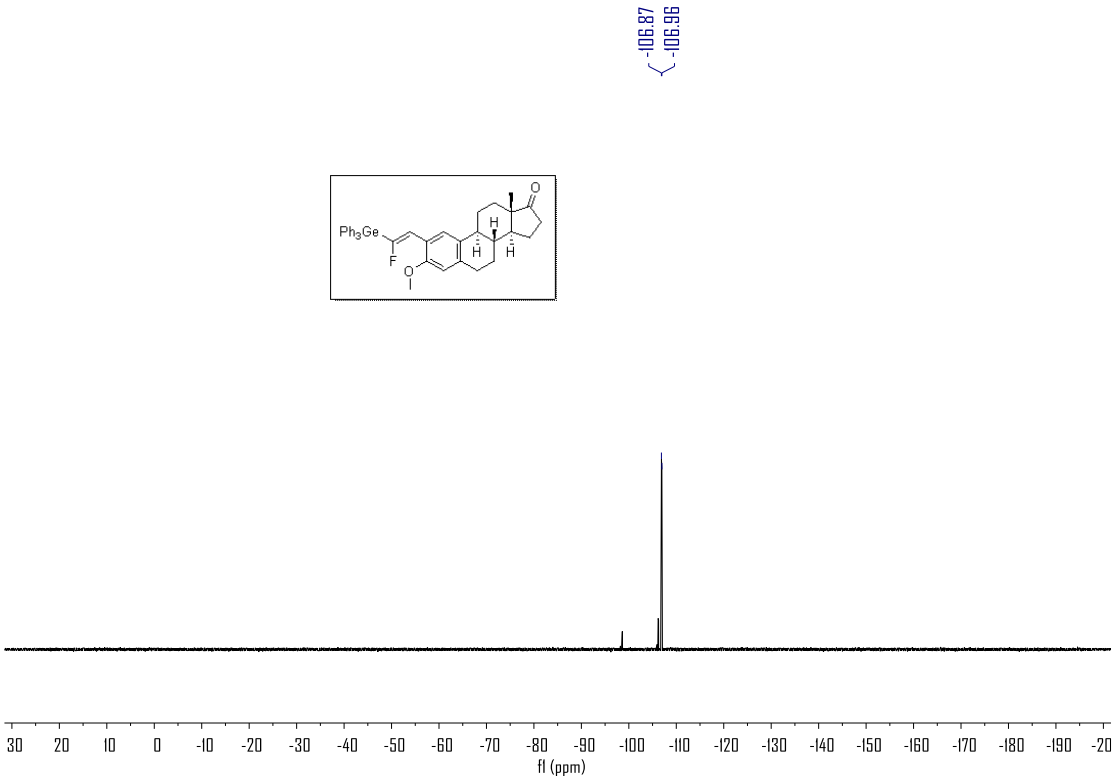
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.61 (dd, *J* = 7.1, 2.2 Hz, 6H), 7.50 – 7.36 (m, 9H), 6.57 (s, 1H), 6.40 (d, *J* = 54.0 Hz, 1H), 3.70 (s, 3H), 2.94 – 2.84 (m, 2H), 2.56 – 2.39 (m, 2H), 2.29 – 1.93 (m, 6H), 1.70 – 1.39 (m, 5H), 0.91 (s, 3H).

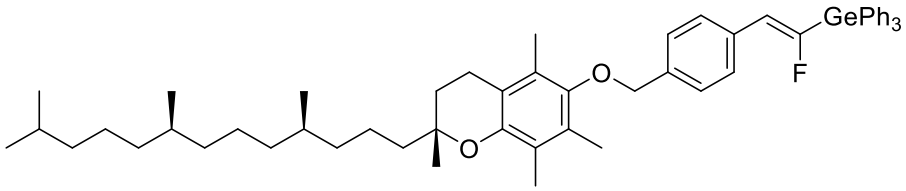
^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.92 (d, *J* = 53.8 Hz).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.87 (d, *J* = 308.2 Hz), 154.23, 137.61, 134.99, 134.37, 131.77, 129.64, 128.52, 128.17, 127.81 (d, *J* = 13.8 Hz), 119.63, 110.96, 55.74, 50.45, 48.17, 44.06, 38.46, 36.04, 31.60, 29.96, 26.63, 26.05, 21.70, 13.97.

HRMS (APCI) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{39}FGeNaO_2$: 655.2038; found: 655.2046.


7.92 7.62 7.61 7.60 7.60 7.47 7.45 7.43 7.43 7.41 7.39 7.39 7.26 6.57 6.47 6.34 3.70 2.90 2.89 2.88 2.49 2.47 2.24 2.17 2.03 2.02 1.96 1.62 1.60 1.59 1.58 1.57 1.55 1.54 1.52 1.51 1.49 1.47 1.46 1.46 1.44 1.43 0.91
Ph3Ge
F
O
H
H
H
O
0.91 6.02 9.06 0.99 1.00 3.01 2.01 2.01 5.99 5.24 3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
167.40 164.34 154.23 137.61 135.32 134.99 134.37 131.77 129.68 129.64 128.52 128.17 127.88 127.75 119.63 116.42 116.36 110.96 77.48 77.16 76.84 55.74 50.45 48.17 44.06 38.46 36.04 31.60 29.96 26.63 26.05 21.70 13.97
Ph3Ge
F
O
H
H
H
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-106.87
-106.96
Ph3Ge
F
O
H
H
H
O
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)



((E)-1-fluoro-2-(4-((((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)vinyl)triphenylgermane

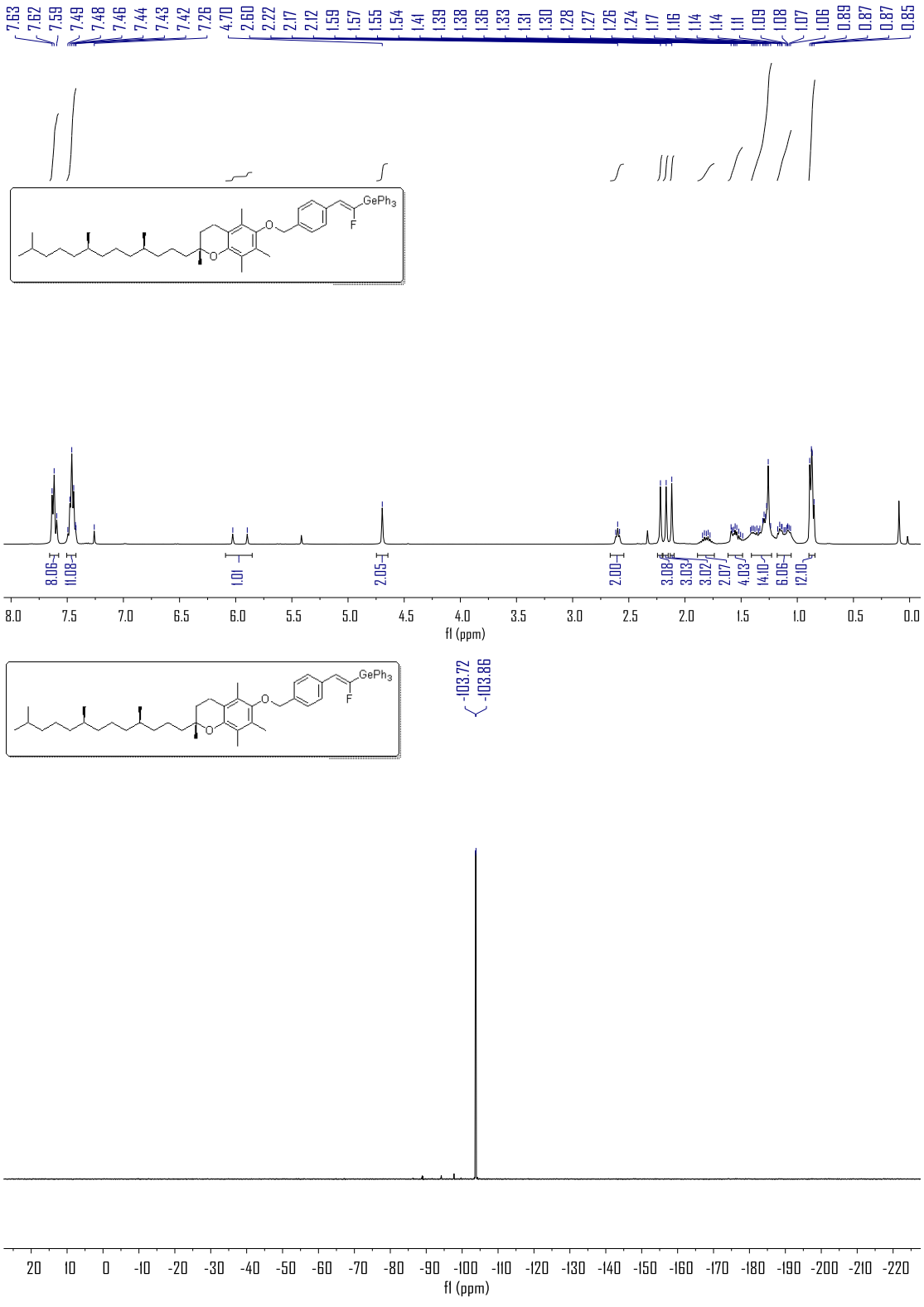
Following the general procedure (**5b**, pale-yellow solid, 35 mg, 41%, E/Z > 30:1). The residue was purified by silica gel-columun chromatography using PE/DCM (20:1) as an eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.57 (m, 8H), 7.52 – 7.41 (m, 11H), 5.96 (d, *J* = 51.6 Hz, 1H), 4.70 (s, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 3H), 2.12 (s, 3H), 1.81 (dt, *J* = 13.1, 6.8 Hz, 2H), 1.62 – 1.50 (m, 4H), 1.42 – 1.22 (m, 14H), 1.18 – 1.02 (m, 6H), 0.93 – 0.83 (m, 12H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.35 (d, *J* = 48.9 Hz, 1F), -134.77 (dd, *J* = 20.6, 9.0 Hz, 2F), -160.59 (tt, *J* = 20.4, 7.0 Hz, 1F).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.16 (d, *J* = 310.4 Hz), 148.08 (d, *J* = 19.0 Hz), 137.68, 135.29, 134.02, 133.07 (d, *J* = 71.7 Hz), 129.87, 129.82, 129.34 (d, *J* = 7.4 Hz), 128.66, 128.31 (d, *J* = 53.3 Hz), 127.79, 126.10, 123.03, 122.64 (d, *J* = 4.2 Hz), 117.71, 74.94, 74.52, 40.08, 39.48, 37.57, 37.53, 37.39, 32.92, 32.82, 31.38, 28.12, 24.95, 24.58, 24.02, 22.89, 22.79, 21.16, 20.80, 19.89, 19.81, 13.04, 12.18, 11.98.

HRMS (APCI) m/z: $[M + Na]^+$ Calcd for $C_{56}H_{71}FGeNaO_2$: 891.4542; found: 891.4549.


7.63
7.62
7.59
7.49
7.48
7.46
7.44
7.43
7.42
7.26
4.70
2.60
2.22
2.17
2.12
1.59
1.57
1.55
1.54
1.41
1.39
1.38
1.36
1.33
1.31
1.30
1.28
1.27
1.26
1.24
1.17
1.16
1.14
1.14
1.11
1.09
1.08
1.07
1.06
0.89
0.87
0.87
0.85
GePh3
F
O
O
8.06
11.08
1.01
2.05
2.00
3.08
3.03
3.02
2.07
4.03
14.10
6.06
12.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
GePh3
F
O
O
-103.72
-103.86
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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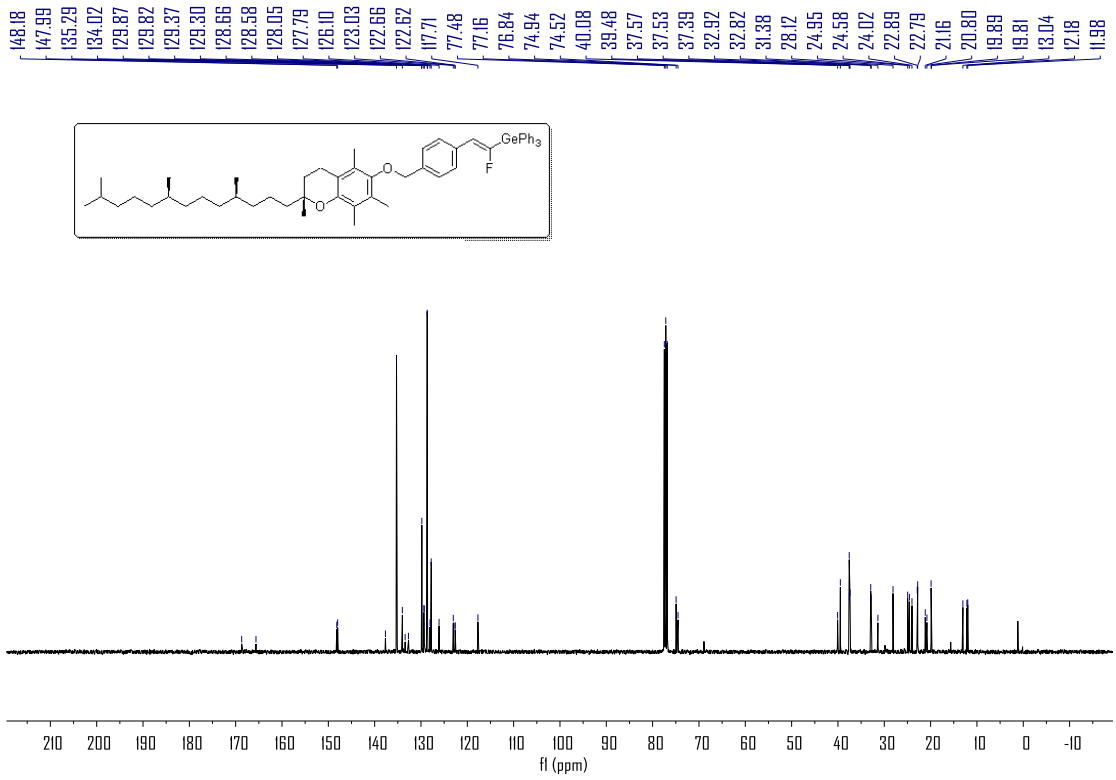
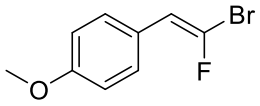
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


148.18
147.99
135.29
134.02
129.87
129.82
129.37
129.30
128.66
128.58
128.05
127.79
126.10
123.03
122.66
122.62
117.71
77.48
77.16
76.84
74.94
74.52
40.08
39.48
37.57
37.53
37.39
32.92
32.82
31.38
28.12
24.95
24.58
24.02
22.89
22.79
21.16
20.80
19.89
19.81
13.04
12.18
11.98
GePh3
F
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



(E)-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene

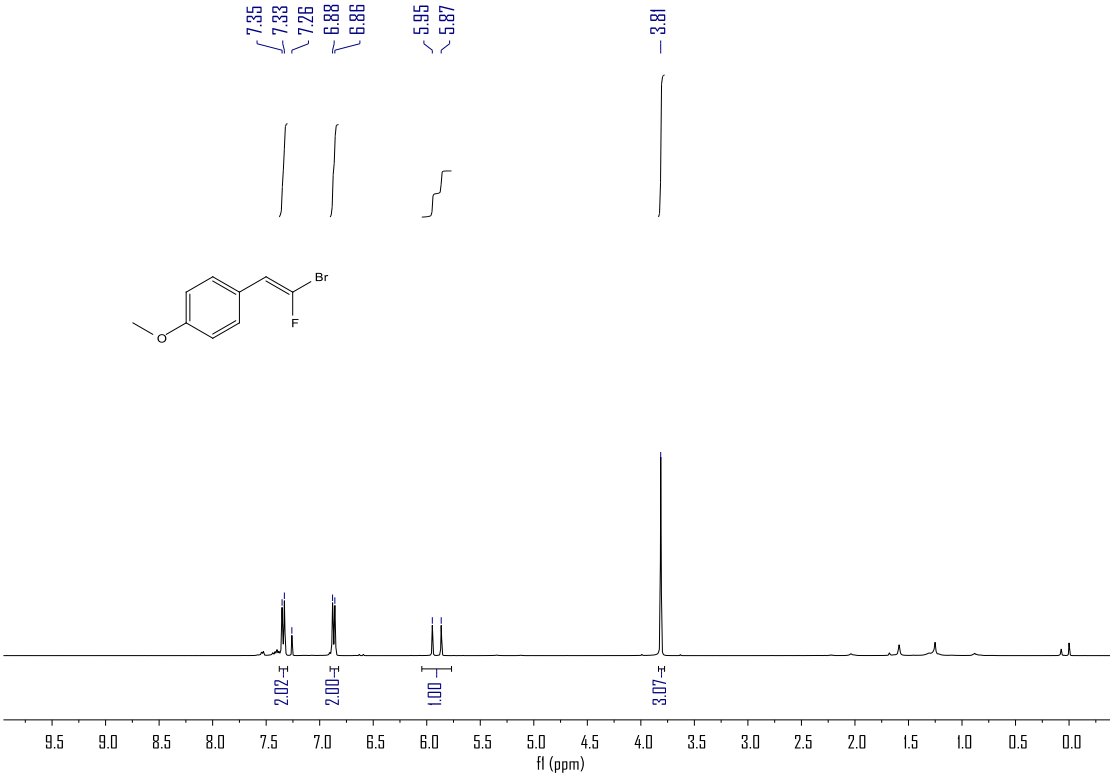
(**3ba**, pale-yellow liquid, 22 mg, 95%). The residue was purified by silica gel-columun chromatography using PE/EtOAc (50:1) as an eluent.

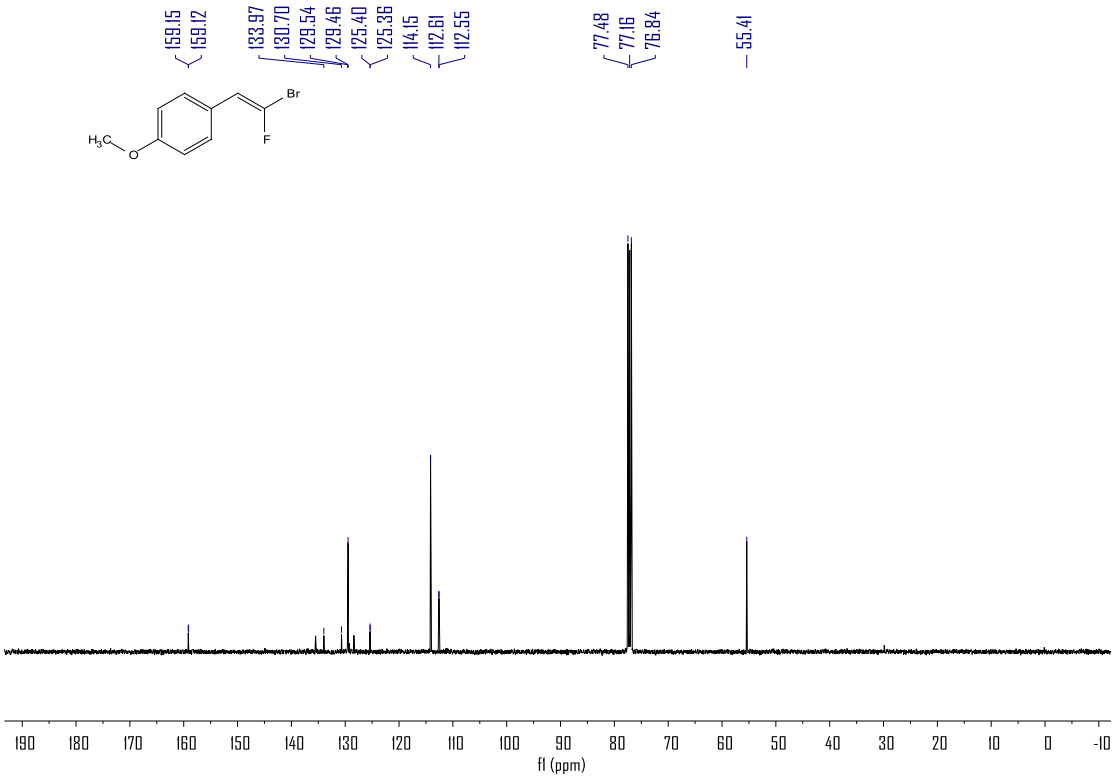
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.91 (d, *J* = 33.2 Hz, 1H), 3.81 (s, 3H).

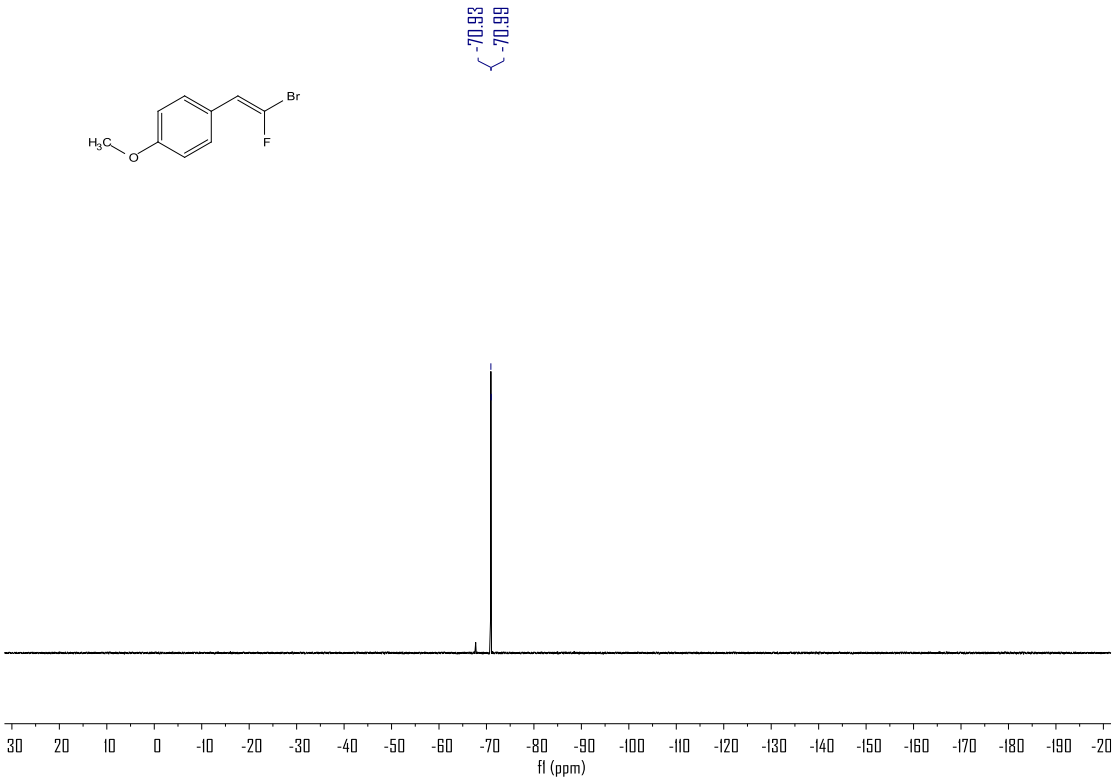
^{19}F NMR (376 MHz, Chloroform-*d*) δ -70.96 (d, *J* = 33.1 Hz).

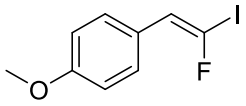
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.13 (d, *J* = 2.9 Hz), 132.33 (d, *J* = 329.2 Hz), 129.50 (d, *J* = 7.2 Hz), 125.38 (d, *J* = 4.5 Hz), 114.15, 112.58 (d, *J* = 6.6 Hz), 55.41.

These data are in agreement with those reported previously in the literature.[6]




159.15
159.12
133.97
130.70
129.54
129.46
125.40
125.36
114.15
112.61
112.55
77.48
77.16
76.84
55.41
Br
F
H3C
O
f1 (ppm)


-70.93
-70.99
Br
F
H3C
O
f1 (ppm)



(E)-1-(2-fluoro-2-iodovinyl)-4-methoxybenzene

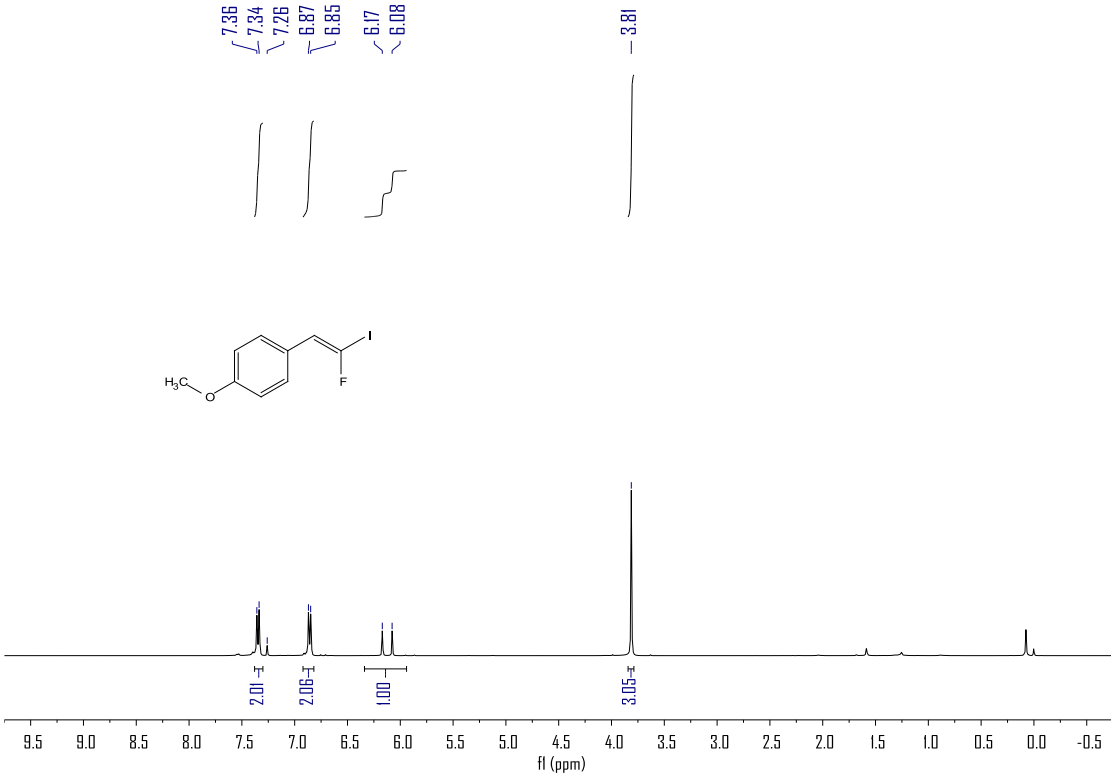
(**3ca**, pale-yellow liquid, 20 mg, 72%). The residue was purified by silica gel-columun chromatography using PE/EtOAc (50:1) as an eluent.

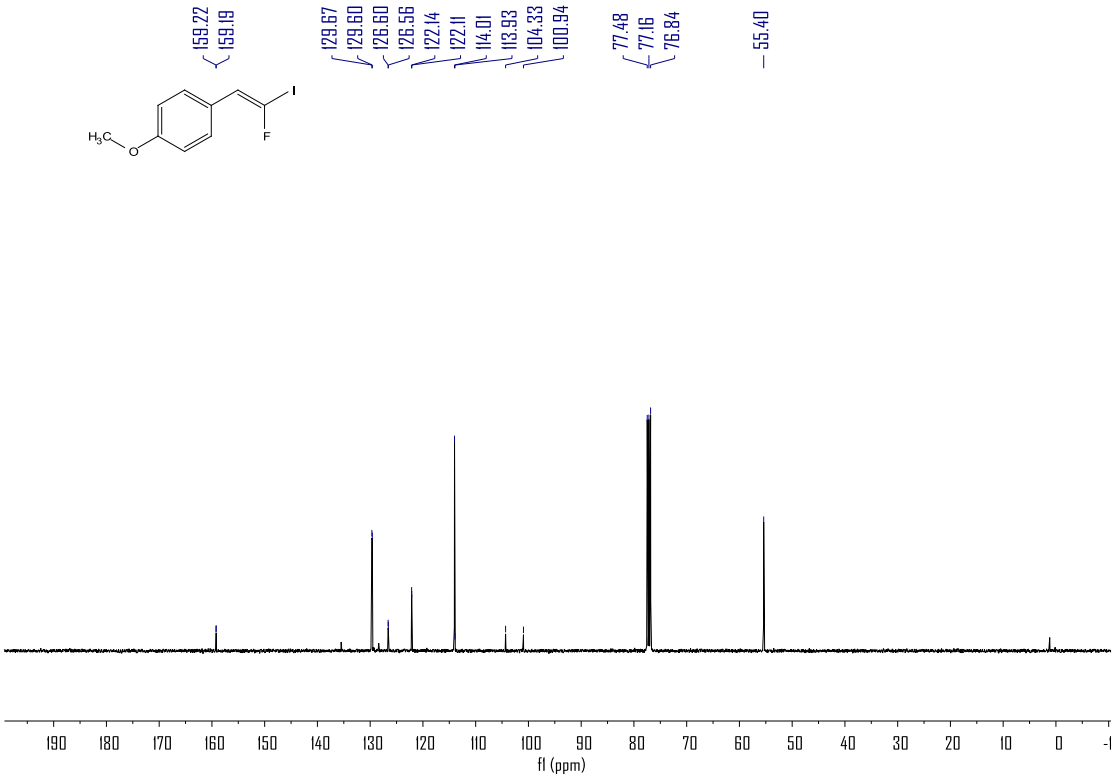
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (s, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.12 (d, *J* = 37.2 Hz, 1H), 3.81 (s, 3H).

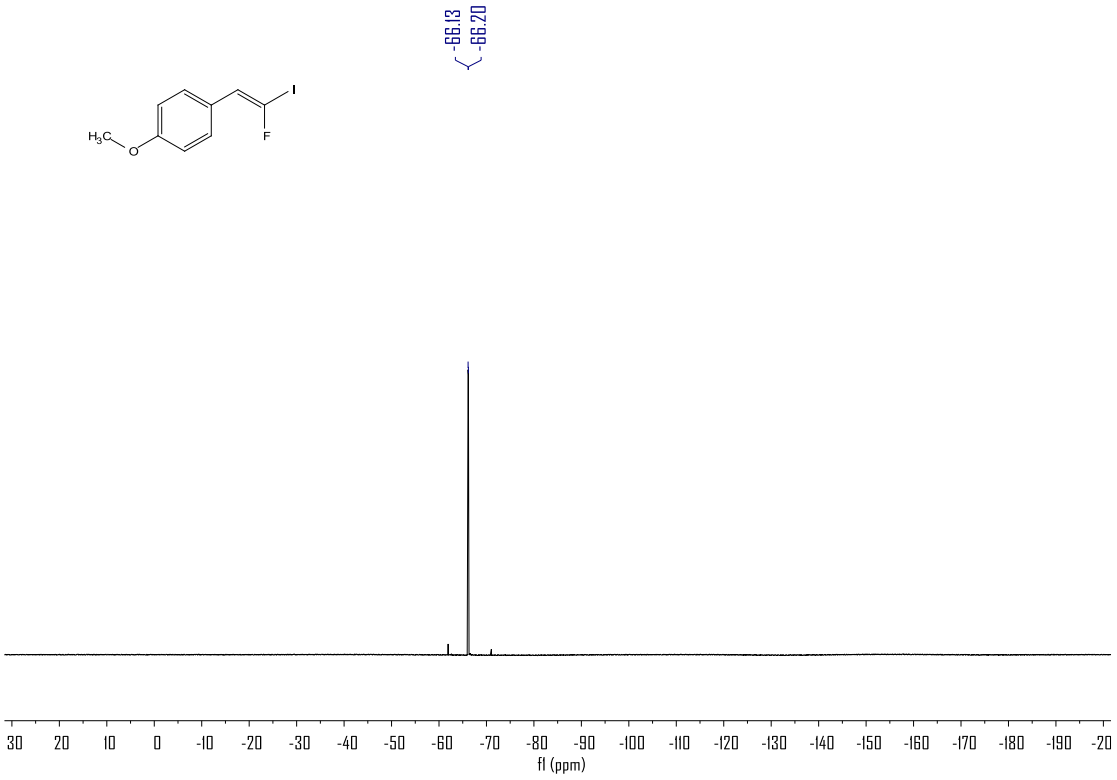
^{19}F NMR (376 MHz, Chloroform-*d*) δ -66.16 (d, *J* = 37.1 Hz).

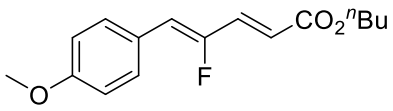
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.21 (d, *J* = 3.1 Hz), 129.64 (d, *J* = 7.4 Hz), 126.58 (d, *J* = 3.6 Hz), 122.13 (d, *J* = 2.8 Hz), 114.01, 102.63 (d, *J* = 341.1 Hz), 55.40.

These data are in agreement with those reported previously in the literature.[6]




159.22
159.19
129.67
129.60
126.60
126.56
122.14
122.11
114.01
113.93
104.33
100.94
77.48
77.16
76.84
55.40
I
F
O
H3C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


-66.13
-66.20
I
F
O
H3C
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)



Butyl-(2E,4Z)-4-fluoro-5-(4-methoxyphenyl)penta-2,4-dienoate

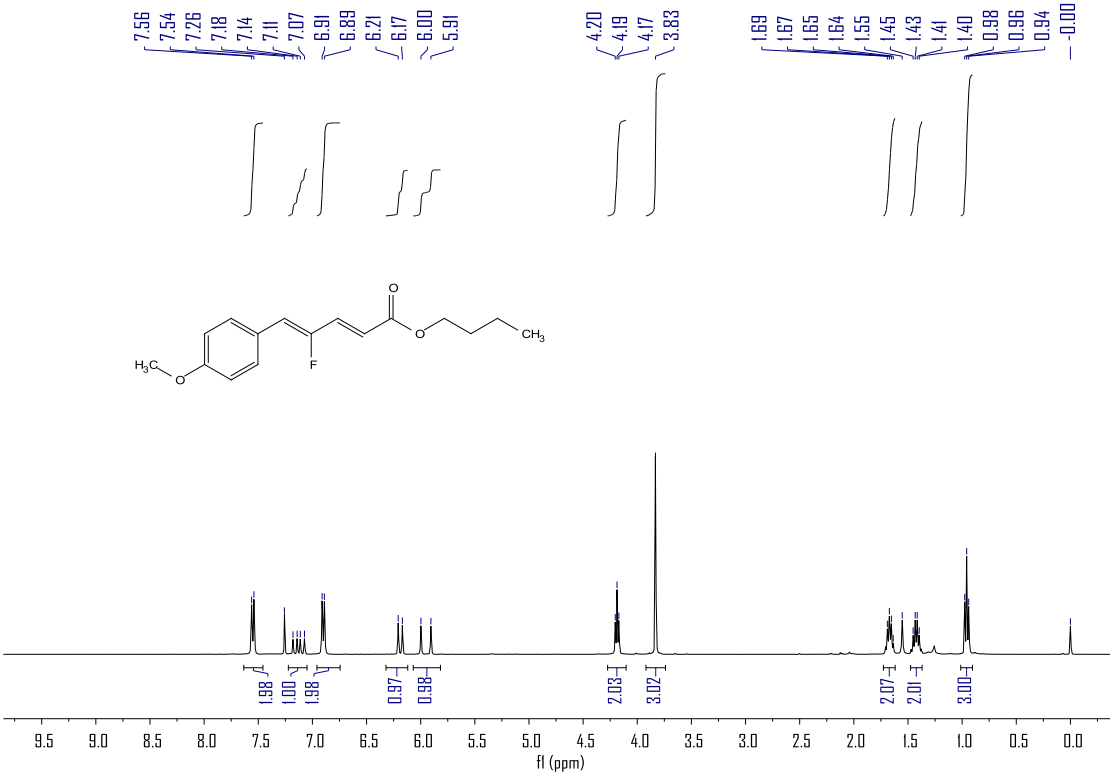
(**3ea**, pale-yellow liquid, 12 mg, 45%). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent.

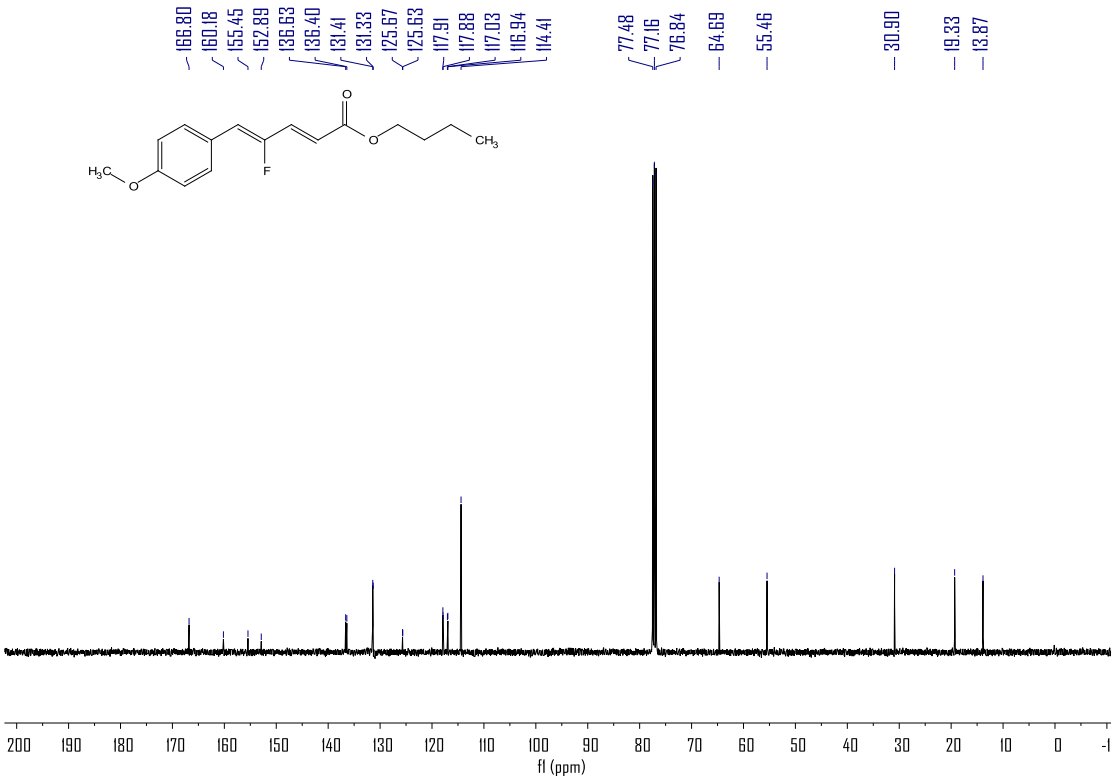
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.13 (dd, *J* = 27.1, 15.5 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.19 (d, *J* = 15.3 Hz, 1H), 5.95 (d, *J* = 36.9 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.83 (s, 3H), 1.72 – 1.59 (m, 2H), 1.49 – 1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.30 – -122.14 (m).

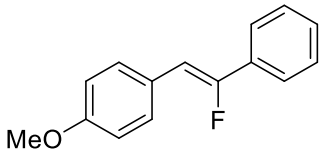
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.80, 160.18, 154.17 (d, *J* = 257.4 Hz), 136.52 (d, *J* = 22.8 Hz), 131.37 (d, *J* = 8.1 Hz), 125.65 (d, *J* = 3.7 Hz), 117.89 (d, *J* = 2.4 Hz), 116.99 (d, *J* = 9.0 Hz), 114.41, 64.69, 55.46, 30.90, 19.33, 13.87.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}FO_3$: 279.1391; found: 279.1397.




166.80
160.18
155.45
152.89
136.63
136.40
131.41
131.33
125.67
125.63
117.91
117.88
117.03
116.94
114.41
77.48
77.16
76.84
64.69
55.46
30.90
19.33
13.87
O
O
CH3
H3C
O
F
f1 (ppm)

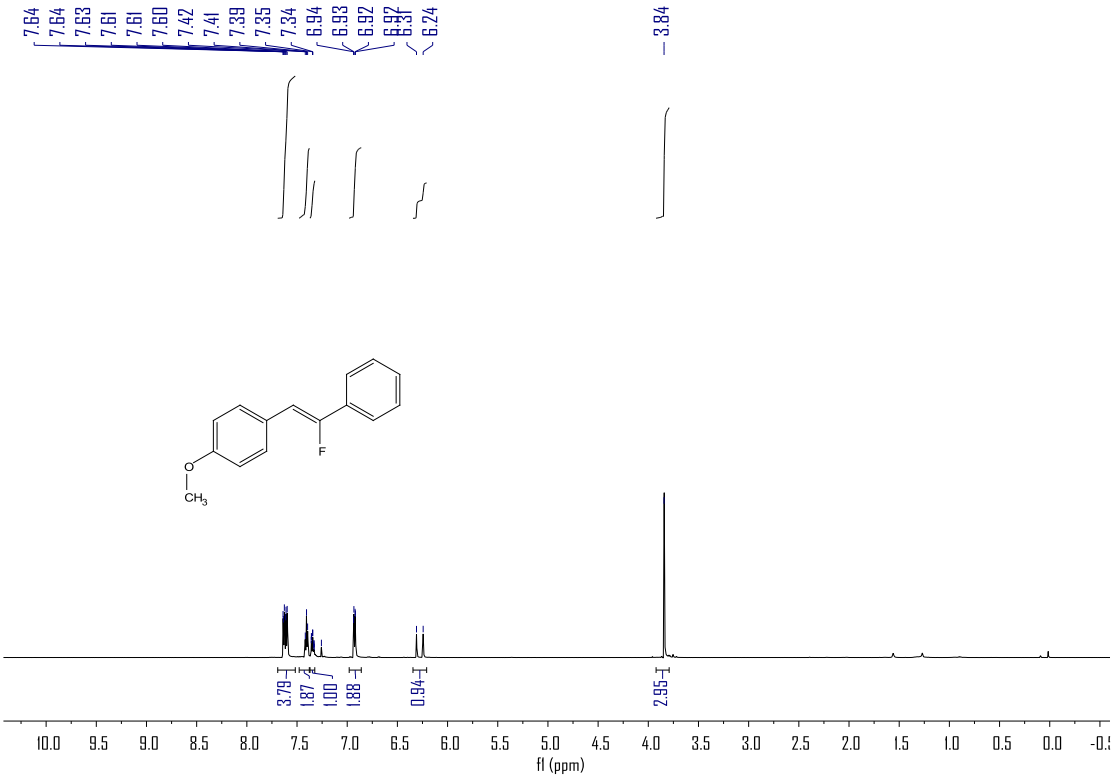

-120.64
-120.67
-120.68
-120.69
-120.70
-120.75
O
O
CH3
H3C
O
F
f1 (ppm)

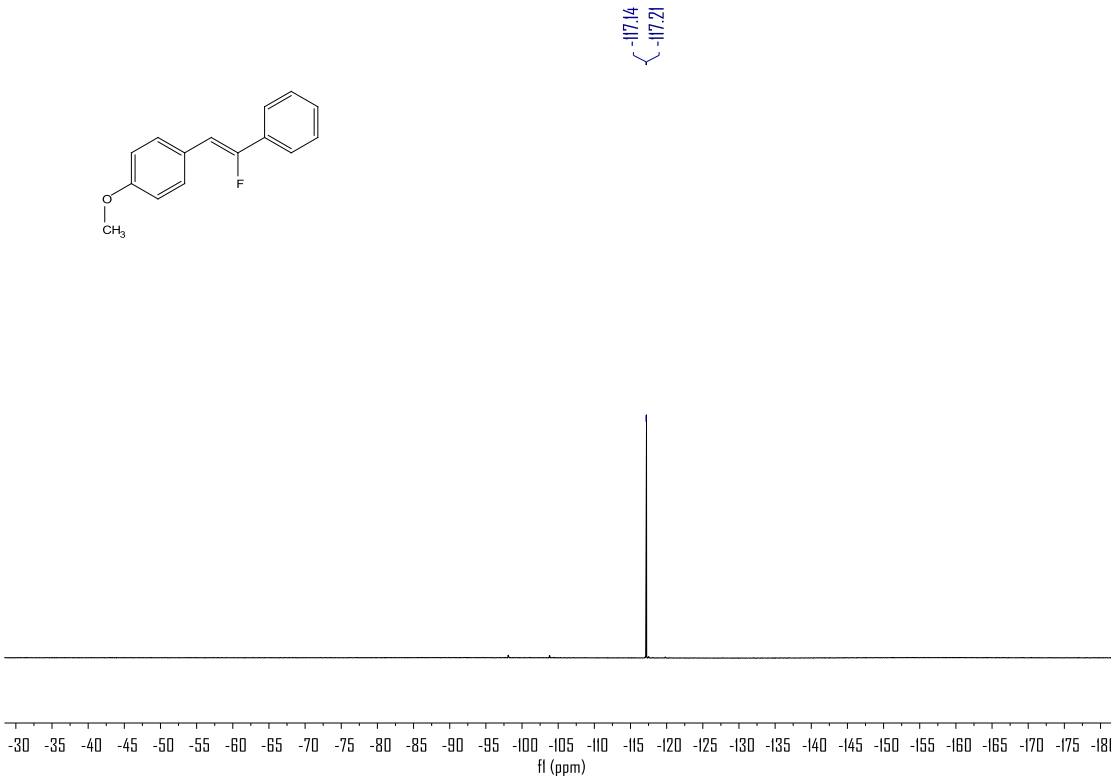


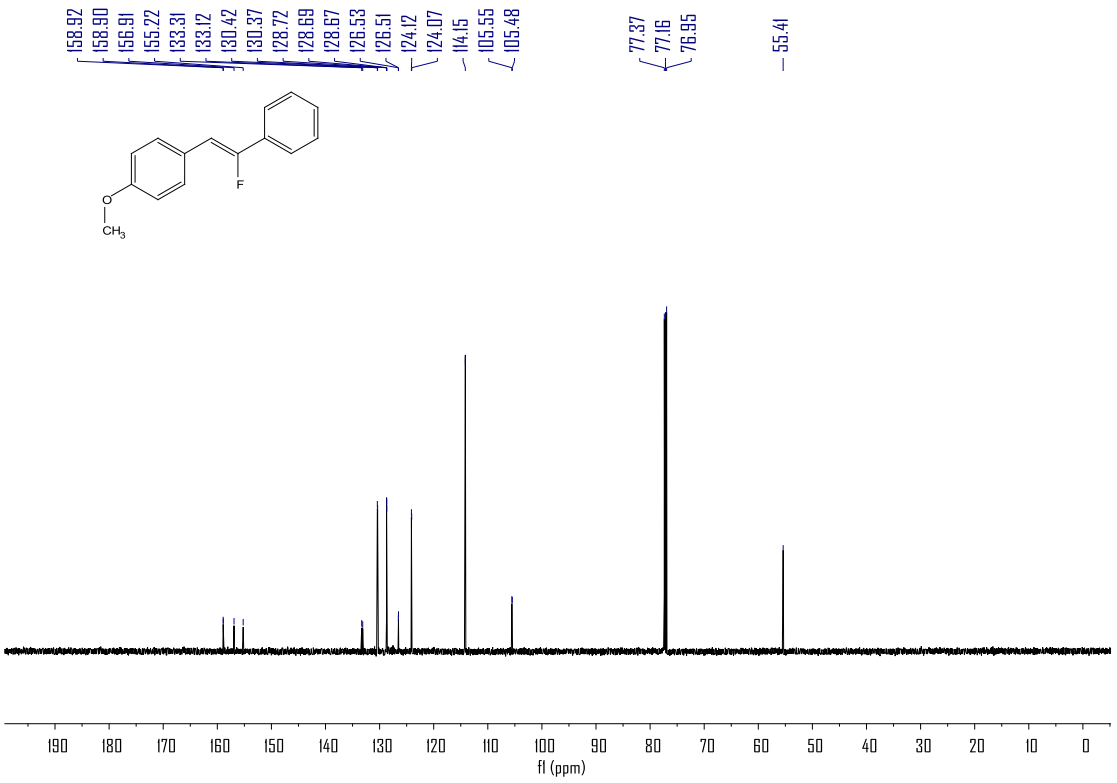
(Z)-1-(2-fluoro-2-phenylvinyl)-4-methoxybenzene

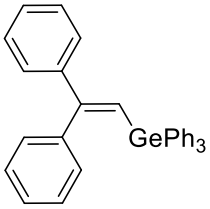
(**3da**, pale-yellow liquid). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.69 – 7.56 (m, 4H), 7.41 (t, *J* = 6.9 Hz, 2H), 7.36 – 7.32 (m, 1H), 6.93 (dd, *J* = 8.8, 1.7 Hz, 2H), 6.28 (d, *J* = 39.9 Hz, 1H), 3.84 (s, 1H). **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -117.18 (d, *J* = 39.8 Hz). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 158.91 (d, *J* = 2.9 Hz), 156.06 (d, *J* = 255.7 Hz), 133.22 (d, *J* = 28.1 Hz), 130.39 (d, *J* = 8.1 Hz), 128.72, 128.68 (d, *J* = 2.0 Hz), 126.52 (d, *J* = 2.9 Hz), 124.09 (d, *J* = 7.5 Hz), 114.15, 105.52 (d, *J* = 10.6 Hz), 55.41.

These data are in agreement with those reported previously in the literature.[7]




-117.14
-117.21
F
O
CH3
f1 (ppm)


158.92
158.90
156.91
155.22
133.31
133.12
130.42
130.37
128.72
128.69
128.67
126.53
126.51
124.12
124.07
114.15
105.55
105.48
77.37
77.16
76.95
55.41
F
O
CH3
f1 (ppm)



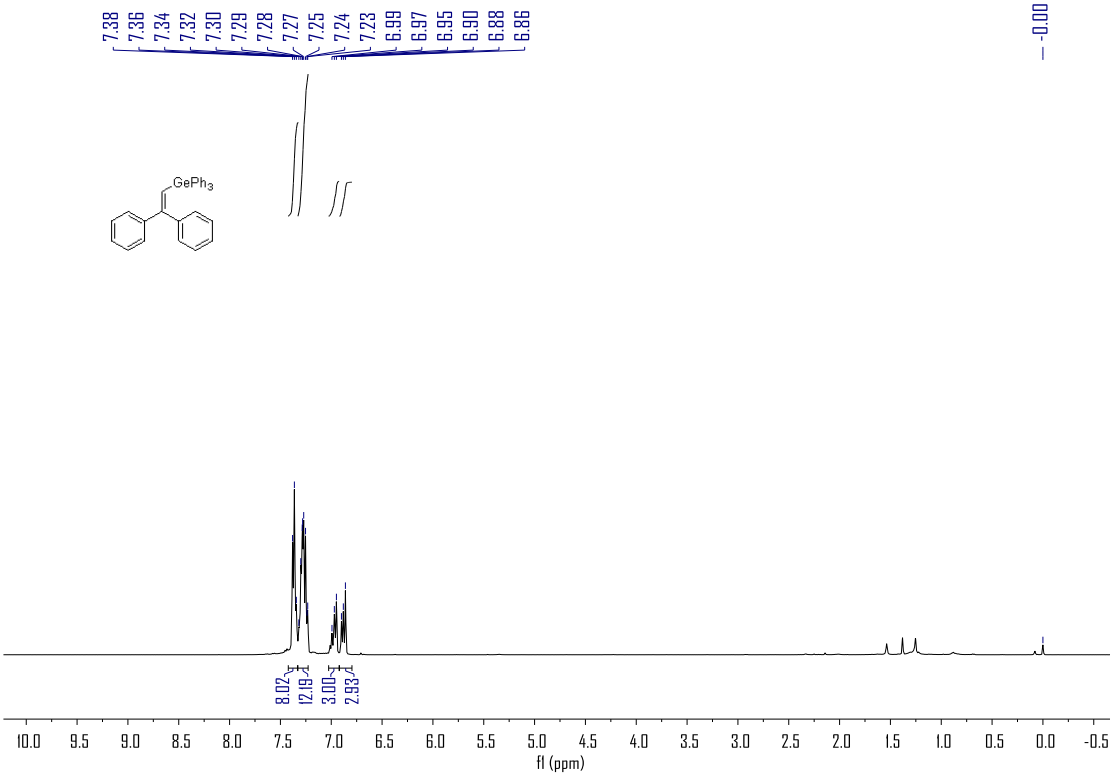
(2,2-diphenylvinyl)triphenylgermane

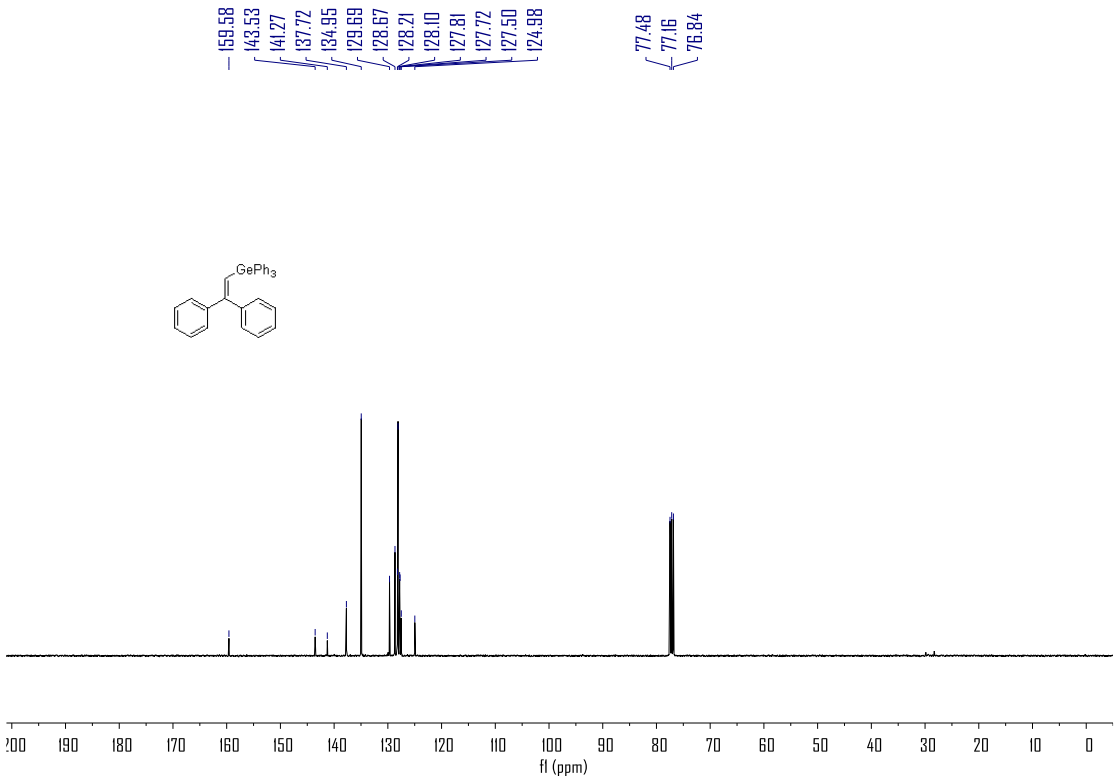
Following the general procedure (**7a**, pale-yellow liquid, 6 mg, 12%). The residue was purified by silica gel-columun chromatography using PE/DCM (30:1) as an eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 8H), 7.35 – 7.24 (m, 12H), 7.04 – 6.96 (m, 3H), 6.94 – 6.83 (m, 3H).

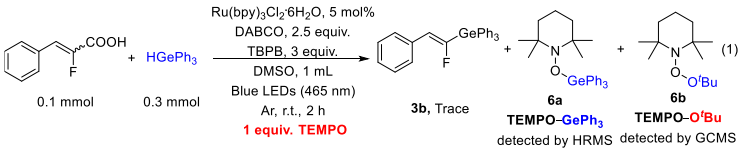
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.58, 143.53, 141.27, 137.72, 134.95, 129.69, 128.67, 128.21, 128.10, 127.81, 127.72, 127.50, 124.98.

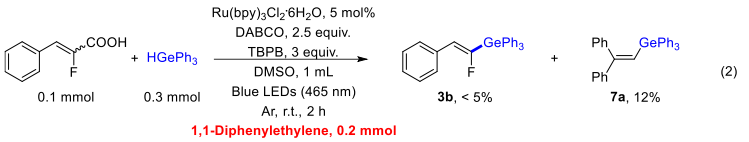
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{26}GeNa$: 507.1139; found: 507.1135.



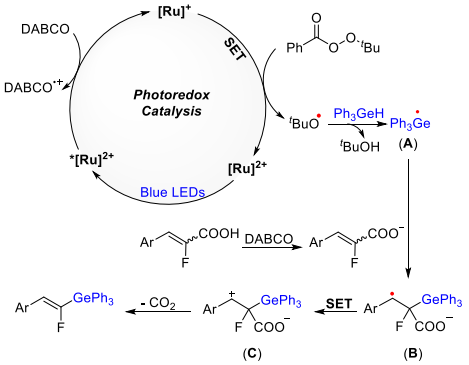

159.58
143.53
141.27
137.72
134.95
129.69
128.67
128.21
128.10
127.81
127.72
127.50
124.98
77.48
77.16
76.84
GePh3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

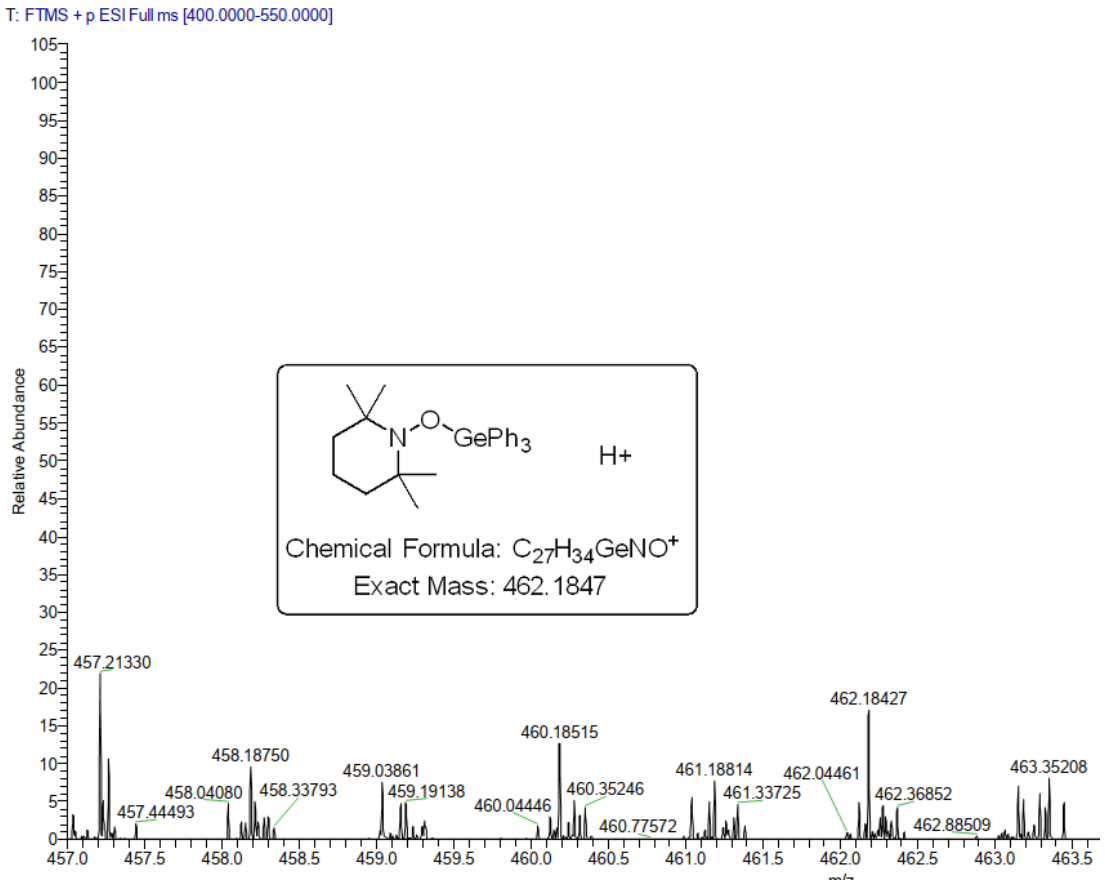
VIII. Mechanistic experiments and proposed catalytic cycle

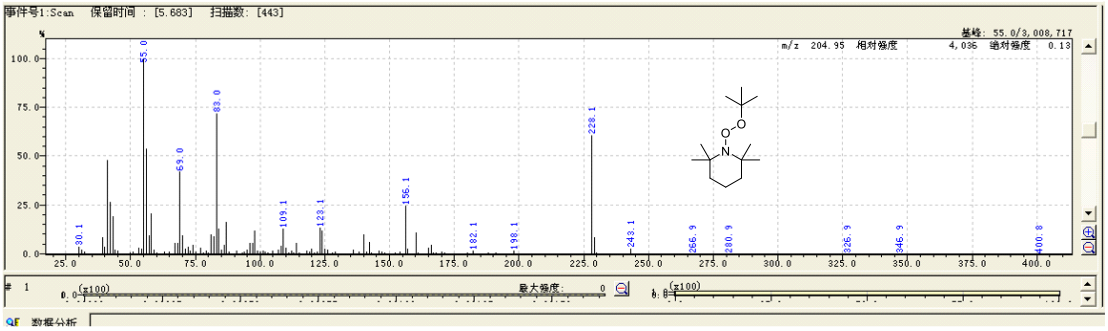




Proposed mechanism



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50.0
25.0
0.0
55.0
83.0
69.0
109.1
123.1
156.1
182.1
198.1
228.1
243.1
266.9
280.9
326.9
346.9
400.8
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
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275.0
300.0
325.0
350.0
375.0
400.0
(x100)
最大强度: 0
(x100)
数据分析

IX. References

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