Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Transition metal free hydrodefluorination of acid fluorides and organofluorines by Ph_3GeH promoted by catalytic $[Ph_3C][B(C_6F_5)_4]$

By

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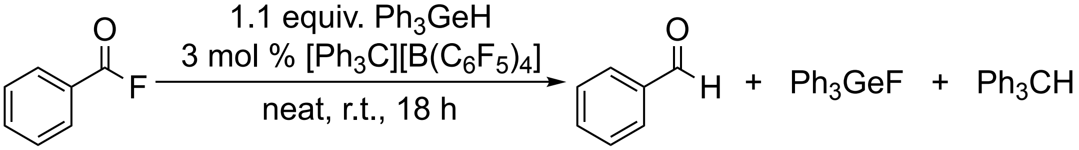
Experimental Procedures and Data

General Considerations

All reactions were carried out using standard Schlenk, syringe, and glovebox techniques. The reagents benzoyl fluoride, pentanoyl fluoride, 1-fluorooctane, 1-fluorocyclohexane, 1,1,1-trifluoromethyltoluene, and 1,3-bis(trifluoromethyl)xylene were purchased from Alfa Aesar. The reagents triphenylgermanium hydride and $[Ph_3C][B(C_6F_5)_4]$ were purchased from Aldrich. All reagents were used without further purification. All NMR solvents were dried over activated molecular sieves and non-deuterated solvents were purified using a Glass Contour Solvent Purification System. NMR spectra were acquire using a Bruker Avance III spectrometer operating at 400.00 (^{1}H) or 376.31 (^{19}F) MHz. GC/MS data were acquired using a Shimadzu QP2010 instrument.

1). Experimental Procedures, NMR, and GC/MS data for the reaction



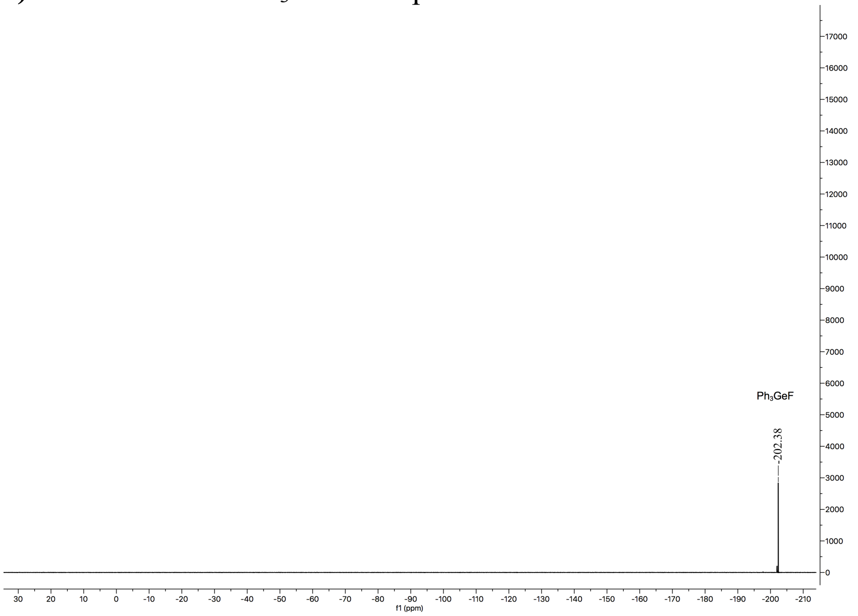
a). Reaction to determine conversion

In a 20 mL vial equipped with a stir bar, benzoyl fluoride (0.200 g, 1.62 mmol) was added via pipette to Ph_3GeH (0.545 g, 1.79 mmol) resulting in the formation of a liquid mixture. To the mixture was added $[Ph_3C][B(C_6F_5)_4]$ (0.045 g, 0.049 mmol) resulting in a yellow liquid. The reaction mixture was stirred at room temperature under nitrogen for 18 h. An aliquot of the product mixture was analyzed by ^{1}H and ^{19}F NMR spectroscopy in benzene-*d*$_6$. The percent conversion (>99 %) was determined by integration of the ^{19}F NMR signals for the benzoyl fluoride starting material and the Ph_3GeF product. An aliquot of the product mixture was also analyzed by GC/MS in CH_2Cl_2 solution.

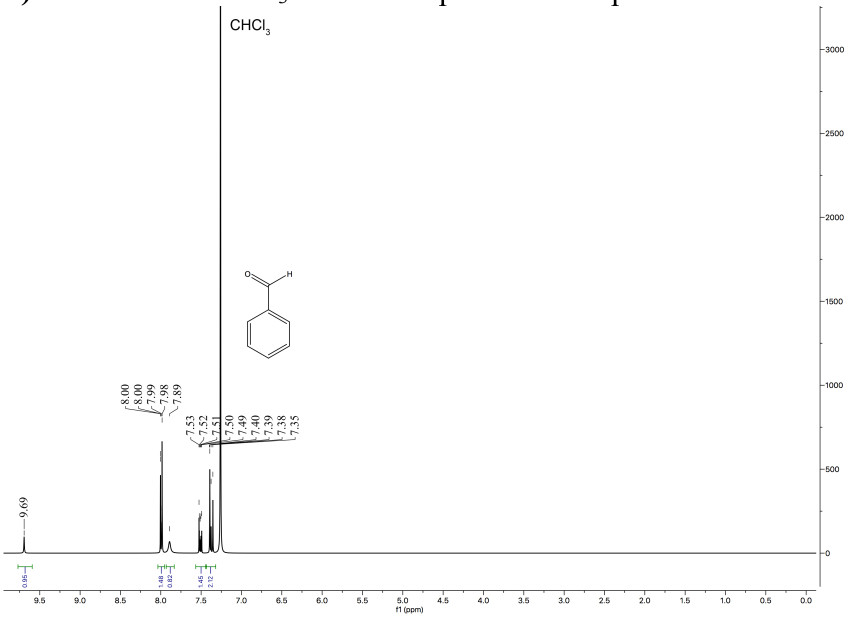
b). Reaction to provide isolated product

A Schlenk flask was charged with Ph_3GeH (0.811 g, 2.66 mmol) and to this was added benzoyl fluoride (0.300 g, 2.42 mmol) via pipette, resulting in a liquid mixture. To this was added $[Ph_3C][B(C_6F_5)_4]$ (0.030 g, 0.033 mmol), resulting in the formation of a yellow liquid mixture. The mixture was stirred at room temperature for 18 h under nitrogen and then was washed with water to separate benzaldehyde from the Ph_3GeF and Ph_3CH byproducts. The benzaldehyde was then extracted from the water layer with Et_2O. The ethereal layer was separated and the solvent was removed *in vacuo* to yield a clear liquid, which was identified to be pure benzaldehyde by NMR (^{1}H and ^{19}F) spectroscopy in $CDCl_3$. Yield: 0.121 g, 46.8%.

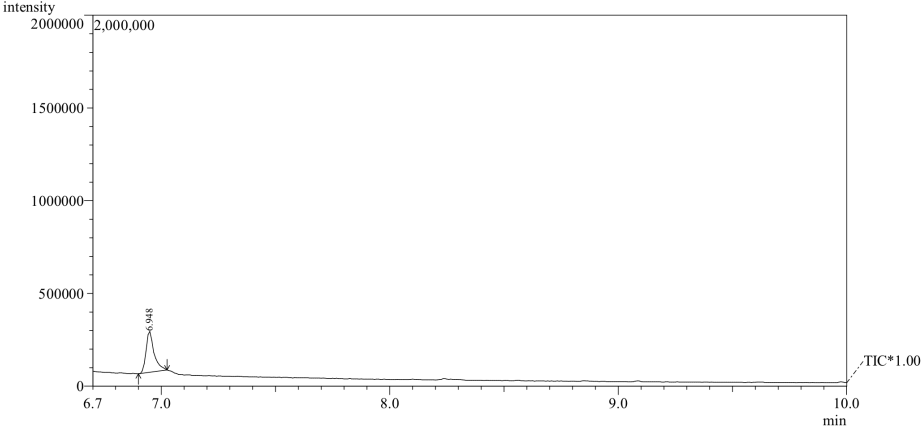
c). ^{19}F NMR in $CDCl_3$ of crude product mixture:



d). ^{1}H NMR in $CDCl_3$ of isolated product after purification:



e). GC of isolated product after purification:



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                                          542305  100.00      220332  100.00
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f). MS of isolated product after purification:

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RawMode:Single 7.0(115)  BasePeak:96(46076)
BG Mode:None
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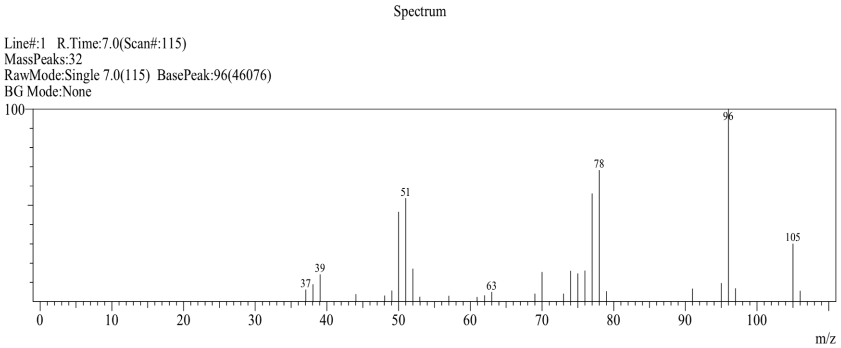

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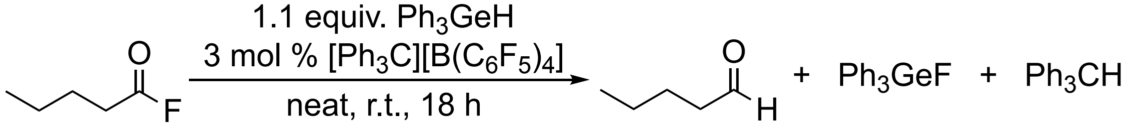
   6    49.05      2573        5.58
   7    50.00     21473       46.60
   8    51.00     24671       53.54
   9    52.00      7842       17.02
  10    52.95      1093        2.37
  11    57.00      1340        2.91
  12    60.95      1052        2.28
  13    62.00      1426        3.09
  14    63.00      2268        4.92
  15    69.00      1836        3.98
  16    70.00      7006       15.21
  17    73.00      1857        4.03
  18    74.00      7316       15.88
  19    75.00      6692       14.52
  20    76.00      7390       16.04
  21    77.00     25817       56.03
  22    78.00     31402       68.15
  23    79.00      2391        5.19
  24    91.00      3052        6.62
  25    95.00      4367        9.48
  26    96.00     46076      100.00
  27    97.00      3106        6.74
  28   105.00     13782       29.91
  29   106.00      2535        5.50
  30   123.00      7422       16.11
  31   124.00     39910       86.62
  32   125.00      3004        6.52
```

2). Experimental Procedure, NMR, and GC/MS data for the reaction

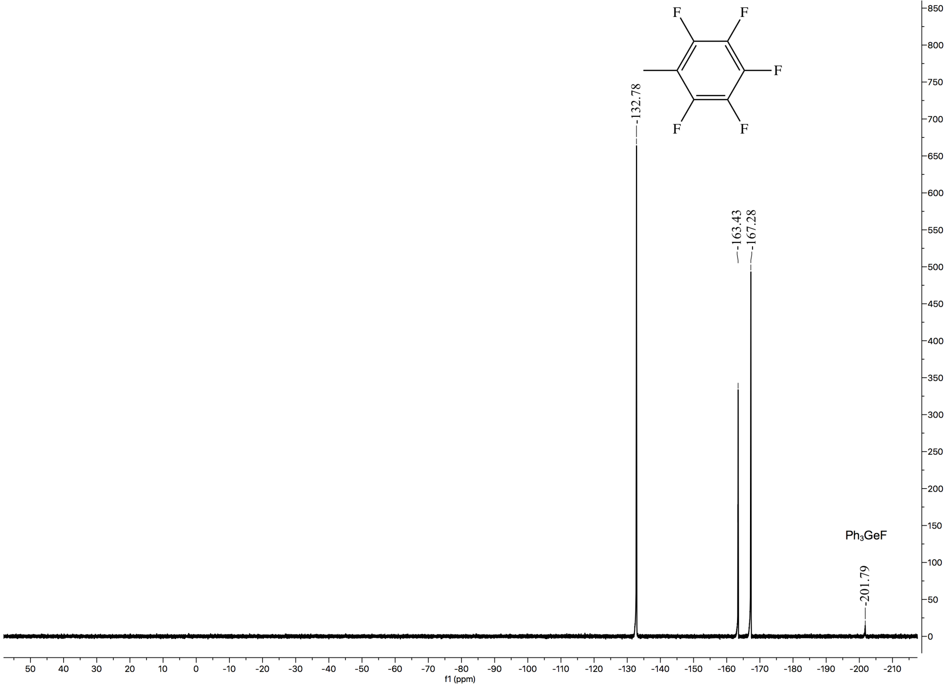


a). Experimental procedure

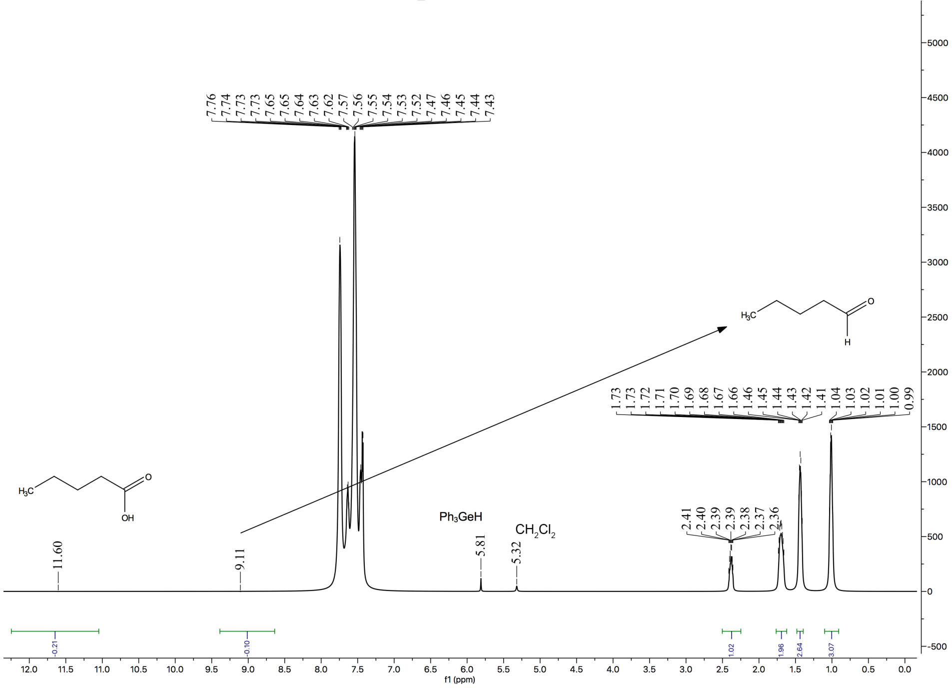
In a 20 mL vial equipped with a stir bar, pentanoyl fluoride (0.100 g, 0.960 mmol) was added via pipette to Ph_3GeH (0.322 g, 1.06 mmol) resulting in the formation of a liquid mixture. To the mixture was added $[Ph_3C][B(C_6F_5)_4]$ (0.026 g, 0.029 mmol) resulting in a yellow liquid. The reaction mixture was stirred at room temperature under nitrogen for

18 h. An aliquot of the product mixture was analyzed by ^{1}H and ^{19}F NMR spectroscopy in CD_2Cl_2. The percent conversion (>99 %) was determined by integration of the ^{19}F NMR signals for the pentanoyl fluoride starting material and the Ph_3GeF product. An aliquot of the product mixture was also analyzed by GC/MS in CH_2Cl_2 solution.

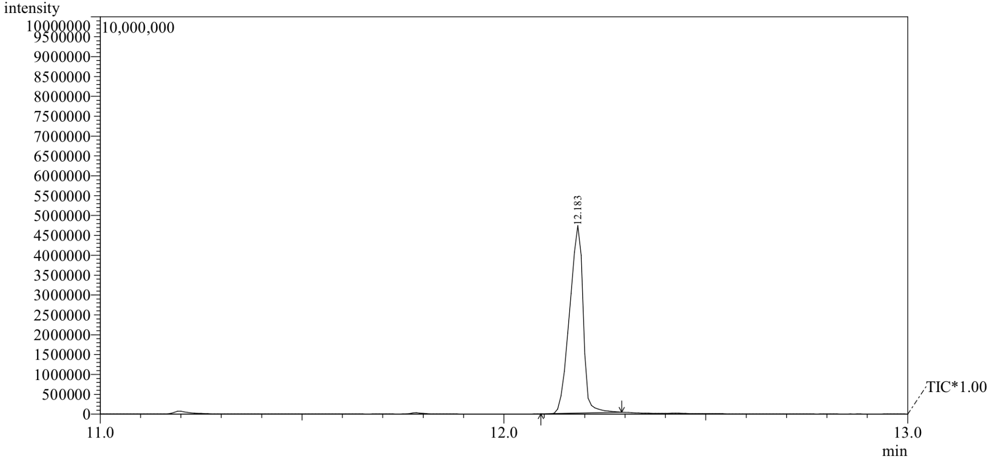
b). ^{19}F NMR in CD_2Cl_2 of crude product mixture:



c). ^{1}H NMR in CD_2Cl_2 of crude product mixture:



d). GC of product mixture:



Peak Report TIC

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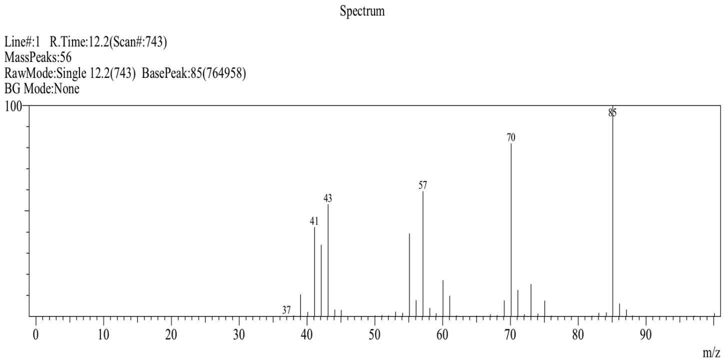
				10920510	100.00	4720668	100.00			

e). MS of product mixture:



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3	39.05	79211	10.35	31	74.05	9266	1.21
4	40.10	15153	1.98	32	75.05	55995	7.32
5	41.10	322906	42.21	33	76.10	1930	0.25
6	42.10	258852	33.84	34	82.05	1717	0.22
7	43.10	405434	53.00	35	83.05	11564	1.51
8	44.10	23420	3.06	36	84.15	13413	1.75
9	45.05	22300	2.92	37	85.10	764958	100.00
10	50.05	2230	0.29	38	86.10	46201	6.04
11	51.05	3781	0.49	39	87.10	23404	3.06
12	52.05	2187	0.29	40	88.05	2599	0.34
13	53.05	16000	2.09				
14	54.10	12303	1.61				
15	55.10	299666	39.17				
16	56.10	58033	7.59				
17	57.10	453754	59.32				
18	58.10	29655	3.88				
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20	60.05	130569	17.07				
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23	65.00	1284	0.17				
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25	68.05	3804	0.50				
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27	70.10	626282	81.87				
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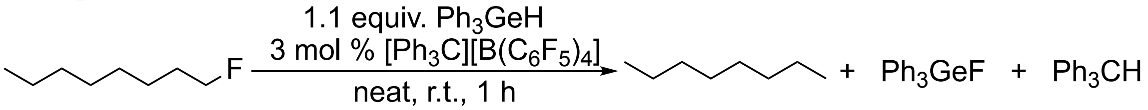
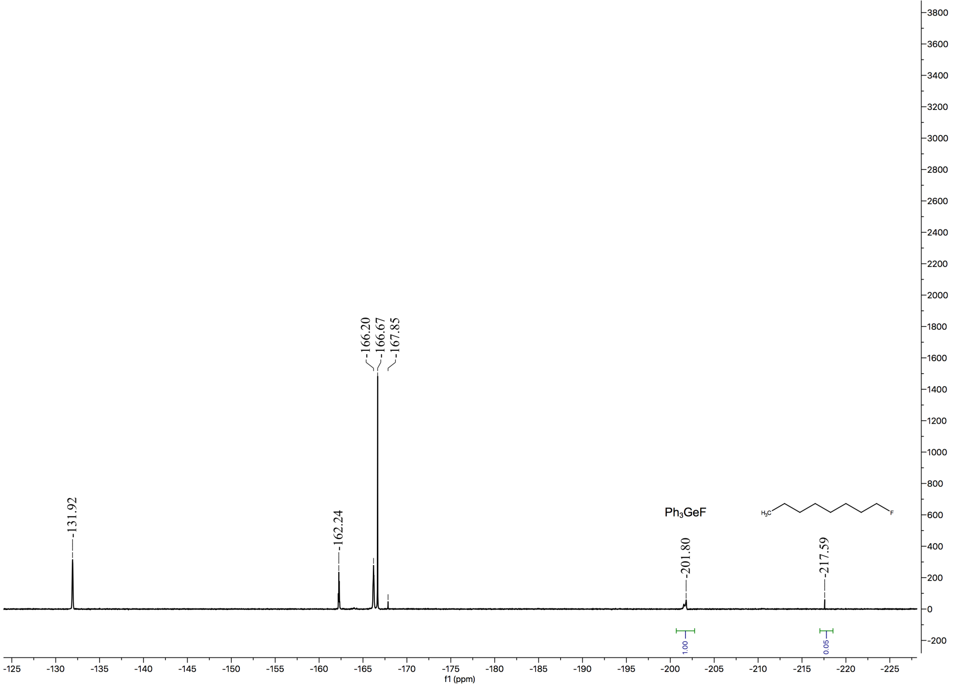
3). Experimental Procedure, NMR, and GC/MS data for the reaction



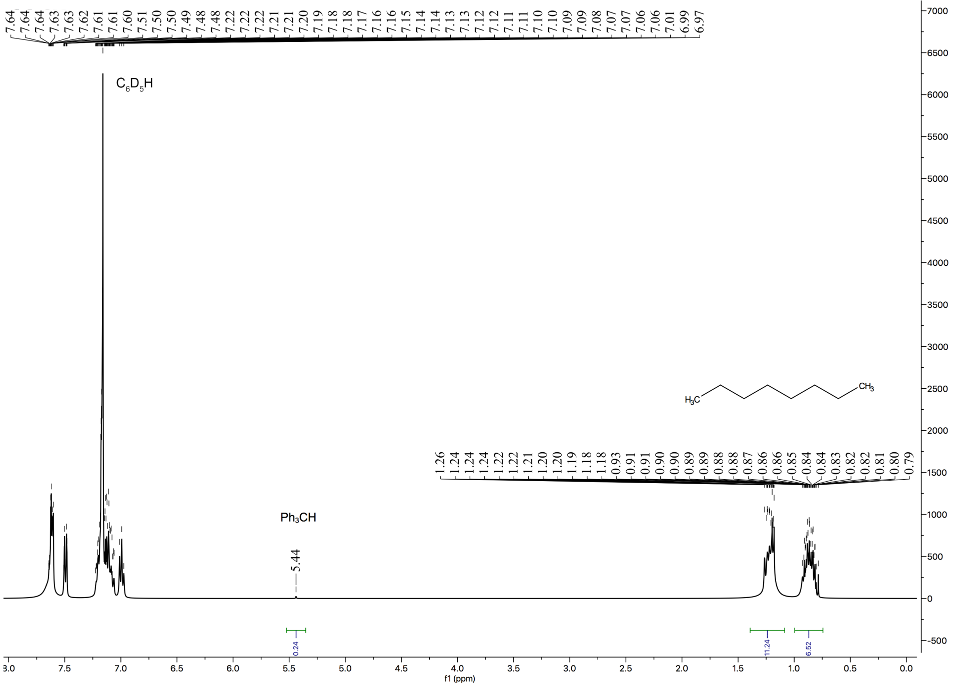
a). Experimental procedure

In a 20 mL vial equipped with a stir bar, 1-fluorooctane (0.110 g, 0.833 mmol) was added via pipette to Ph_3GeH (0.270 g, 0.886 mmol) resulting in the formation of a liquid mixture. To the mixture was added $[Ph_3C][B(C_6F_5)_4]$ (0.020 g, 0.022 mmol) and a white solid formed. The reaction mixture was stirred at room temperature under nitrogen for 1 h. An aliquot of the product mixture was analyzed by ^1H and ^{19}F NMR spectroscopy in benzene-d_6 after filtration of the benzene-d_6 solution through Celite. The percent conversion (>99 %) was determined by integration of the ^{19}F NMR signals for the 1-fluorooctane starting material and the Ph_3GeF product. An aliquot of the product mixture was also analyzed by GC/MS in CH_2Cl_2 solution, which was filtered through Celite prior to injection of the sample.

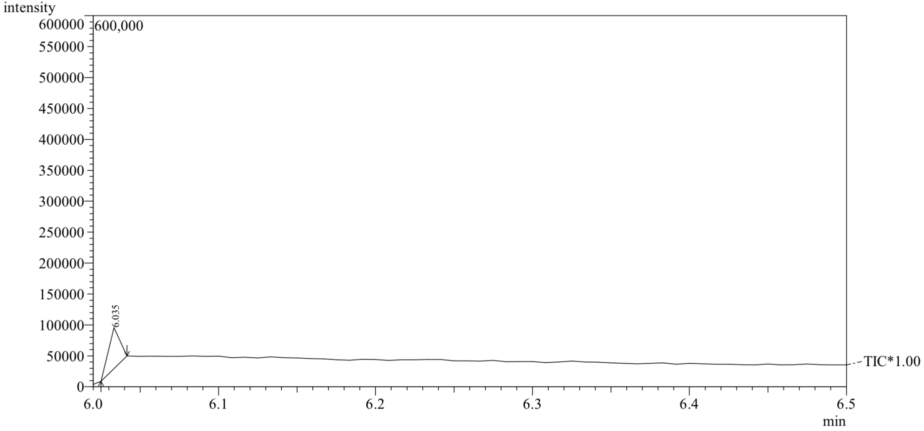
b). ^{19}F NMR in C_6D_6 of crude product mixture:



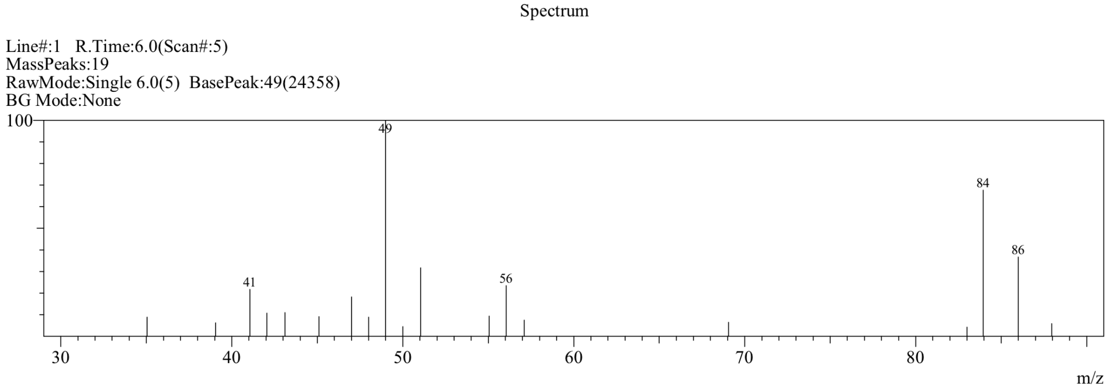
c). ^1H NMR in C_6D_6 of crude product mixture:



d). GC of product mixture:



e). MS of product mixture:



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     6    45.10        2226         9.14
     7    47.00        4450        18.27
     8    48.00        2159         8.86
     9    49.00       24358       100.00
    10    50.00        1098         4.51
    11    51.05        7734        31.75
    12    55.05        2294         9.42
    13    56.05        5704        23.42
    14    57.10        1814         7.45
    15    69.05        1578         6.48
    16    83.00        1031         4.23
    17    83.95       16483        67.67
    18    86.00        8926        36.65
    19    87.95        1443         5.92
```
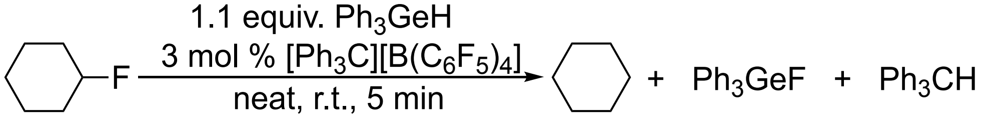
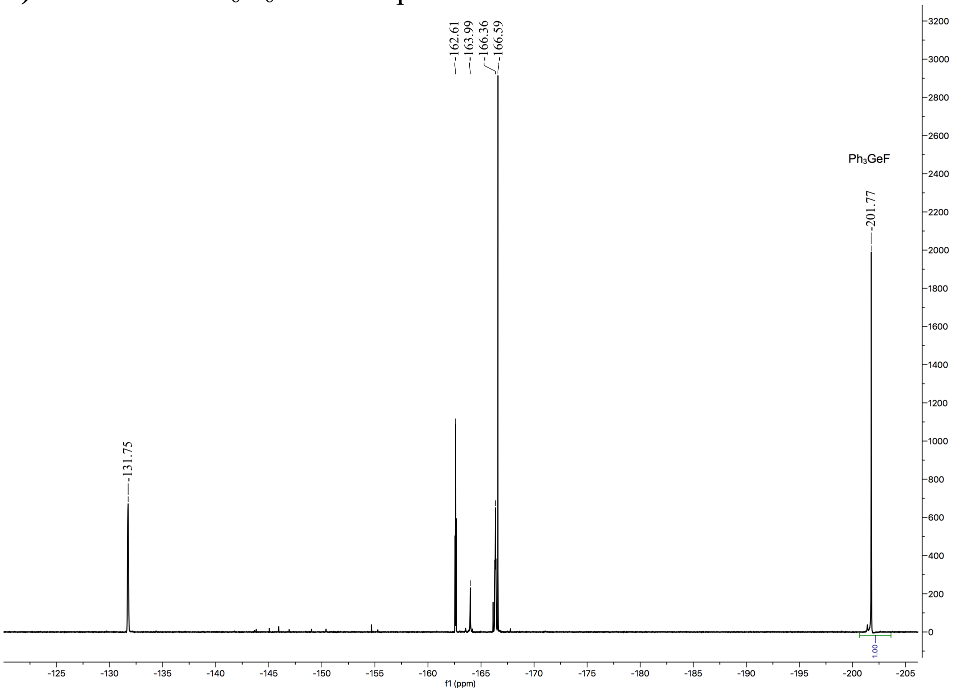

4). Experimental Procedure, NMR, and GC/MS data for the reaction



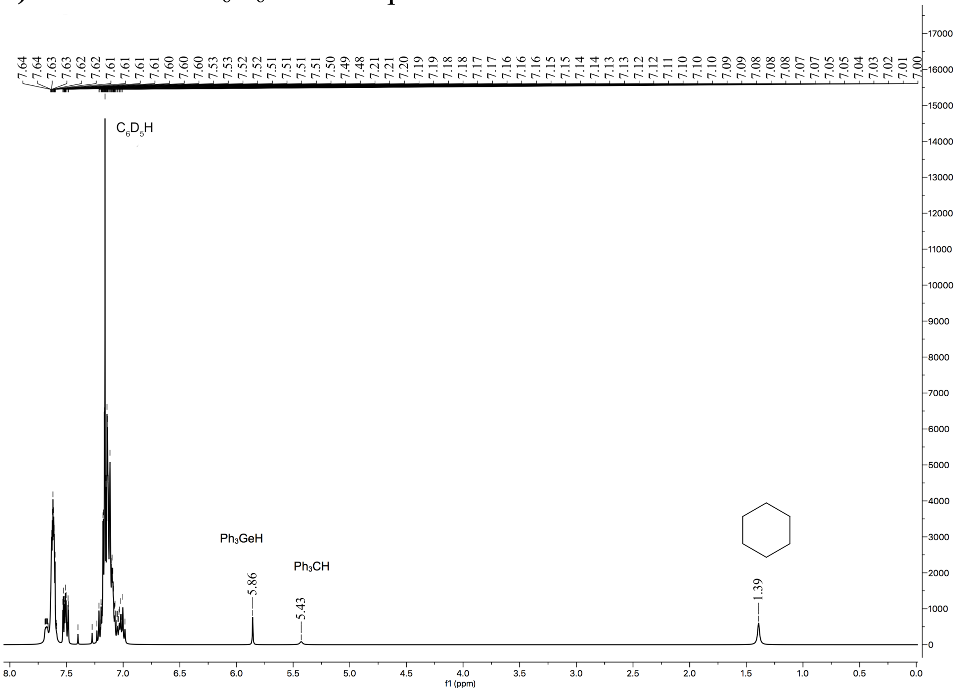
a). Experimental procedure

In a 20 mL vial equipped with a stir bar, 1-fluorocyclohexane (0.100 g, 0.978 mmol) was added via pipette to Ph_3GeH (0.328 g, 1.08 mmol) resulting in the formation of a liquid mixture. To the mixture was added $[Ph_3C][B(C_6F_5)_4]$ (0.027 g, 0.029 mmol) and a white solid formed. The reaction mixture was stirred at room temperature under nitrogen for 5 min. An aliquot of the product mixture was analyzed by ^1H and ^{19}F NMR spectroscopy in benzene-*d*$_6$ after filtration of the benzene-*d*$_6$ solution through Celite. The percent conversion (>99 %) was determined by integration of the ^{19}F NMR signals for the 1-fluorocyclohexane starting material and the Ph_3GeF product. An aliquot of the product mixture was also analyzed by GC/MS in CH_2Cl_2 solution, which was filtered through Celite prior to injection of the sample.

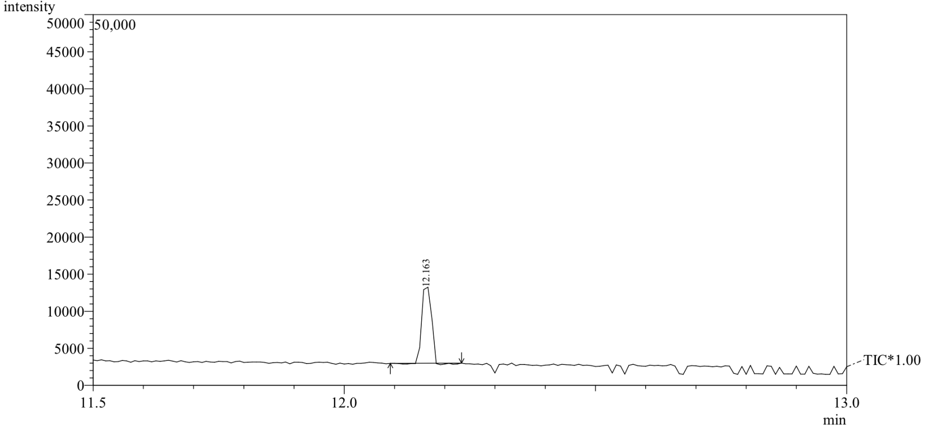
b). ^{19}F NMR in C_6D_6 of crude product mixture:



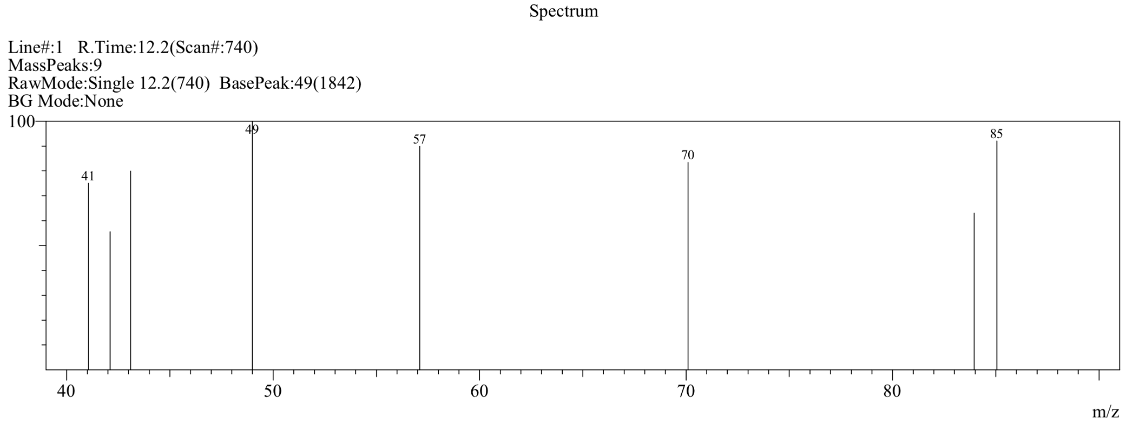
c). ^{1}H NMR in C_6D_6 of crude product mixture:



d). GC of product mixture:



e). MS of product mixture:



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   4     49.00        1842      100.00
   5     57.10        1655       89.85
   6     70.10        1537       83.44
   7     83.95        1162       63.08
   8     85.05        1695       92.02
   9    103.10        1161       63.03
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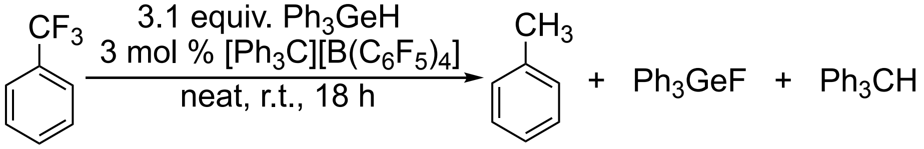
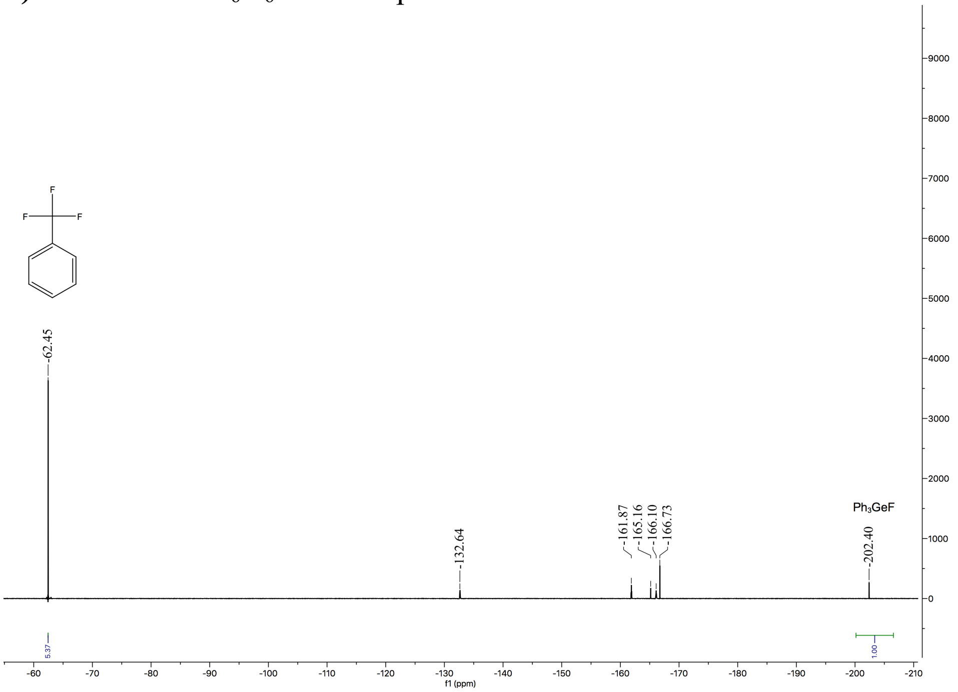
5). Experimental Procedure, NMR, and GC/MS data for the reaction



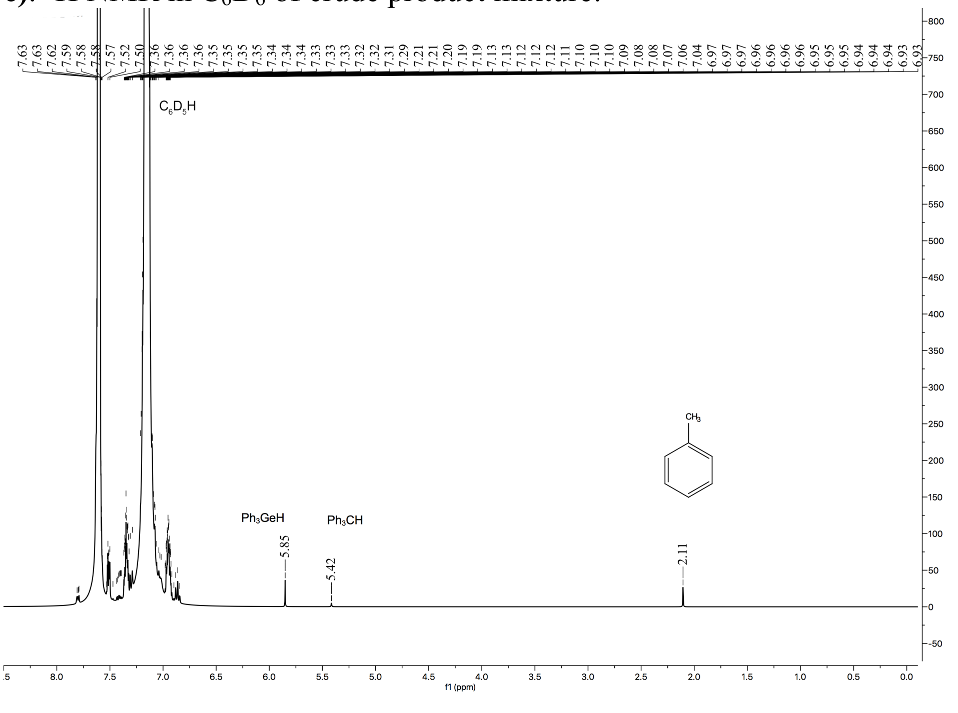
a). Experimental procedure

In a 20 mL vial equipped with a stir bar, 1,1,1-trifluorotoluene (0.060 g, 0.41mmol) was added via pipette to Ph_3GeH (0.388 g, 1.27 mmol) resulting in the formation of a liquid mixture. To the mixture was added $[Ph_3C][B(C_6F_5)_4]$ (0.011 g, 0.012 mmol) and a white solid formed. The reaction mixture was stirred at room temperature under nitrogen for 18 h. An aliquot of the product mixture was analyzed by ^1H and ^{19}F NMR spectroscopy in benzene-d_6 after filtration of the benzene-d_6 solution through Celite. The percent conversion (56 %) was determined by integration of the ^{19}F NMR signals for the 1,1,1-trifluorotoluene starting material and the Ph_3GeF product. An aliquot of the product mixture was also analyzed by GC/MS in hexane solution, which was filtered through Celite prior to injection of the sample.

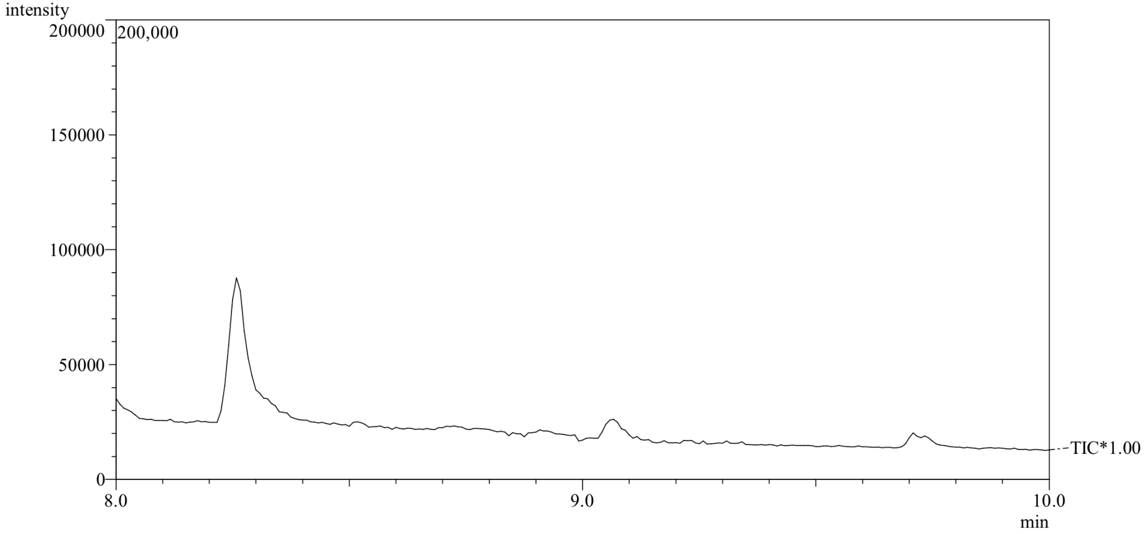
b). ^{19}F NMR in C_6D_6 of crude product mixture:



c). ^{1}H NMR in C_6D_6 of crude product mixture:



d). GC of product mixture:



e). MS of product mixture:

Spectrum

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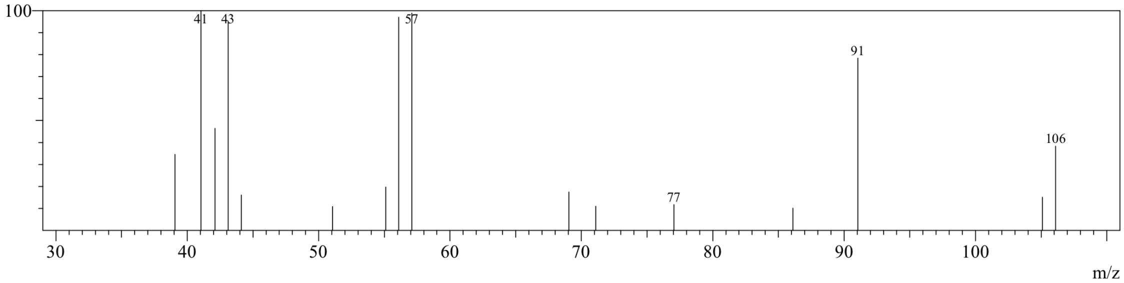

Mass Table
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BG Mode:None

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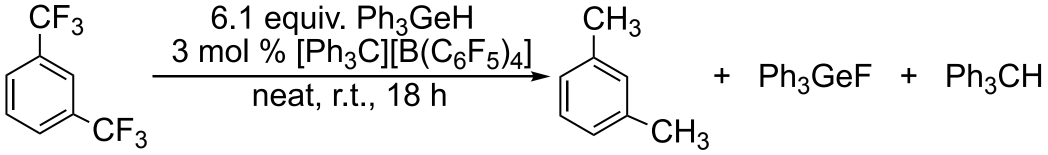
4	43.10	9546	95.22
5	44.10	1609	16.05
6	51.05	1091	10.88
7	55.10	1980	19.75
8	56.10	9719	96.95
9	57.10	9916	98.91
10	69.05	1757	17.53
11	71.10	1097	10.94
12	77.05	1180	11.77
13	86.10	1020	10.17
14	91.05	7854	78.34
15	105.10	1510	15.06
16	106.10	3846	38.36

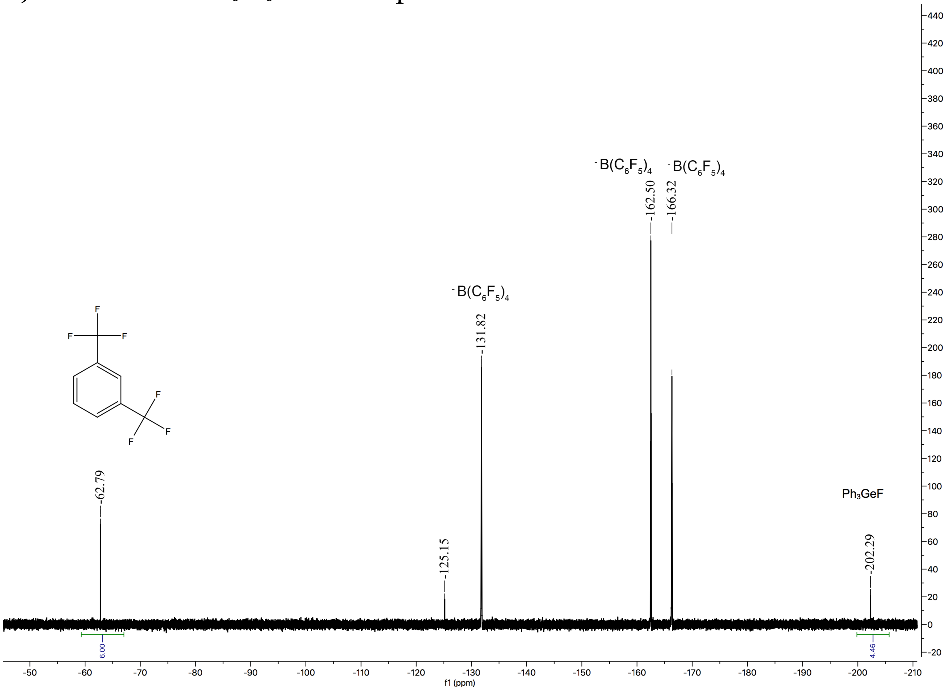
6). Experimental Procedure, NMR, and GC/MS data for the reaction



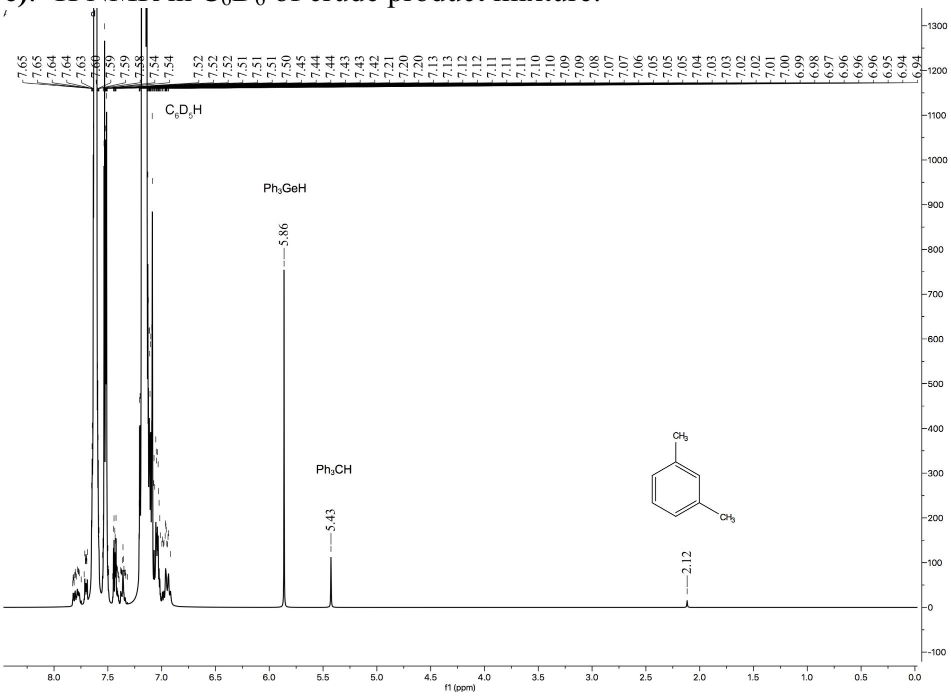
a). Experimental procedure

In a 20 mL vial equipped with a stir bar, 1,3-bis(trifluoromethyl)xylene (0.080 g, 0.37 mmol) was added via pipette to Ph_3GeH (0.695 g, 2.28 mmol) resulting in the formation of a liquid mixture. To the mixture was added $[Ph_3C][B(C_6F_5)_4]$ (0.010 g, 0.011 mmol) and a white solid formed. The reaction mixture was stirred at room temperature under nitrogen for 18 h. An aliquot of the product mixture was analyzed by ^1H and ^{19}F NMR spectroscopy in benzene-d_6 after filtration of the benzene-d_6 solution through Celite. The percent conversion (74 %) was determined by integration of the ^{19}F NMR signals for the 1,3-bis(trifluoromethyl)xylene starting material and the Ph_3GeF product. An aliquot of the product mixture was also analyzed by GC/MS in hexane solution, which was filtered through Celite prior to injection of the sample.

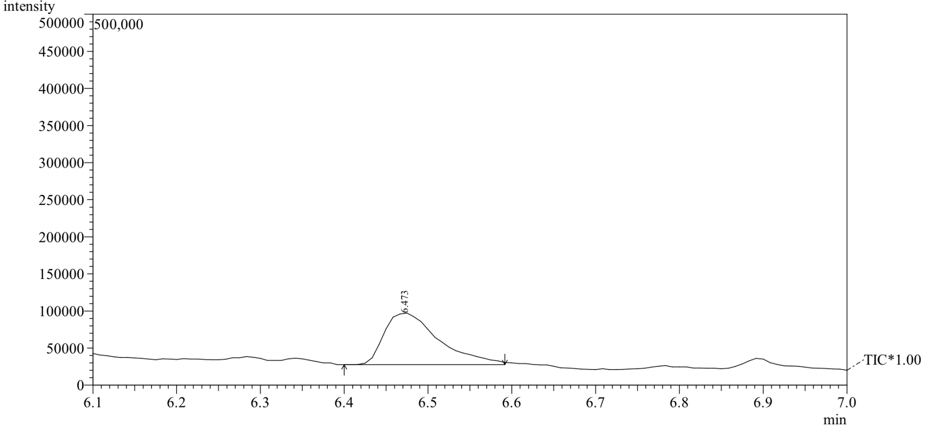
b). ^{19}F NMR in C_6D_6 of crude product mixture:



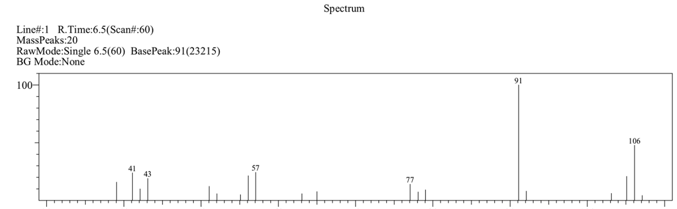
c). ^{1}H NMR in C_6D_6 of crude product mixture:



d). GC of product mixture:



e). MS of product mixture:



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BG Mode:None

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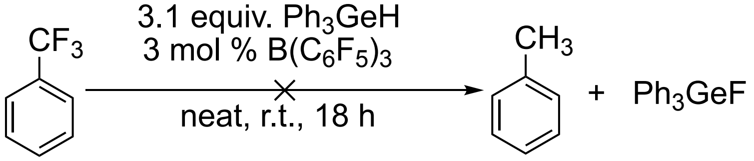
3	42.10	2316	9.98
4	43.10	4417	19.03
5	51.05	2846	12.26
6	52.05	1341	5.78
7	55.10	1159	4.99
8	56.10	4954	21.34
9	57.05	5649	24.33
10	63.05	1343	5.79
11	65.00	1764	7.60
12	77.05	3263	14.06
13	78.10	1706	7.35
14	79.05	2128	9.17
15	91.10	23215	100.00
16	92.10	1862	8.02
17	103.10	1433	6.17
18	105.10	4833	20.82
19	106.10	11089	47.77
20	107.10	1001	4.31

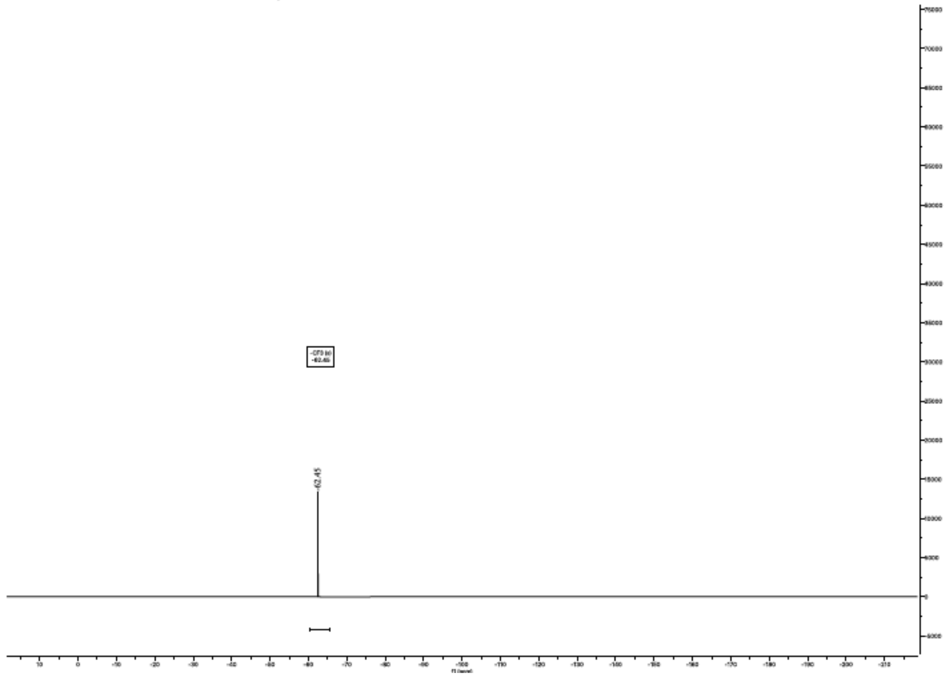
7). Experimental Procedure and ^{19}F NMR data for the reaction



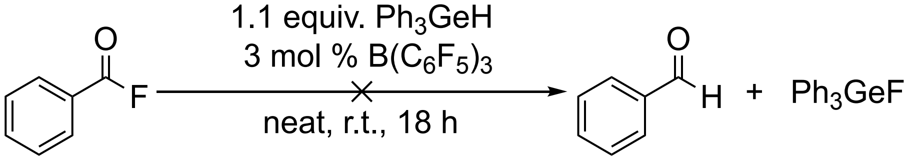
a). Experimental procedure

In a 20 mL vial equipped with a stir bar, 1,1,1-trifluorotoluene (0.100 g, 0.684 mmol) was added via pipette to Ph_3GeH (0.647 g, 2.12 mmol) resulting in the formation of a liquid mixture. To the mixture was added $B(C_6F_5)_3$ (0.011 g, 0.021 mmol). The reaction mixture was stirred at room temperature under nitrogen for 18 h. An aliquot of the product mixture was analyzed by ^{19}F NMR spectroscopy in benzene-d_6 after filtration of the benzene-d_6 solution through Celite. No formation of Ph_3GeF was detected.

b). ^{19}F NMR in C_6D_6 of crude product mixture:



8). Experimental Procedure and ^{19}F NMR data for the reaction

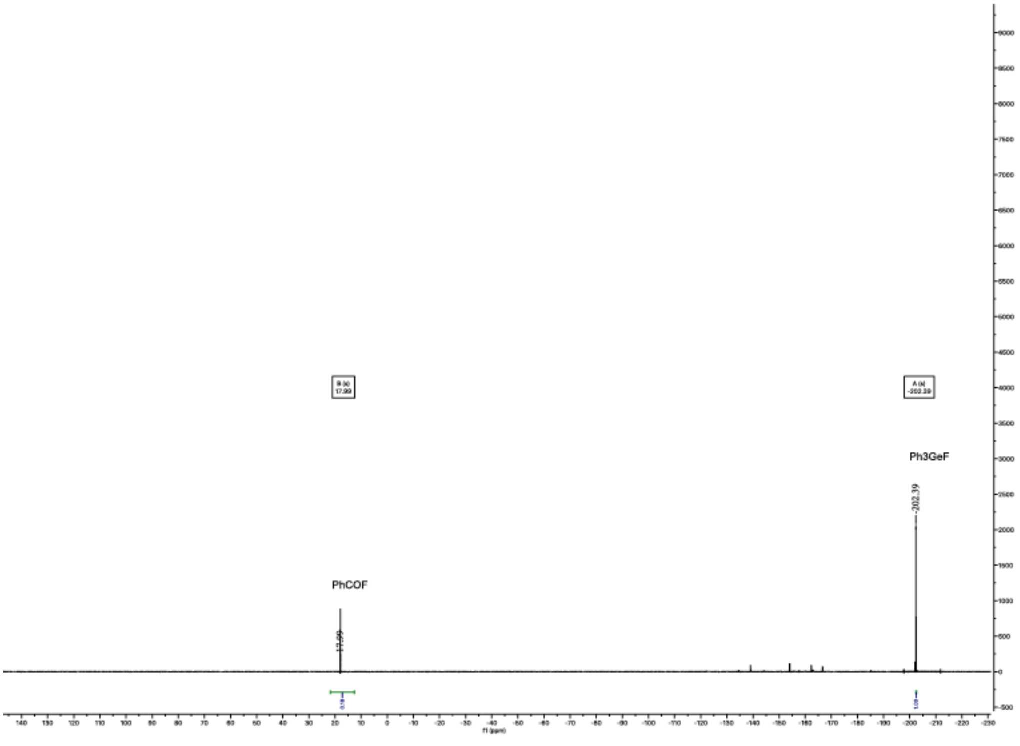


a). Experimental procedure

In a 20 mL vial equipped with a stir bar, benzoyl fluoride (0.120 g, 0.967 mmol) was added via pipette to Ph_3GeH (0.324 g, 1.06 mmol) resulting in the formation of a liquid mixture. To the mixture was added $B(C_6F_5)_3$ (0.015 g, 0.029 mmol) resulting in a yellow liquid. The reaction mixture was stirred at room temperature under nitrogen for 18 h. An aliquot of the product mixture was analyzed by ^{19}F NMR spectroscopy in benzene-d_6.

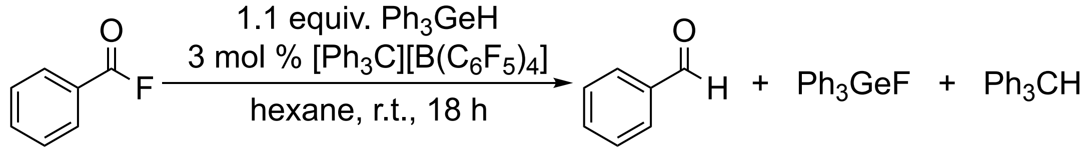
The percent conversion was determined by integration of the ^{19}F NMR signals for the benzoyl fluoride starting material and the Ph_3GeF product.

b). ^{19}F NMR in C_6D_6 of crude product mixture:



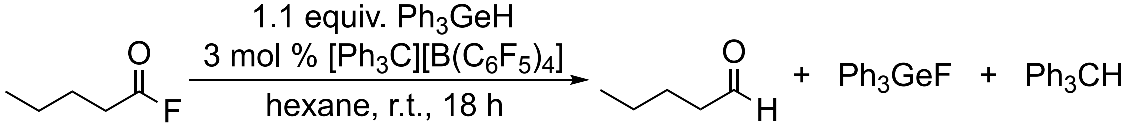
9). Reactions in hexane solvent

a). Experimental Procedure for the reaction



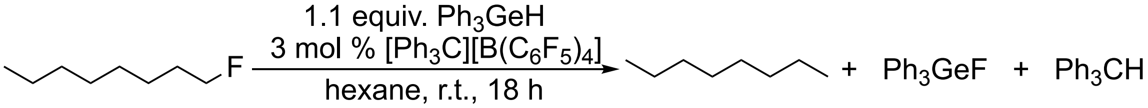
In a 20 mL screw-cap vial, benzoyl fluoride (0.243 g, 1.96 mmol) and Ph_3GeH (0.657 g, 2.16 mmol) were combined in hexane (10 mL) and solid $[Ph_3C][B(C_6F_5)_4]$ was added (0.054 g, 0.059 mmol) to the reaction mixture. After stirring at room temperature for 18 h under nitrogen, the vial was opened, the reaction mixture was filtered through Celite, and the hexane was removed *in vacuo*. The resulting pale yellow liquid was analyzed by NMR (^{1}H and ^{19}F) spectroscopy and GC/MS.

b). Experimental Procedure for the reaction



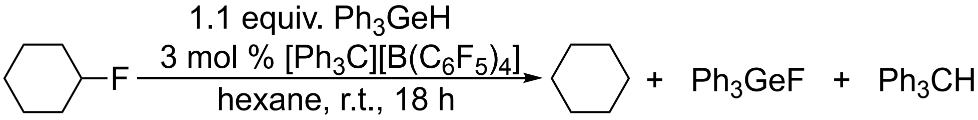
In a 20 mL screw-cap vial, pentanoyl fluoride (0.481 g, 4.62 mmol) and Ph_3GeH (1.55 g, 5.09 mmol) were combined in hexane (15 mL) and solid $[Ph_3C][B(C_6F_5)_4]$ was added (0.127 g, 0.138 mmol) to the reaction mixture. After stirring at room temperature for 18 h under nitrogen, the vial was opened, the reaction mixture was filtered through Celite, and the hexane was removed *in vacuo*. The resulting clear liquid was analyzed by NMR (^1H and ^{19}F) spectroscopy and GC/MS.

c). Experimental Procedure for the reaction



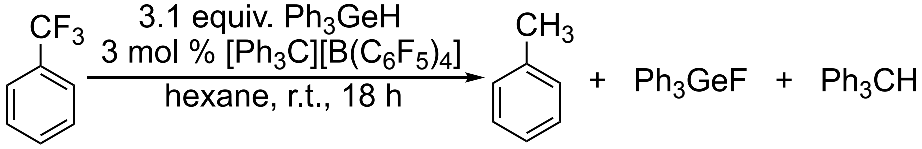
In a 20 mL screw-cap vial, 1-fluorooctane (0.650 g, 4.92 mmol) and Ph_3GeH (1.65 g, 5.41 mmol) were combined in hexane (15 mL) and solid $[Ph_3C][B(C_6F_5)_4]$ was added (0.136 g, 0.148 mmol) to the reaction mixture. After stirring at room temperature for 18 h under nitrogen, the vial was opened, the reaction mixture was filtered through Celite, and the hexane was removed *in vacuo*. The resulting clear liquid was analyzed by NMR (^1H and ^{19}F) spectroscopy and GC/MS.

d). Experimental Procedure for the reaction



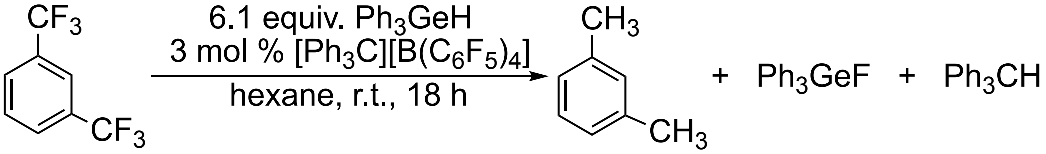
In a 20 mL screw-cap vial, 1-fluorocyclohexane (0.477 g, 4.67 mmol) and Ph_3GeH (1.57 g, 5.14 mmol) were combined in hexane (10 mL) and solid $[Ph_3C][B(C_6F_5)_4]$ was added (0.136 g, 0.129 mmol) to the reaction mixture. After stirring at room temperature for 18 h under nitrogen, the vial was opened, the reaction mixture was filtered through Celite, and the hexane was removed *in vacuo*. The resulting clear liquid was analyzed by NMR (^1H and ^{19}F) spectroscopy and GC/MS.

e). Experimental Procedure for the reaction



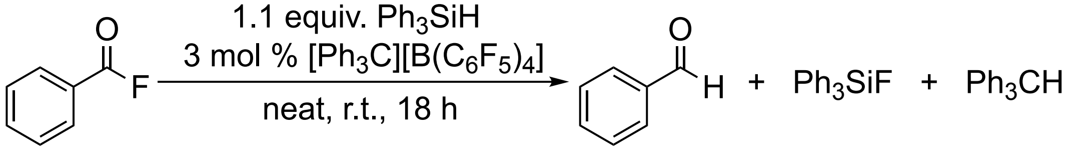
In a 20 mL screw-cap vial, 1,1,1-trifluorotoluene (0.187 g, 1.28 mmol) and Ph_3GeH (1.20 g, 3.97 mmol) were combined in hexane (15 mL) and solid $[Ph_3C][B(C_6F_5)_4]$ was added (0.0351 g, 0.0381 mmol) to the reaction mixture. After stirring at room temperature for 18 h under nitrogen, the vial was opened, the reaction mixture was filtered through Celite, and the hexane was removed *in vacuo*. The resulting clear liquid was analyzed by NMR (^1H and ^{19}F) spectroscopy and GC/MS.

f). Experimental Procedure for the reaction



In a 20 mL screw-cap vial, 1,3-bis(trifluoromethyl)xylene (0.211 g, 0.986 mmol) and Ph_3GeH (1.83 g, 6.00 mmol) were combined in hexane (15 mL) and solid $[Ph_3C][B(C_6F_5)_4]$ was added (0.0273 g, 0.0296 mmol) to the reaction mixture. After stirring at room temperature for 18 h under nitrogen, the vial was opened, the reaction mixture was filtered through Celite, and the hexane was removed *in vacuo*. The resulting clear liquid was analyzed by NMR (^1H and ^{19}F) spectroscopy and GC/MS.

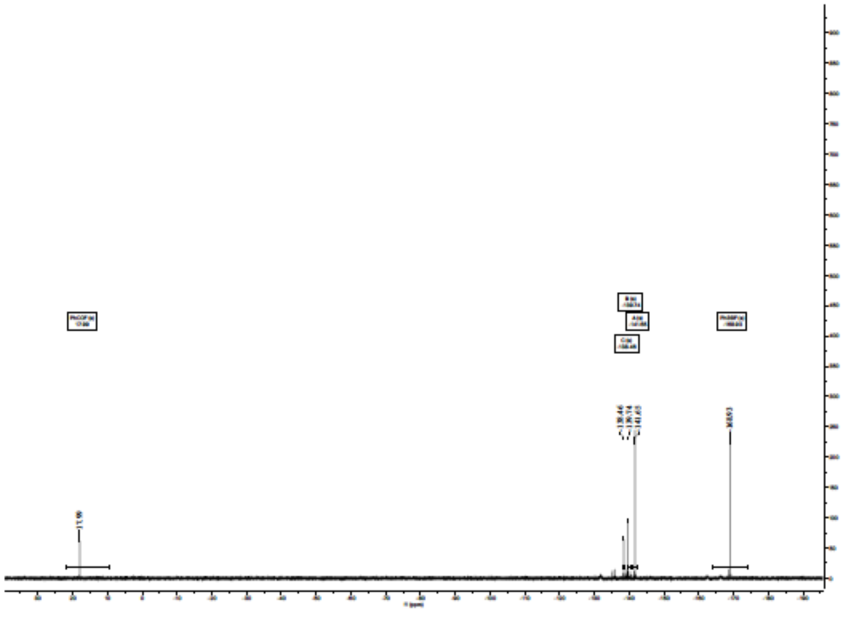
10). Experimental Procedure and ^{19}F NMR data for the reaction



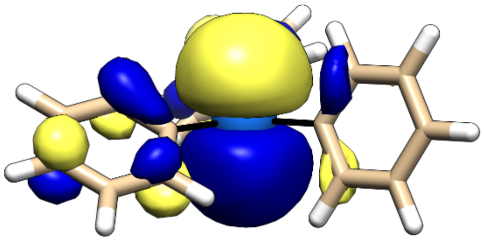
a). Experimental procedure

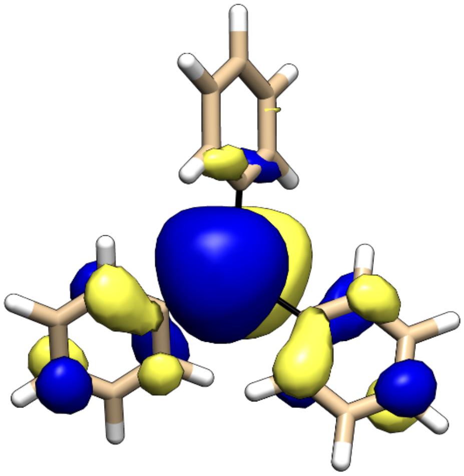
In a 20 mL screw-cap vial, benzoyl fluoride (0.321 g, 2.59 mmol) and Ph_3SiH (0.741 g, 2.85 mmol) were combined and solid $[Ph_3C][B(C_6F_5)_4]$ (0.079 g, 0.086 mmol) was added to the reaction mixture and the reaction mixture immediately became exothermic. After stirring at room temperature for 18 h under nitrogen, the vial was opened and an aliquot of the reaction mixture was analyzed by ^{19}F NMR spectroscopy in C_6D_6 solvent.

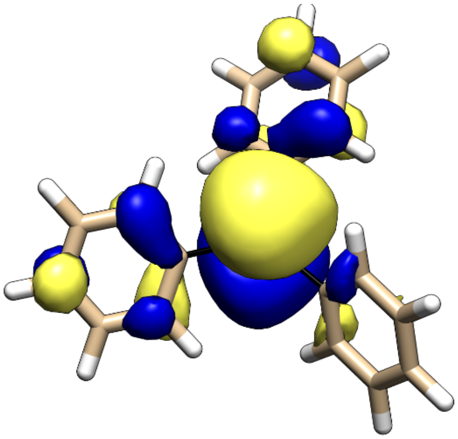
b). ^{19}F NMR in C_6D_6 of crude product mixture:

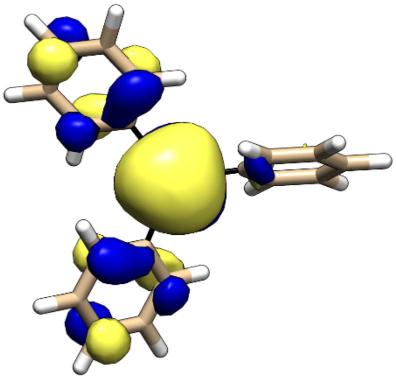


11). Views of the LUMO of the free Ph_3Ge^+ calculated by DFT using the using B3LYP/6-31G(d) basis set[1]:









Minimized geometry of Ph$_3$Ge$^+$ using B3LYP/6-31G(d)

1 C1	4.0853	-2.275	-0.0007	C
2 C2	4.0043	-0.9936	0.5546	C
3 C3	2.793	-0.3097	0.5483	C
4 C4	1.6438	-0.9172	-0.0001	C
5 C5	1.7336	-2.2136	-0.5488	C
6 C6	2.9536	-2.8819	-0.5554	C
7 H7	3.0262	-3.8745	-0.9888	H
8 H8	0.8566	-2.6843	-0.9836	H
9 Ge9	0	-0.0005	-0.0014	Ge
10 C10	-0.0287	1.8812	0.0002	C
11 C11	-1.1339	2.5737	0.5379	C
12 C12	-1.1454	3.9646	0.5442	C
13 C13	-0.0696	4.6744	0.0002	C
14 C14	1.0265	3.9968	-0.5438	C
15 C15	1.0558	2.606	-0.5373	C
16 H16	1.9056	2.0809	-0.9638	H
17 H17	1.8549	4.555	-0.9688	H
18 H18	-0.0858	5.7603	0.0003	H
19 H19	-1.9896	4.4984	0.9694	H
20 H20	-1.9672	2.0238	0.9655	H
21 C21	-1.6159	-0.9659	-0.002	C
22 C22	-2.7842	-0.3932	-0.5471	C
23 C23	-3.9743	-1.1133	-0.5503	C
24 C24	-4.0152	-2.3968	0.0045	C
25 C25	-2.8642	-2.9699	0.5553	C
26 C26	-1.6649	-2.265	0.5458	C
27 H27	-0.7732	-2.7092	0.9784	H

28	H28	-2.9056	-3.9645	0.9881	H
29	H29	-4.9481	-2.9528	0.0074	H
30	H30	-4.8707	-0.6781	-0.9809	H
31	H31	-2.7525	0.6012	-0.9829	H
32	H32	2.7302	0.6833	0.9838	H
33	H33	4.8859	-0.532	0.9882	H
34	H34	5.0345	-2.8028	-0.0015	H

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