Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for the article

Direct amidation of acid fluorides using germanium amides

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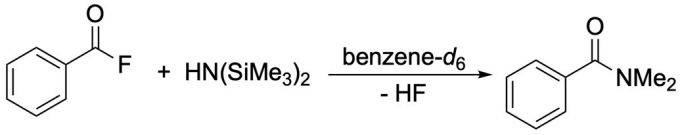


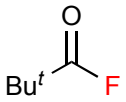
Experimental Procedures

1). General Considerations

The reagents benzoyl fluoride, pivaloyl chloride, propionyl chloride, 3-phenylpropionyl chloride were purchased from TCI America and used without further purification. The reagents *N*-bromosuccinimide, triphenylphosphine, benzoic acid, lithium di*iso*propylamide, triphenylgermanium chloride, and tetrabutylammonium fluoride were purchased from Sigma Aldrich and used without further purification. The germylamine Ph_3GeNMe_2 was synthesized according to the literature procedure.[1, 2] NMR spectra were acquired using a Bruker Advance spectrometer operating at 400.1 MHz (^{1}H), 100.6 MHz (^{13}C), 376.4 MHz (^{19}F), 79.5 MHz (^{29}Si) or 162.0 MHz (^{31}P). GC/MS data were acquired using a Shimadzu QP2010 GC/MS and HRAM-MS were collected using a Thermo Fisher Q Exactive Hybrid Quadrupole Orbitrap mass spectrometer.

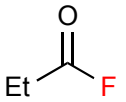
2). Starting Material Syntheses

a). Synthesis of pivaloyl fluoride



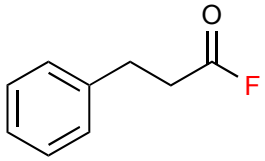
Pivaloyl chloride (2.00 g, 16.6 mmol, 1 equiv.) was dissolved in dichloromethane in a screw-cap vial. Sodium fluoride (1.04 g, 24.9 mmol, 1.5 equiv) was slowly added as a solid and the mixture was stirred overnight at room temperature. The reaction mixture was then filtered through Celite and the volatiles were removed *in vacuo* to yield pivaloyl fluoride (0.98 g, 57 %). ^{1}H NMR ($CDCl_3$, 25 ºC) δ 1.27 (s, 9H, -C(C*H*$_3$)$_3$) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 173.7 (*C*=O), 26.8 (-*C*(CH$_3$)$_3$), 25.5 (-C(*C*H$_3$)$_3$) ppm. ^{19}F NMR ($CDCl_3$, 25 ºC) δ 25.3 (CO*F*) ppm. The NMR spectra are consistent with the literature data.[3]

b). Synthesis of propionyl fluoride



Propionyl chloride (2.00 g, 21.6 mmol, 1 equiv.) was dissolved in dichloromethane in a screw-cap vial. Sodium fluoride (1.36 g, 32.4 mmol, 1.5 equiv.) was slowly added as a solid and the mixture was stirred overnight at room temperature. The reaction mixture was then filtered through Celite and the volatiles were removed *in vacuo* to yield propionyl fluoride (1.02 g, 62 %). ^{1}H NMR (C_6D_6, 25 ºC) δ 2.12 (q, J = 8.1 Hz, 2H, -C*H*$_2$CH$_3$), 0.62 (t, J = 8.1 Hz, 3H -CH$_2$C*H*$_3$)) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 174.1 (*C*=O), 40.6 (-*C*H$_2$CH$_3$), 9.2 (-CH$_2$*C*H$_3$) ppm. ^{19}F NMR ($CDCl_3$, 25 ºC) δ 42.8 (CO*F*) ppm. The NMR spectra are consistent with the literature data.[4]

c). Synthesis of 3-phenylpropionyl fluoride



3-Phenylpropionyl chloride (2.00 g, 11.9 mmol, 1 equiv.) was dissolved in chloroform in a screw-cap vial. Sodium fluoride (0.747 g, 17.8 mmol, 1.5 equiv) was slowly added to the solution as a solid and the mixture was stirred overnight at room temperature. The reaction mixture was then filtered through Celite and the volatiles were removed *in vacuo* to yield propionyl fluoride (1.19 g, 66 %). ^{1}H NMR (C_6D_6, 25 ºC) δ 7.08 (d, J = 7.2 Hz, 2H, *o*-C_6H_5), 7.05 – 7.01 (m, 2H, *m*-C_6H_5), 6.95 (d, J = 8.4 Hz, 1H, *p*-C_6H_5), 2.79 (t, J = 8.0 Hz, 2H, $PhCH_2CH_2$-), 2.69 (t, J = 8.0 Hz, 2H, $PhCH_2CH_2$-) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 172.7 (*C*=O), 140.5 (*ipso*-C_6H_5), 128.8 (*o*-C_6H_5), 128.7 (*m*-C_6H_5), 126.9 (*p*-C_6H_5), 35.7 ($PhCH_2CH_2$), 30.7 ($PhCH_2CH_2$) ppm. ^{19}F NMR (C_6D_6, 25 ºC) δ 44.9 (CO*F*) ppm. The NMR spectra are consistent with the literature data.[5]

d). Synthesis of *N,N*-di*iso*propyltriphenylgermylamine

$Ph_3GeNPr^i_2$

In a Schlenk flask, triphenylgermanium chloride (2.79 g, 8.22 mmol, 1 equiv.) was dissolved in benzene (35 mL). To this was added a 2 M solution of lithium di*iso*propylamide in THF (1.06 g, 4.93 mL, 9.86 mmol, 1.2 equiv.) via syringe. The reaction mixture was stirred overnight and the reaction mixture was diluted with benzene (40 mL). The reaction mixture was filtered through Celite and the volatiles were removed *in vacuo* to yield *N,N*-di*iso*propyltriphenylgermylamine (2.89 g, 87 %) as a yellow solid. ^{1}H NMR (C_6D_6, 25 ºC) δ 7.82 (d, J = 6.8 Hz, 6H, *o*-C_6H_5), 7.61 – 7.52 (m, 9H, *m*-C_6H_5 and *p*-C_6H_5), 3.38 (sept, J = 6.8 Hz, 2H, -$CH(CH_3)_2$), 1.12 (d, J = 6.8 Hz, 12H, -$CH(CH_3)_2$) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 139.0 (*ipso*-C_6H_5), 135.9 (*o*-C_6H_5), 128.4 (*m*-C_6H_5), 127.9 (*p*-C_6H_5), 48.2 (-$CH(CH_3)_2$), 25.6 (-$CH(CH_3)_2$) ppm. HRAM-MS: Calcd. m/z = 406.1585 ($M + H^+$). Found: 406.1578 ($M + H^+$).

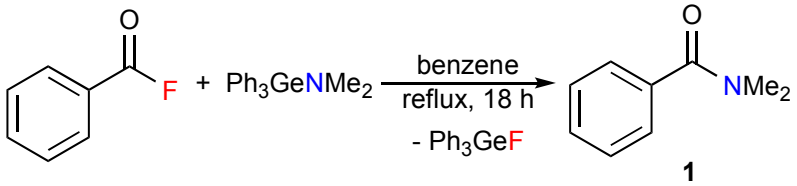
e). Synthesis of *N,N*-bis(trimethylsilyl)triphenylgermylamine

$Ph_3GeN(SiMe_3)_2$

In a Schlenk flask, triphenylgermanium chloride (0.500 g, 1.47 mmol, 1 equiv.) was dissolved in benzene (20 mL). To this was added a solution of lithium bis(trimethylsilyl)amide (0.295 g, 1.77 mmol, 1.2 equiv.) in THF (10 mL) via syringe. The reaction mixture was stirred overnight and the reaction mixture was diluted with benzene (25 mL). The reaction mixture was filtered through Celite and the volatiles were removed *in vacuo* to yield *N,N*-bis(trimethylsilyl)triphentlgermylamine (0.512 g, 75 %) as a pale yellow solid. ^{1}H NMR (C_6D_6, 25 ºC) δ 7.68 (d, J = 7.6 Hz, 6H, *o*-C_6H_5), 7.22 – 7.17 (m, 9H, *m*-C_6H_5 and *p*-C_6H_5), 0.23 (s, 18 H, -$Si(CH_3)_3$) ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 135.3 (*ipso*-C_6H_5), 134.5 (*o*-C_6H_5), 130.6 (*m*-C_6H_5), 128.9 (*p*-C_6H_5), 5.3 (-$Si(CH_3)_3$) ppm. ^{29}Si NMR (C_6D_6, 25 ºC) δ – 111.3 (-$Si(CH_3)_3$) ppm. HRAM-MS: Calcd. m/z = 466.1436 ($M + H^+$). Found: 466.1431 ($M + H^+$).

3). Amidation Reactions

A). Experimental procedure and spectral data for the reaction:

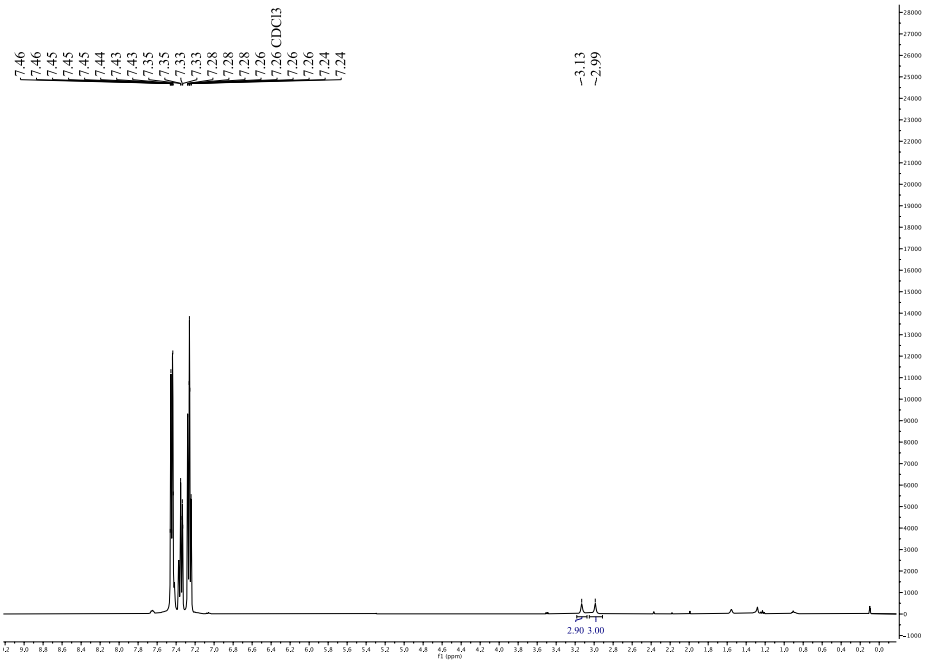


1

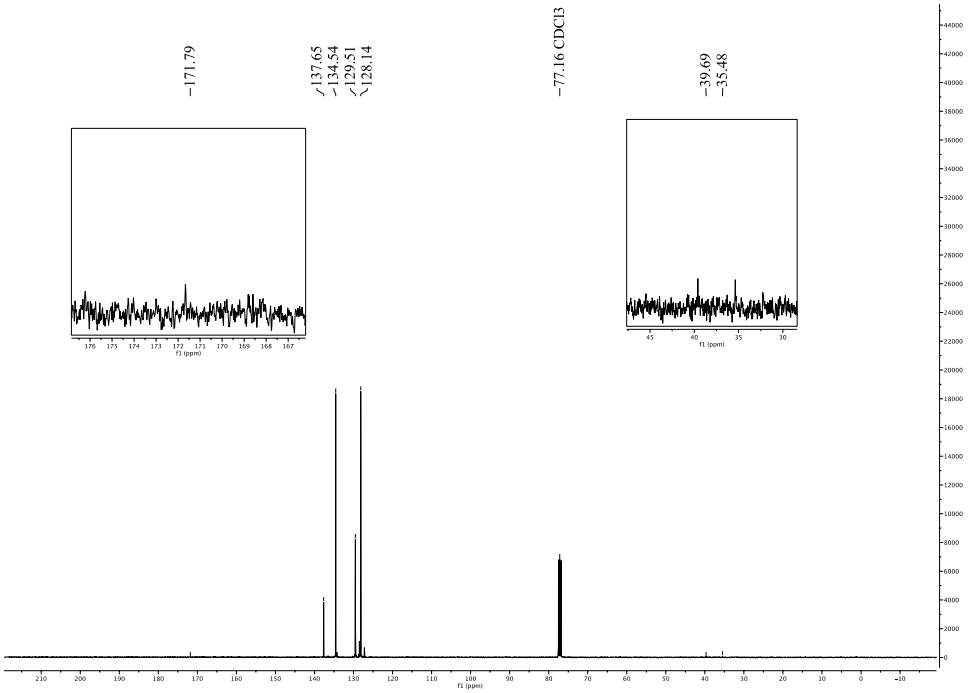
i). Experimental procedure:

Benzoyl fluoride (0.200 g, 1.61 mmol, 1 equiv.) was dissolved in benzene in a Schlenk flask. *N,N*-Dimethyltriphenylgermylamine (Ph_3GeNMe_2, 0.619 g, 1.77 mmol 1.1 equiv.) was slowly added to the reaction mixture and then the mixture was refluxed for 18 h. The solvent was removed *in vacuo* to yield a yellow oil that was purified using a silica gel column with dichloromethane as the eluent. The dichloromethane solution was discarded and the column was washed with ethyl acetate. Removal of the ethyl acetate resulted in the isolation of *N,N*-dimethylbenzamide (**1**) as a white solid. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.52 – 7.32 (m, 5H -C_6H_5), 3.13 (s, 3H, -N(CH_3)$_2$), 2.99 (s, 3H, -N(CH_3)$_2$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.8 (*C*=O), 137.7 (*ipso*-C_6H_5), 134.5 (*o*-C_6H_5), 129.5 (*m*-C_6H_5), 128.1 (*p*-C_6H_5), 39.7 (-N(CH_3)$_2$), 35.5 (-N(CH_3)$_2$) ppm. The NMR spectral data are consistent with the published data.[6]

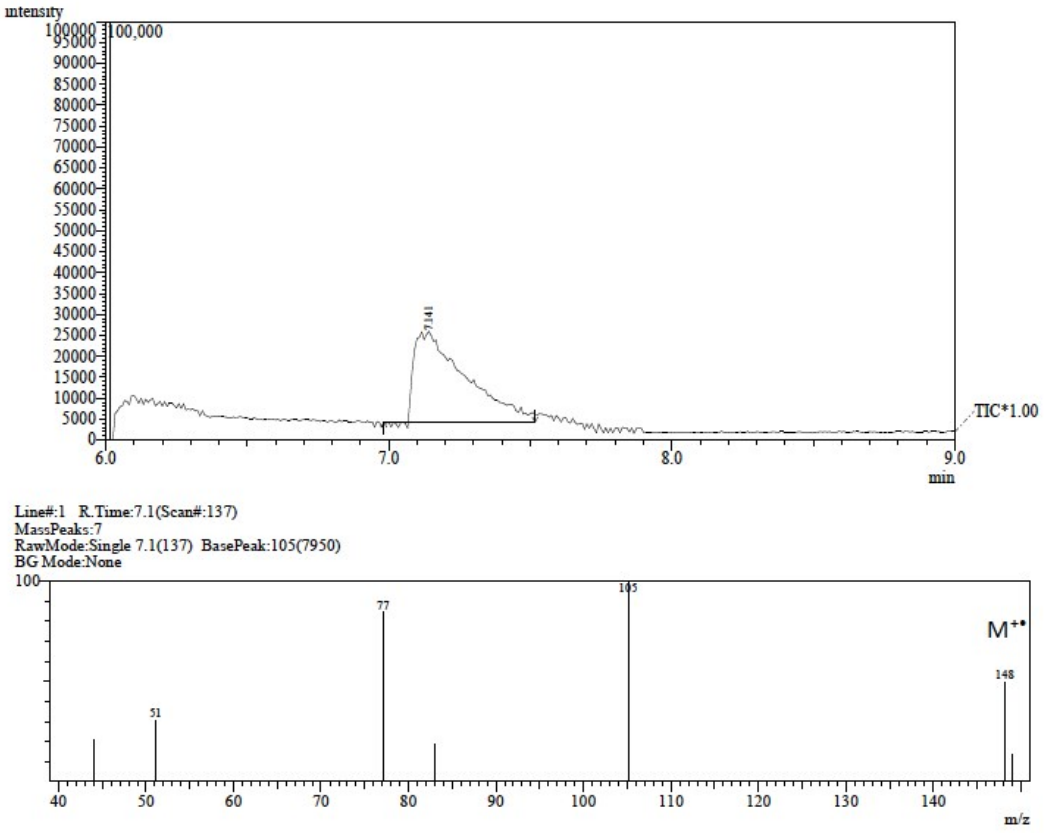
ii). ^{1}H NMR spectrum of 1 (400.1 MHz, $CDCl_3$):



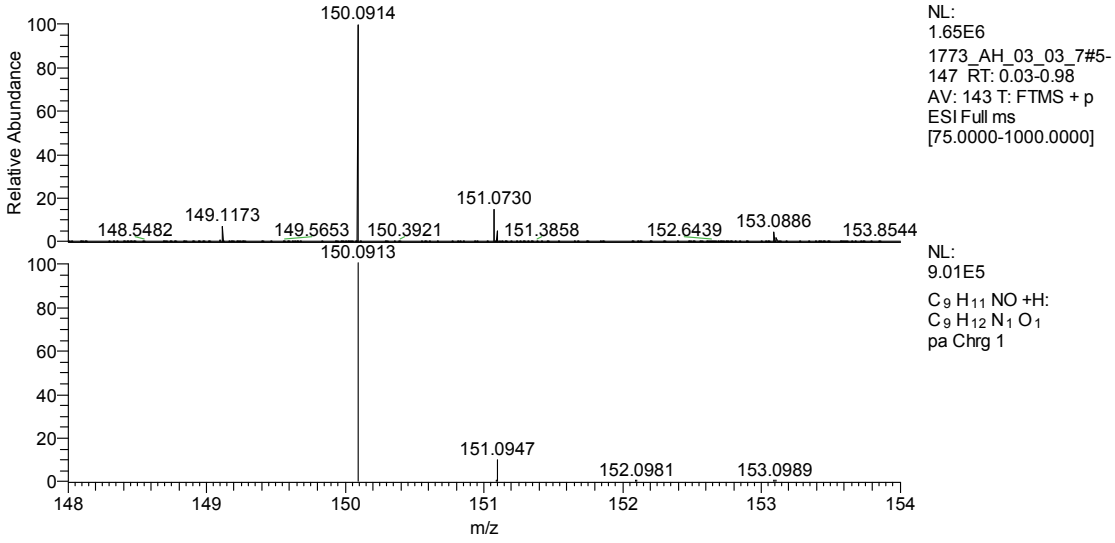
iii). ^{13}C NMR spectrum of 1 (100.6 MHz, $CDCl_3$):



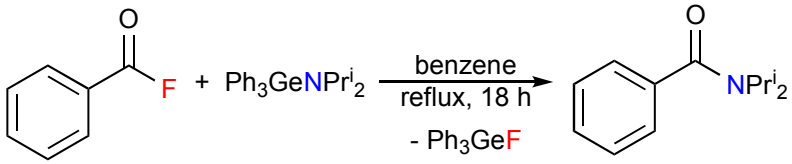
iv). GC/EI-MS of 1:



v). HRAM MS of 1 in water (Top, experimental spectrum; bottom, calculated spectrum):



B). Experimental procedure and spectral data for the reaction:

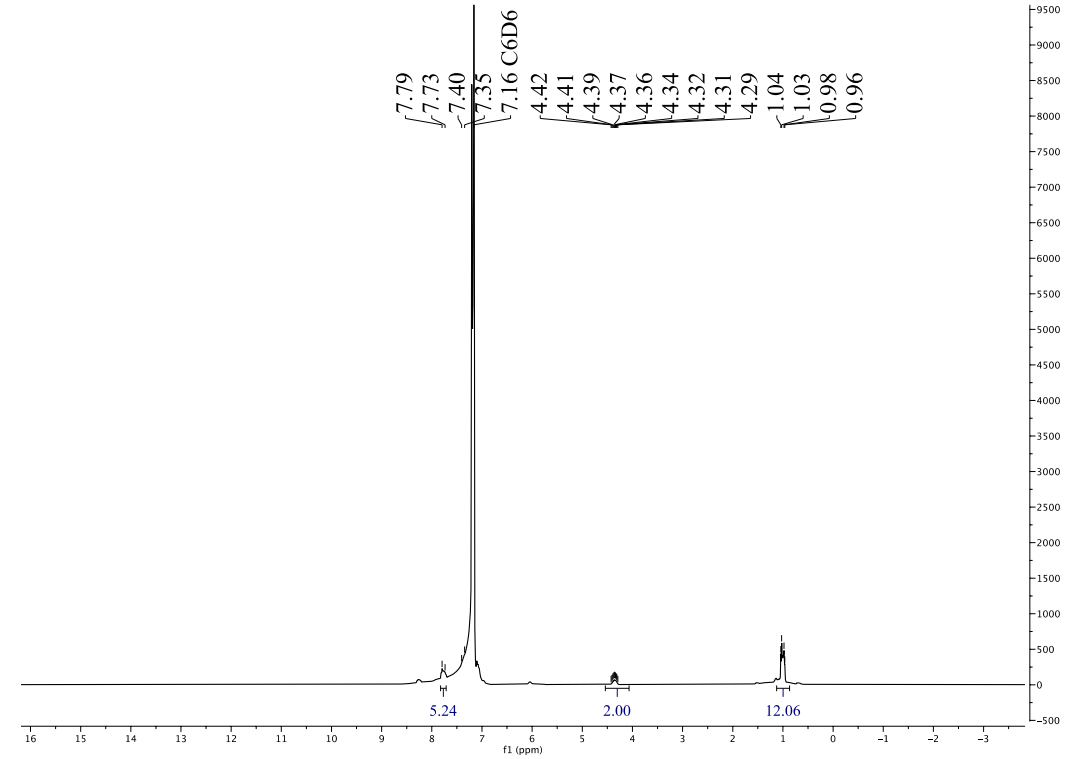


2

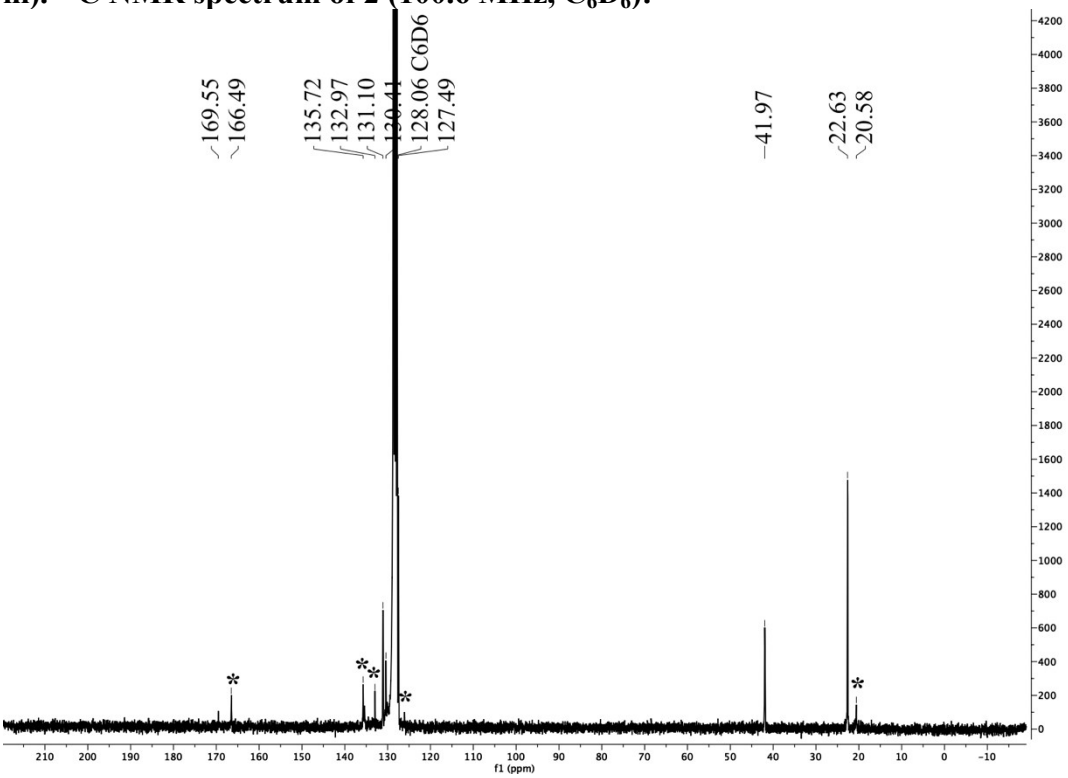
i). Experimental procedure:

Benzoyl fluoride (0.100 g, 0.805 mmol, 1 equiv.) was dissolved in benzene in a Schlenk flask. *N,N*-Di*iso*propyltriphenylgermylamine ($Ph_3GeNPr^i_2$, 0.358 g, 0.866 mmol, 1.1 equiv.) was slowly added to the reaction mixture and then the mixture was refluxed for 18 h. The reaction mixture was filtered through Celite and the solvent was removed *in vacuo*. The resulting yellow oil was purified using a silica gel column using benzene. The benzene washes were discarded and the column was washed with chloroform. Removal of the chloroform *in vacuo* resulted in the isolation of *N,N*-di*iso*propylbenzamide (**2**) as a white solid. ^{1}H NMR (400.1 MHz, C_6D_6) δ 7.85 – 7.65 (m, 5H, -C_6H_5), 4.54 – 4.13 (m, 2H, -C*H*$(CH_3)_2$), 1.11 – 0.86 (m, 12H, -CH(C*H*$_3)_2$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ 169.5 (*C*=O), 135.7 (*ipso*-C_6H_5), 135.72 (*o*-C_6H_5), 131.0 (*m*-C_6H_5), 129.4 (*p*-C_6H_5), 42.0 (-*C*H$(CH_3)_2$), 22.63 42.0 (-CH(*C*H$_3)_2$) ppm. The ^{13}C NMR spectrum contained peaks for some unreacted starting benzoyl fluoride that could not be completely separated. The NMR spectral data for the product are consistent with the published data.[7]

ii). ^{1}H NMR spectrum of 2 (400.1 MHz, C_6D_6):

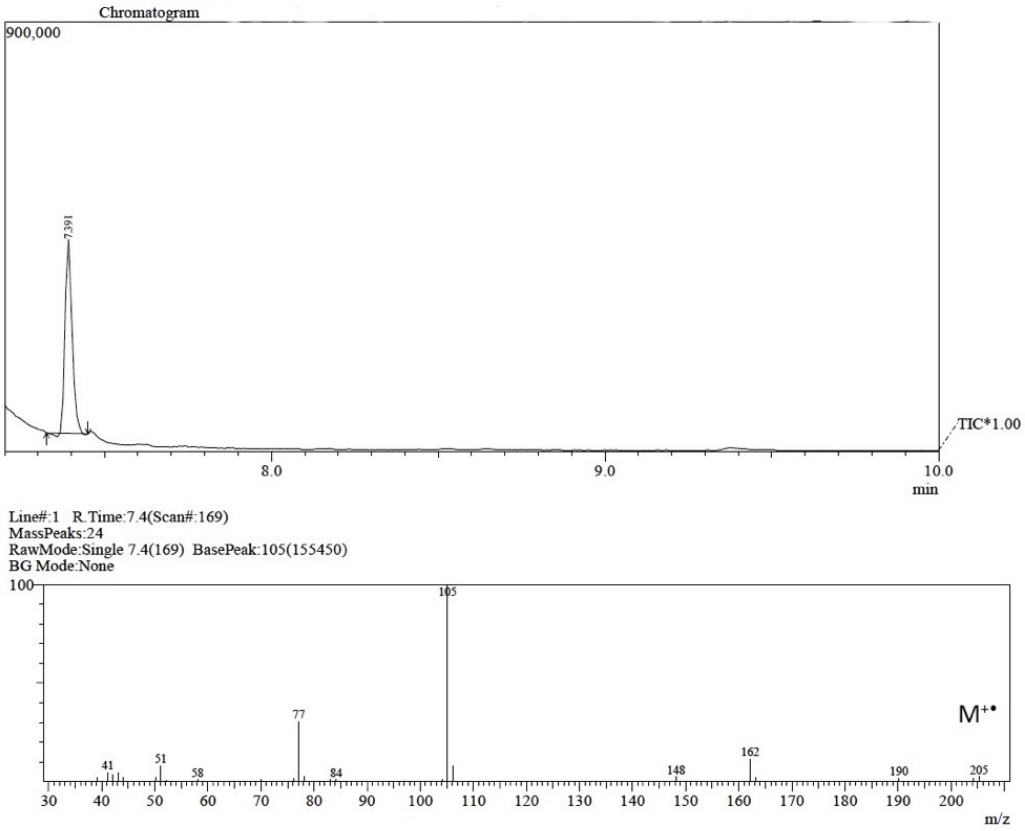


iii). ^{13}C NMR spectrum of 2 (100.6 MHz, C_6D_6):

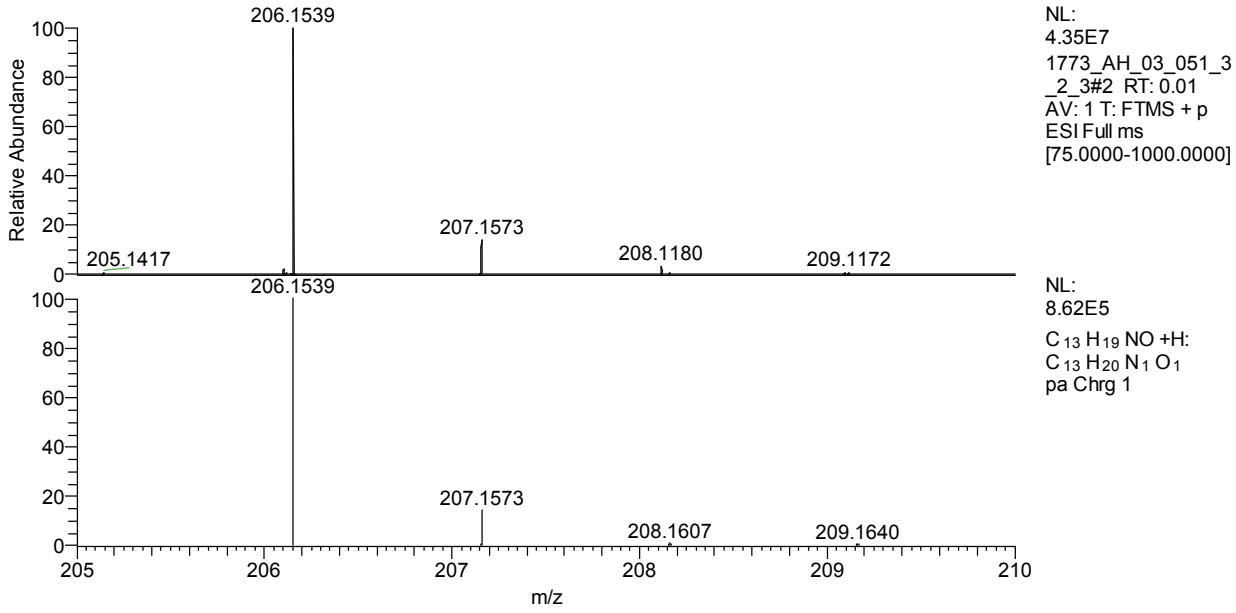


* Peaks marked with an asterisk are due to unreacted benzoyl fluoride.

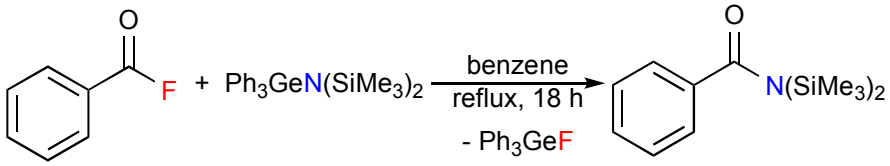
iv). GC/EI-MS of 2:



v). HRAM MS of 2 in water (Top, experimental spectrum; bottom, calculated spectrum):



C). Experimental procedure and spectral data for the reaction:

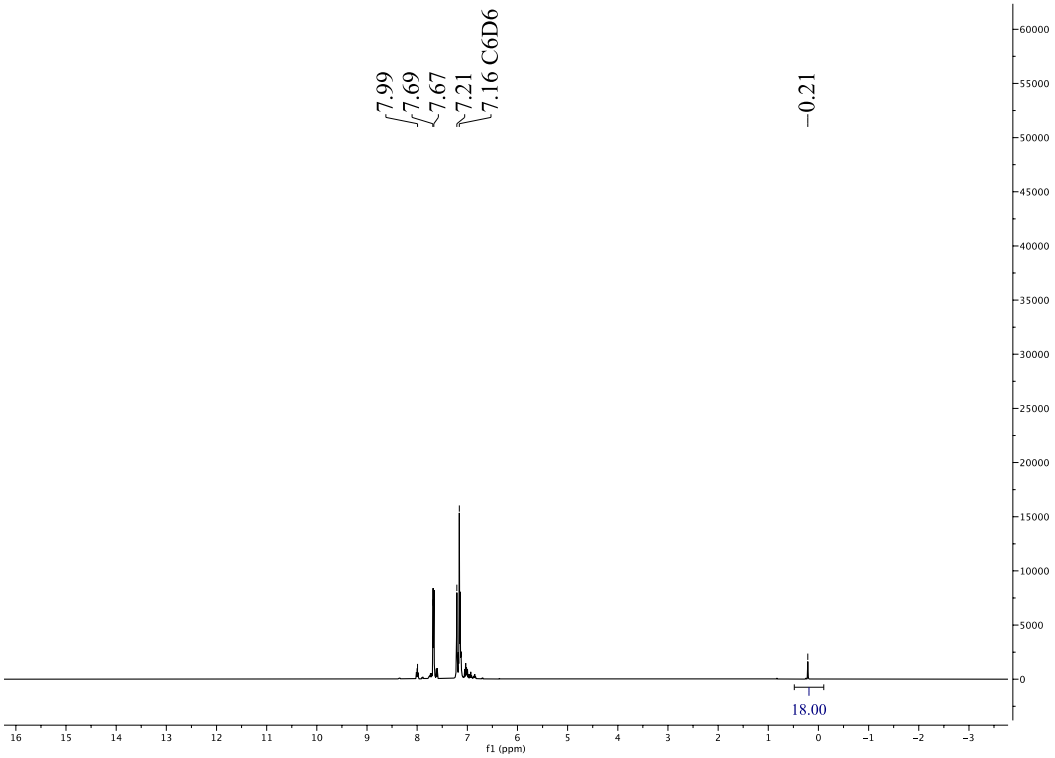


3

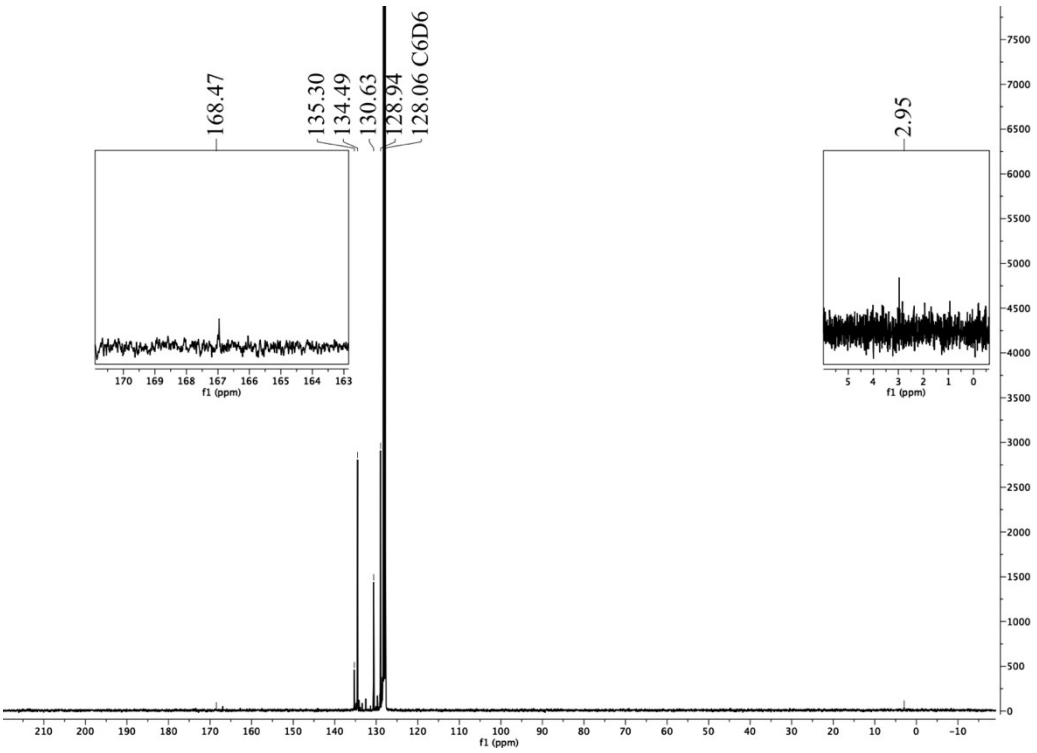
i). Experimental procedure:

Benzoyl fluoride (0.080 g, 0.64 mmol, 1 equiv.) was dissolved in benzene in a Schlenk flask. *N,N*-Bis(trimethylsilyl)triphenylgermylamine ($Ph_3GeN(SiMe_3)_2$, 0.300 g, 0.64 mmol, 1 equiv.) was slowly added to the reaction mixture and then the mixture was refluxed for 18 h and the solvent was removed *in vacuo*. The resulting yellow oil was purified using a silica gel column using benzene followed by chloroform as the eluent. Removal of the solvents resulted in the isolation of *N,N*-bis(trimethylsilyl)benzamide (**3**) as a white solid. ^{1}H NMR (400.1 MHz, C_6D_6) δ 8.05 – 7.19 (m, 5H, -C_6H_5), 0.21 (s, 18H, -N(Si(CH_3)$_3$)$_2$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ 168.5 (*C*=O), 135.3 (*ipso*-C_6H_5), 134.5 (*o*-C_6H_5), 130.6 (*m*-C_6H_5), 128.9 (*p*-C_6H_5), 2.95 (-N(Si(CH_3)$_3$)$_2$) ppm. The NMR spectral data are consistent with the published data.[8]

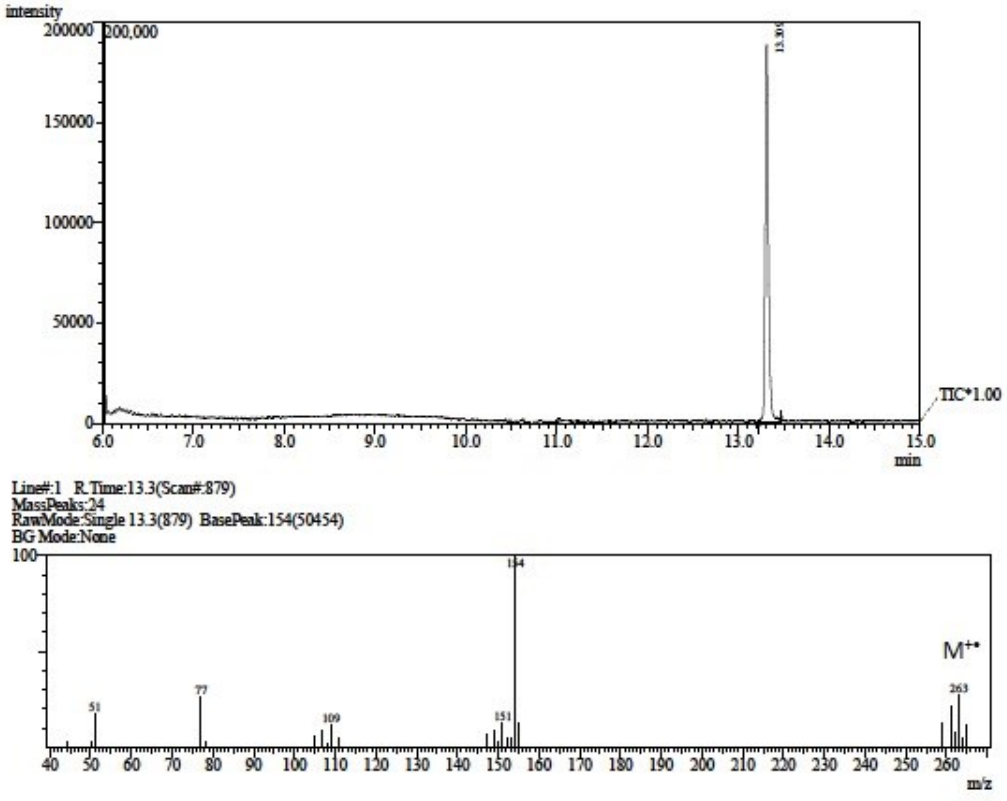
ii). ^{1}H NMR spectrum of 3 (400.1 MHz, C_6D_6):



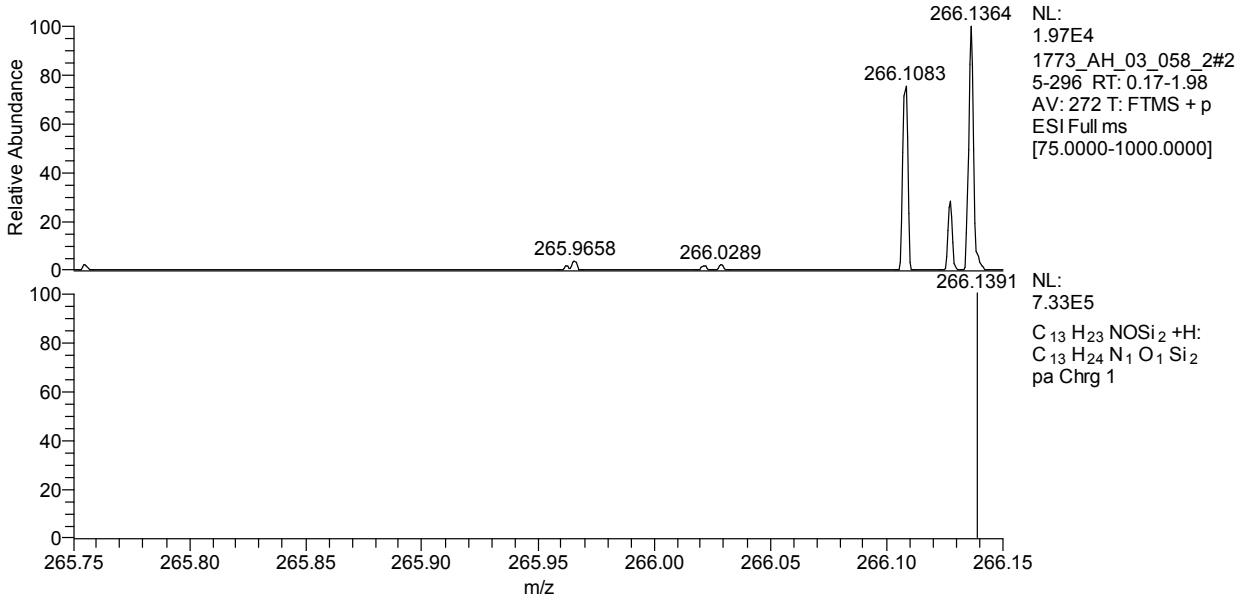
iii). ^{13}C NMR spectrum of 3 (100.6 MHz, C_6D_6):



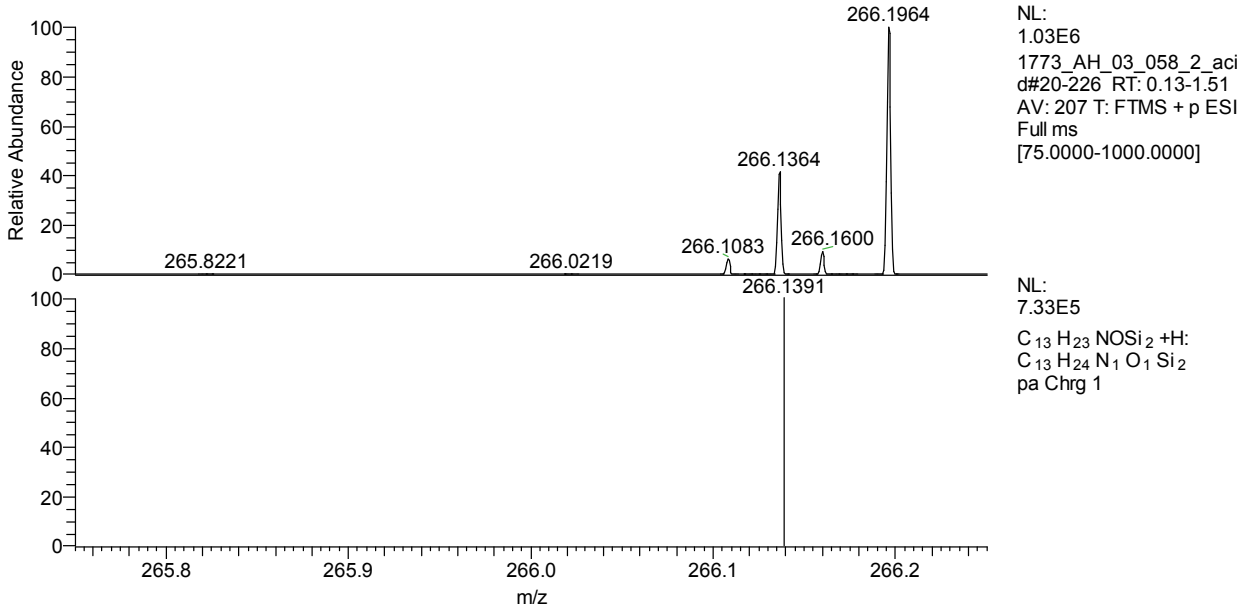
iv). GC/EI-MS of 3:



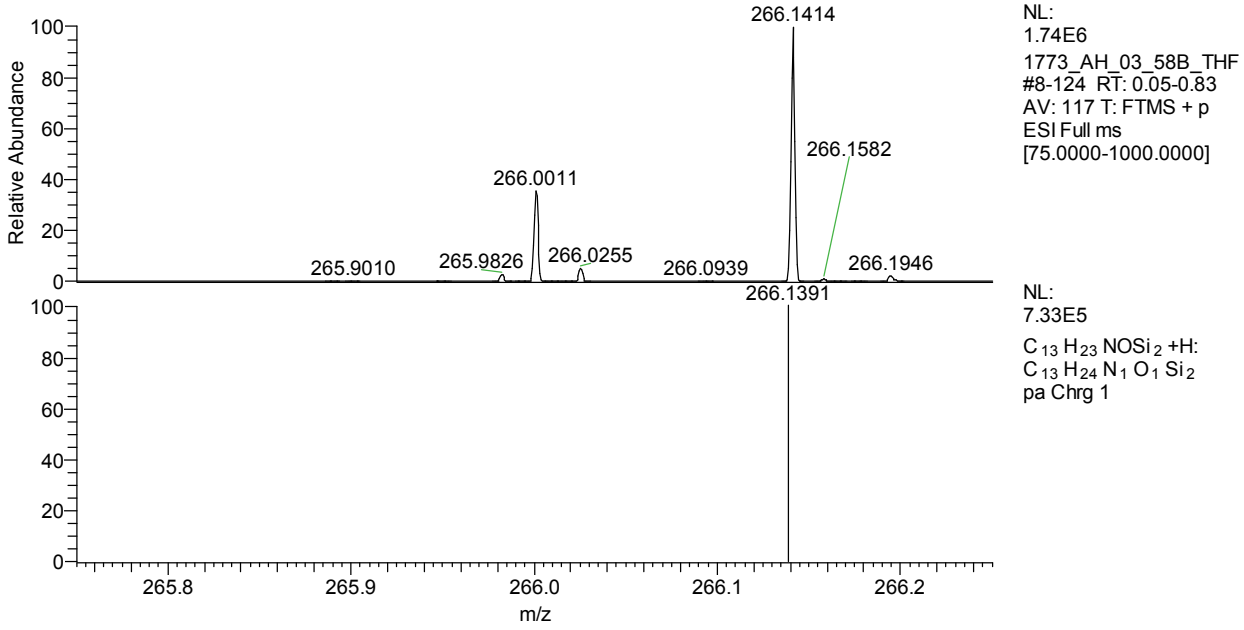
v). HRAM MS of 3 in water (Top, experimental spectrum; bottom, calculated spectrum):



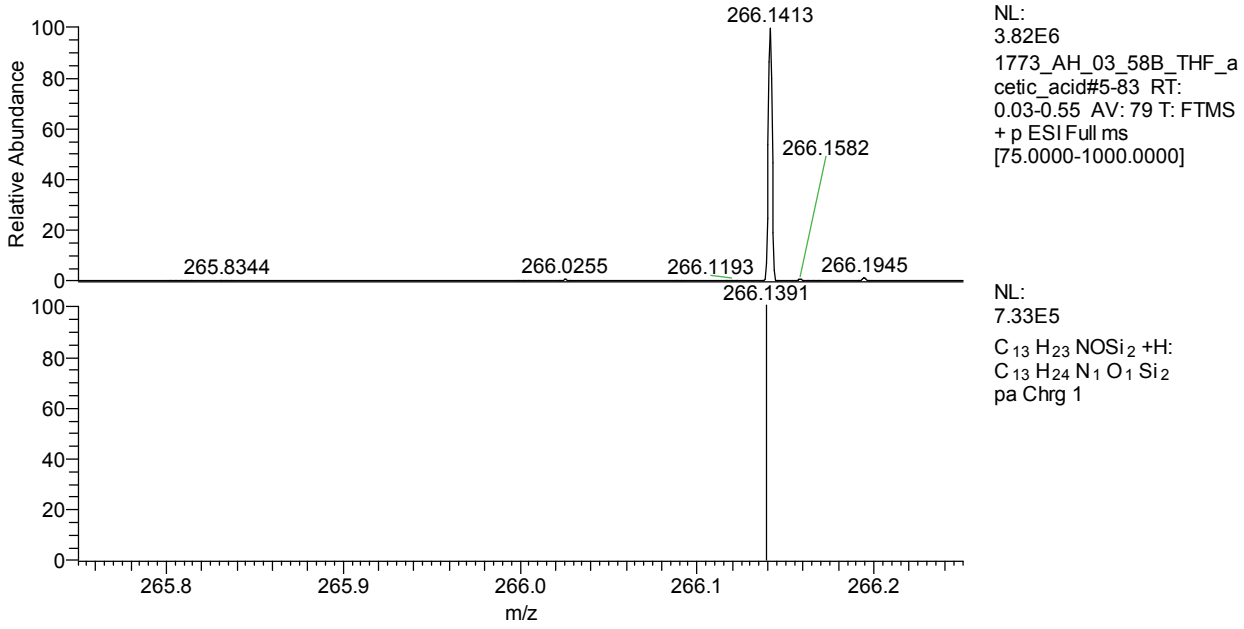
vi). HRAM MS of 3 with added acetic acid (Top, experimental spectrum; bottom, calculated spectrum):



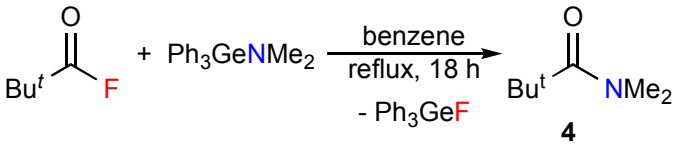
vii). HRAM MS of 3 in THF (Top, experimental spectrum; bottom, calculated spectrum):



viii). HRAM MS of 3 with in THF with added acid (Top, experimental spectrum; bottom, calculated spectrum):



D). Experimental procedure and spectral data for the reaction:

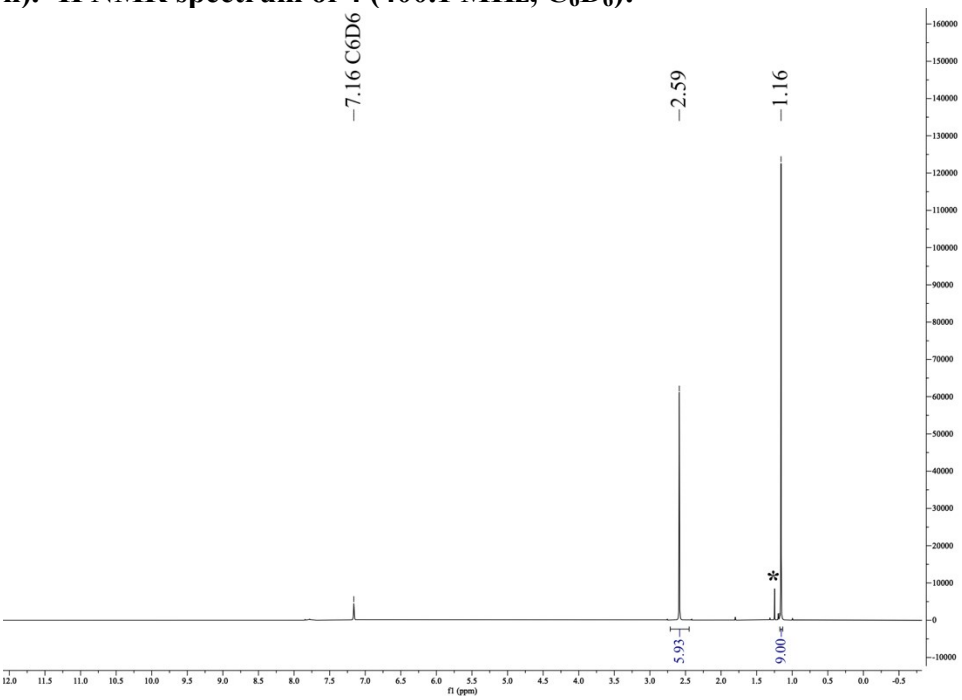


4

i). Experimental procedure:

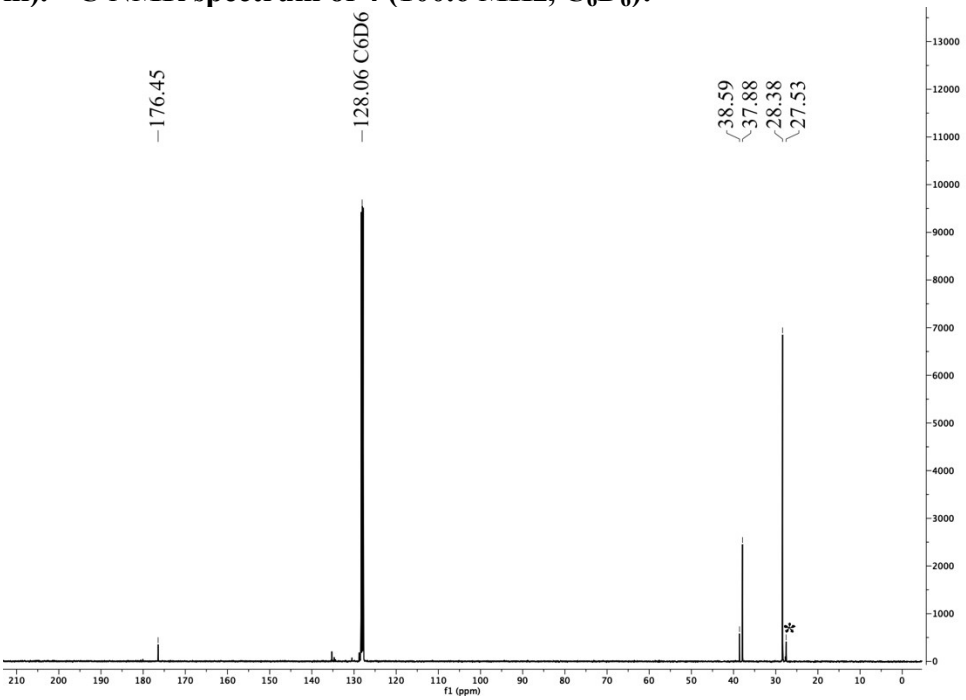
Pivaloyl fluoride (0.200 g, 1.92 mmol, 1 equiv.) was dissolved in benzene in a Schlenk flask. *N,N*- Dimethyltriphenylgermylamine (Ph_3GeNMe_2, 0.735 g, 2.11 mmol, 1.1 equiv.) was slowly added to the reaction mixture and then the mixture was refluxed for 18 h. The solution purified using a silica gel column with benzene as the eluent. The benzene wash was discarded and the column was then washed with ethyl acetate. Removal of the ethyl acetate *in vacuo* resulted in the isolation of *N,N*-dimethylpivalamide (**4**) as a clear oil. ^{1}H NMR (400.1 MHz, C_6D_6) δ 2.59 (s, 6H, -N(C*H*$_3$)$_2$), 1.16 (s, 9H, -C(C*H*$_3$)$_3$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ 176.5 (*C*=*O*), 38.6 (-*C*(CH$_3$)$_3$), 37.9 (-N(*C*H$_3$)$_2$), 28.4 (-C(*C*H$_3$)$_3$) ppm. A trace amount of starting material was present along with the product. The NMR spectral data for the product are consistent with the published data.[9]

ii). ^{1}H NMR spectrum of 4 (400.1 MHz, C_6D_6):



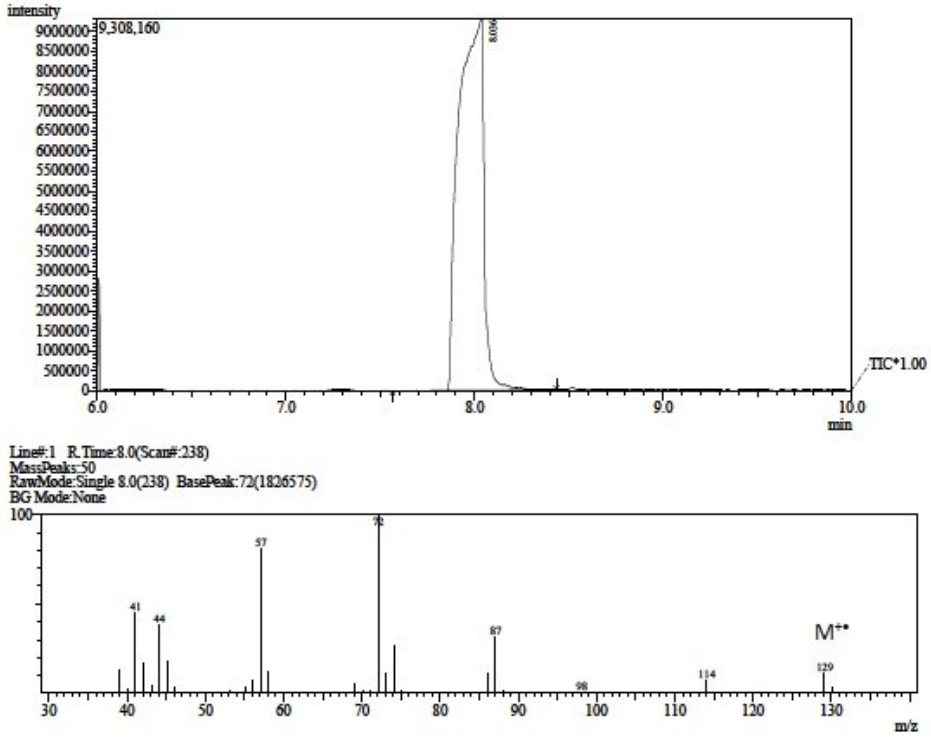
* A peak due to residual starting material is indicated by an asterisk.

iii). ^{13}C NMR spectrum of 4 (100.6 MHz, C_6D_6):

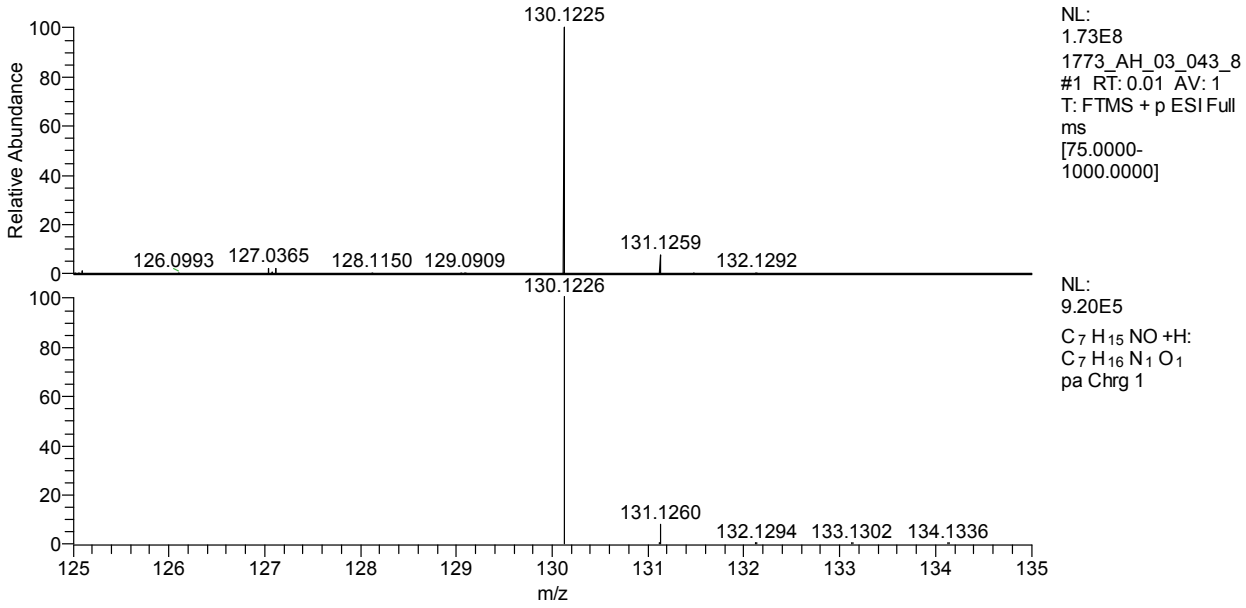


***** A peak due to residual starting material is indicated by an asterisk.

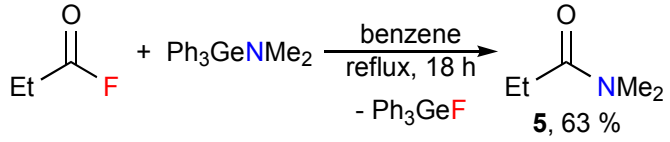
iv). GC/EI-MS of 4:



v). HRAM MS of 4 in water (Top, experimental spectrum; bottom, calculated spectrum):



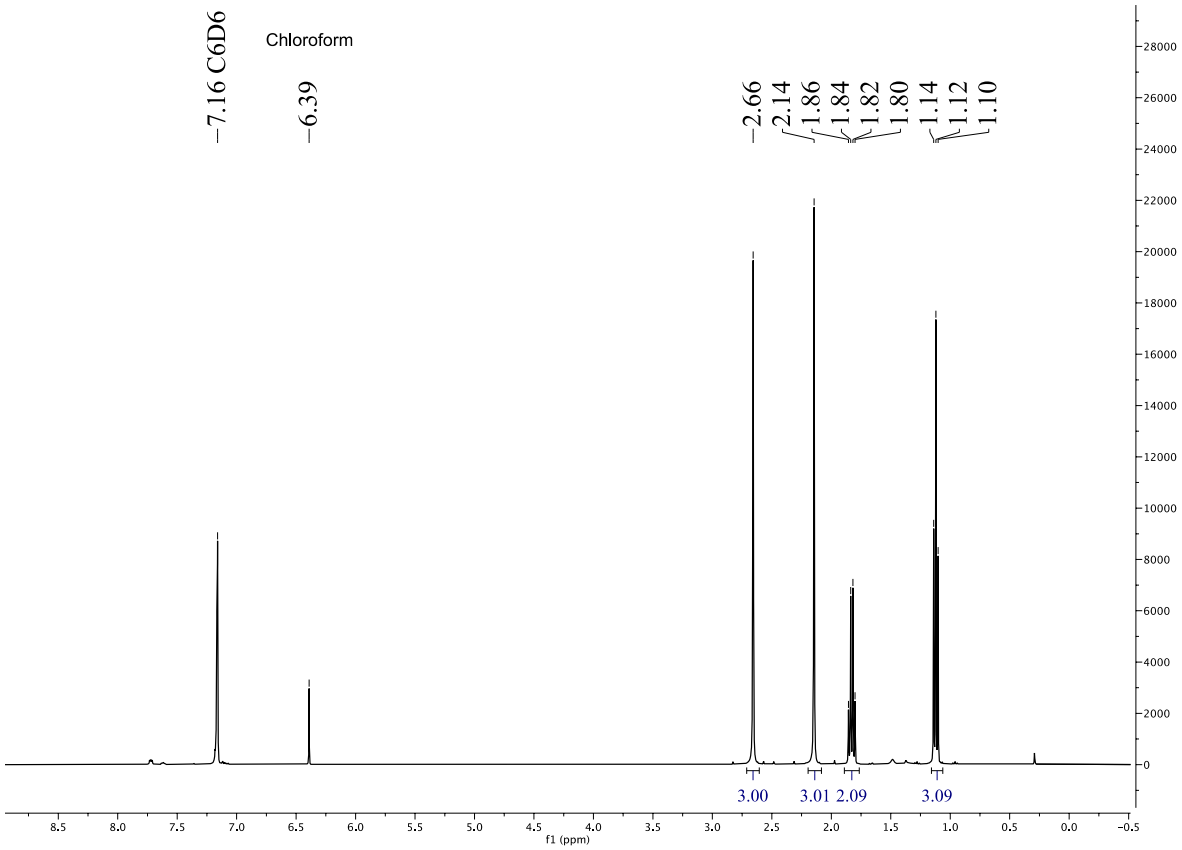
E). Experimental procedure and spectral data for the reaction:



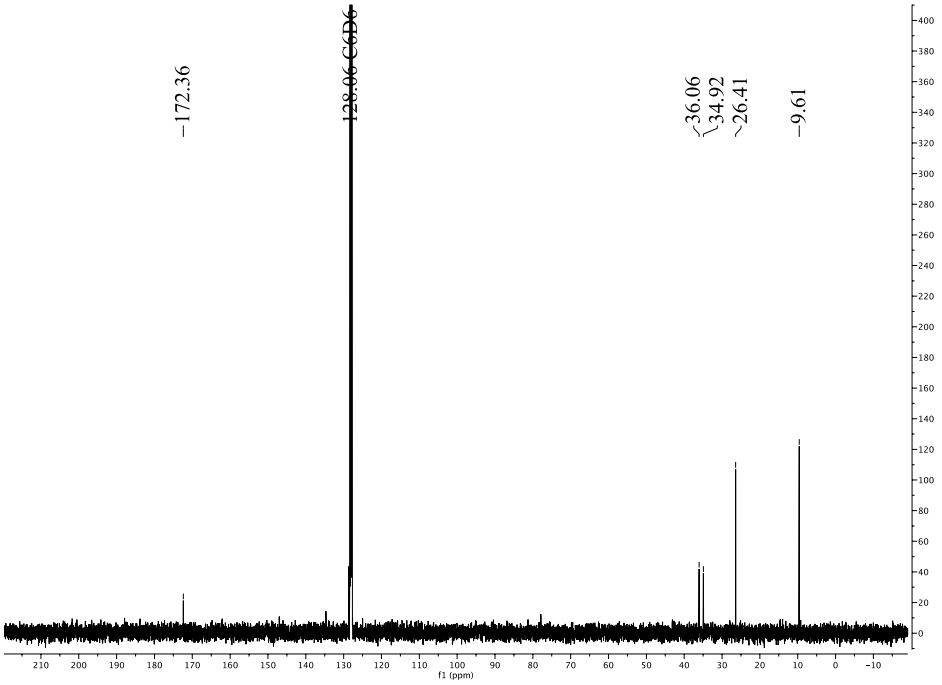
i). Experimental procedure:

Propionyl fluoride (0.160 g, 2.10 mmol, 1 equiv.) was dissolved in benzene in a Schlenk flask. *N,N*- Dimethyltriphenylgermylamine (Ph_3GeNMe_2, 0.805 g, 2.31 mmol, 1.1 equiv.) was slowly added to the reaction mixture and then the mixture was refluxed for 18 h. The solution was purified using a silica gel column with benzene as the eluent. The benzene wash was discarded and the column was then washed with chloroform. The chloroform solvent was distilled away in air resulting in the isolation of *N,N*-dimethylpropionamide (**5**) as a clear oil. ^{1}H NMR (400.1 MHz, C_6D_6) δ 2.66 (s, 3H, -N(CH_3)$_2$), 2.14 (s, 3H, -N(CH_3)$_2$), 1.83 (q, J = 7.4 Hz, 2H, -CH_2CH$_3$), 1.12 (t, J = 7.4 Hz, 3H, -CH$_2$CH_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ 172.4 (*C*=O), 36.1 (-N(*C*H$_3$)$_2$), 34.9 (-N(*C*H$_3$)$_2$), 26.4 (-*C*H$_2$CH$_3$), 9.6 (-CH$_2$*C*H$_3$) ppm. The NMR spectral data are consistent with the published data.[10]

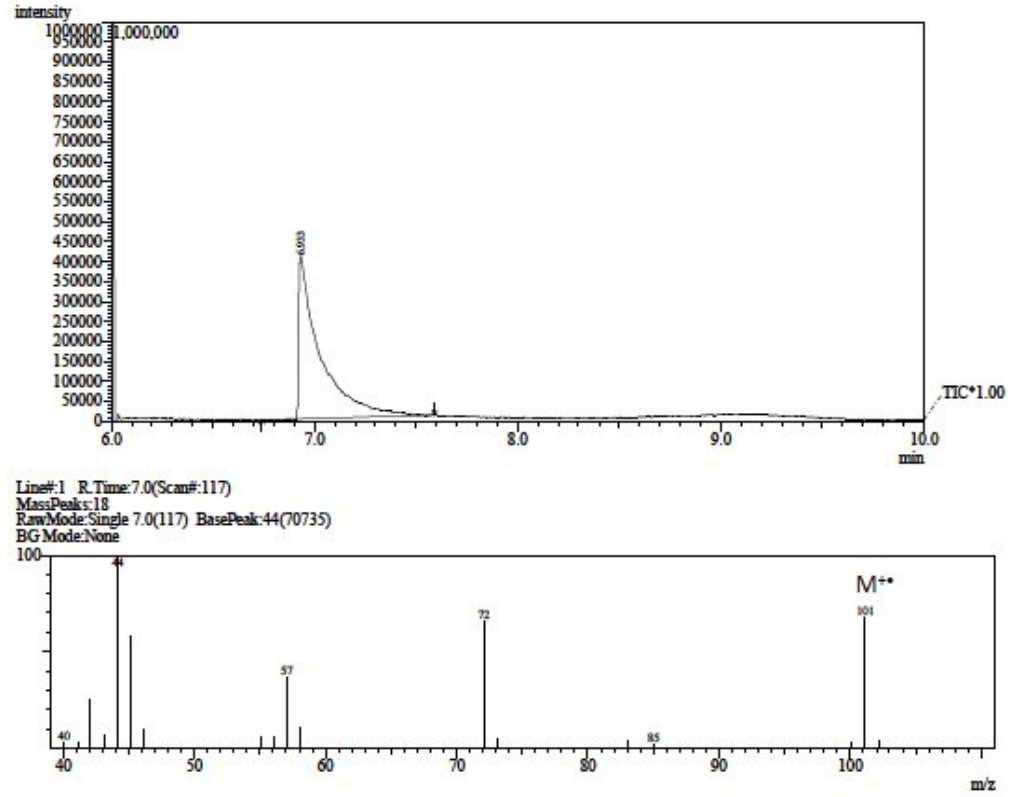
ii). ^{1}H NMR spectrum of 5 (400.1 MHz, C_6D_6):



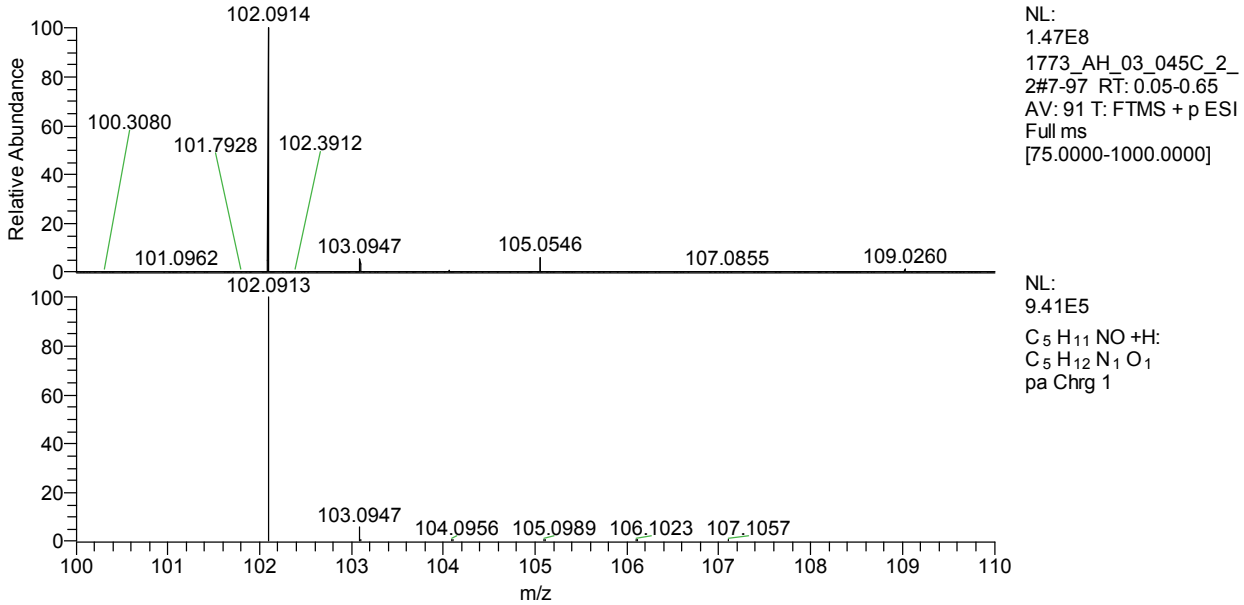
iii). ^{13}C NMR spectrum of 5 (100.6 MHz, C_6D_6):



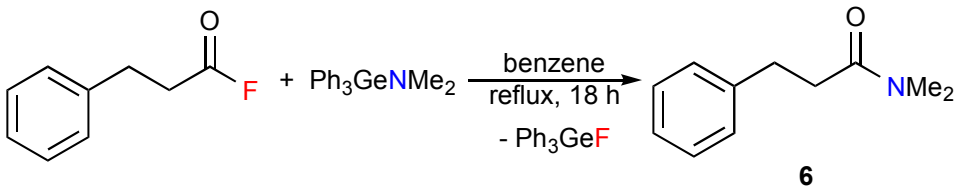
iv). GC/EI-MS of 5:



v). HRAM MS of 5 in water (Top, experimental spectrum; bottom, calculated spectrum):



F). Experimental procedure and spectral data for the reaction:

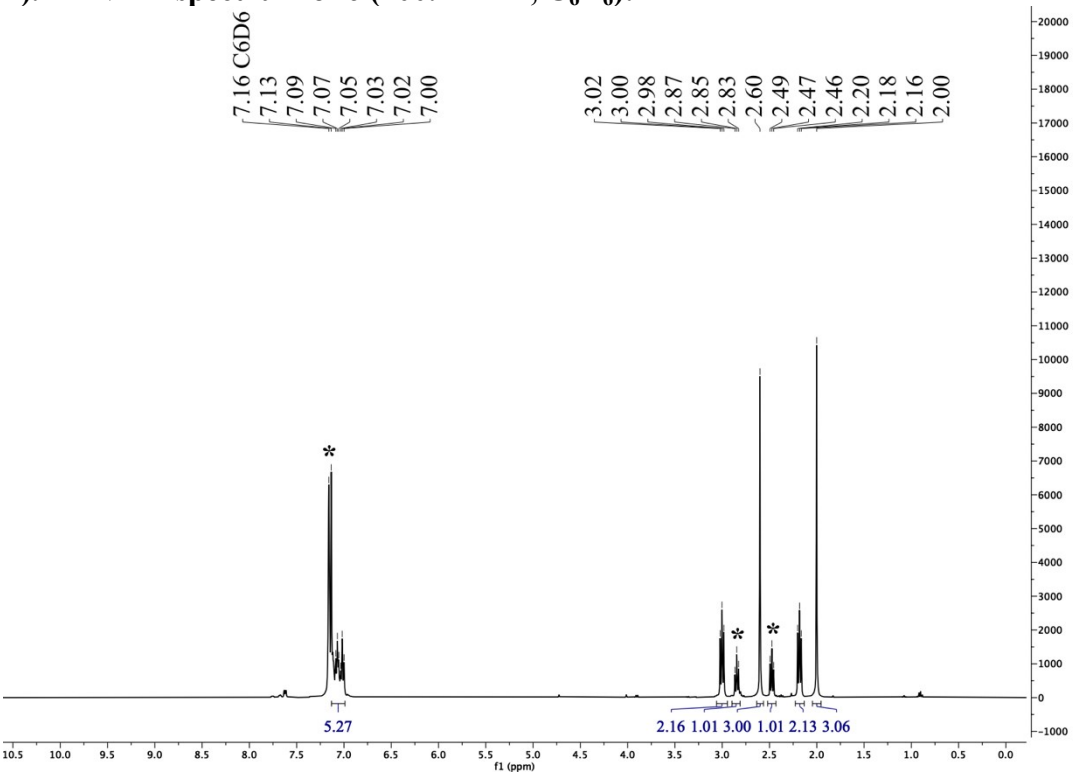


6

i). Experimental procedure:

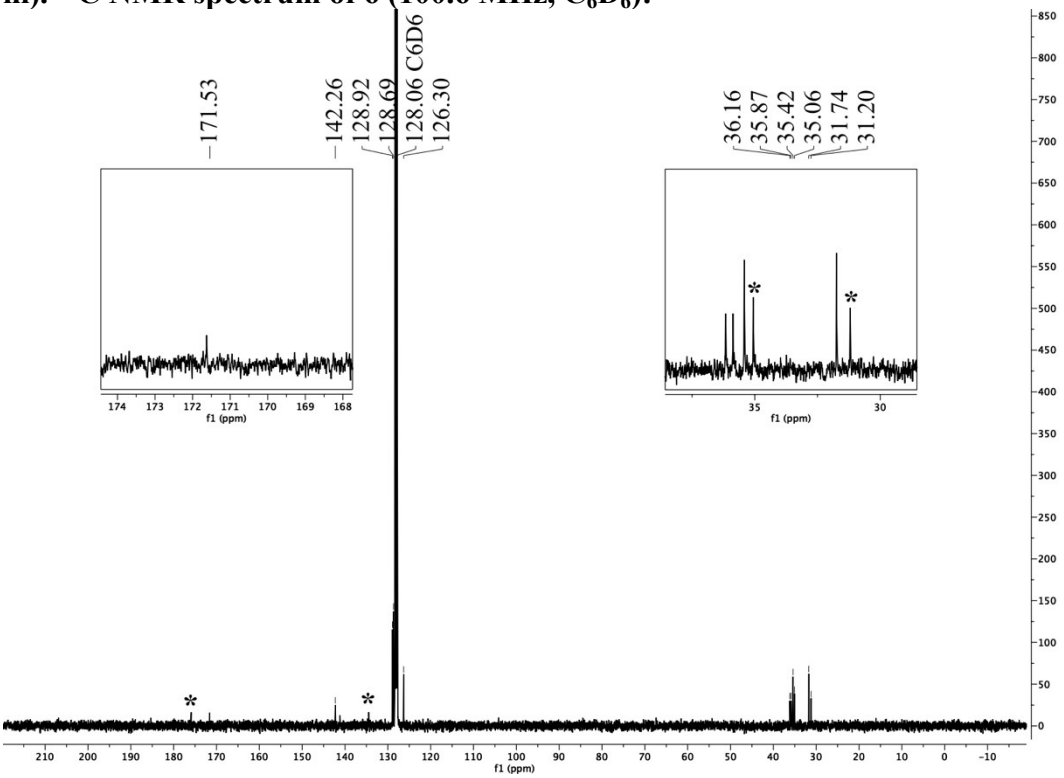
3-Phenylpropionyl fluoride (0.080 g, 0.53 mmol, 1 equiv.) was dissolved in benzene in a Schlenk flask. *N,N*- Dimethyltriphenylgermylamine (Ph_3GeNMe_2, 0.183 g, 0.526 mmol, 1 equiv.) was slowly added to the reaction mixture and then the mixture was refluxed for 18 h. The solution was purified using a silica gel column with benzene as the eluent. The benzene wash was discarded and the column was then washed with chloroform. Removal of the chloroform *in vacuo* resulted in the isolation of *N,N*-dimethyl-3-phenylpropanamide (**6**) as a white solid. ^{1}H NMR (400.1 MHz, C_6D_6) δ 7.10 – 6.99 (m, 5H, -C_6H_5), 3.00 (t, J = 7.8 Hz, 2H, PhCH_2CH_2C(O)-), 2.60 (s, 3H, -N(CH_3)$_2$), 2.18 (t, J = 7.8 Hz, 2H, PhCH_2CH_2C(O)-)), 2.00 (s, 3H, -N(CH_3)$_2$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ 171.5 (*C*=O), 142.3 (*ipso*-C_6H_5), 128.9 (*o*-C_6H_5), 128.7 (*m*-C_6H_5), 126.3 (*p*-C_6H_5), 36.2 (PhCH_2CH_2C(O)), 35.9 (PhCH_2CH_2C(O)), 35.4 (-N(CH_3)$_2$), 31.7 (-N(CH_3)$_2$) ppm. The product was contaminated with residual starting 3-phenylpropionyl fluoride The NMR spectral data for the product are consistent with the published data.[11]

ii). ^{1}H NMR spectrum of 6 (400.1 MHz, C_6D_6):



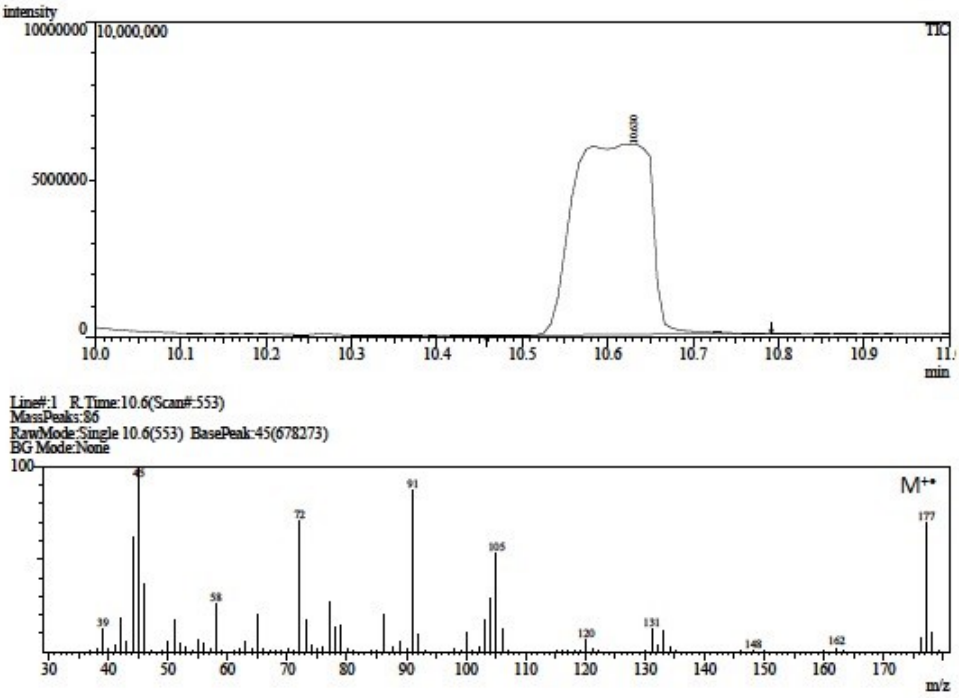
***** Peaks due to residual starting material are indicated by asterisks.

iii). ^{13}C NMR spectrum of 6 (100.6 MHz, C_6D_6):

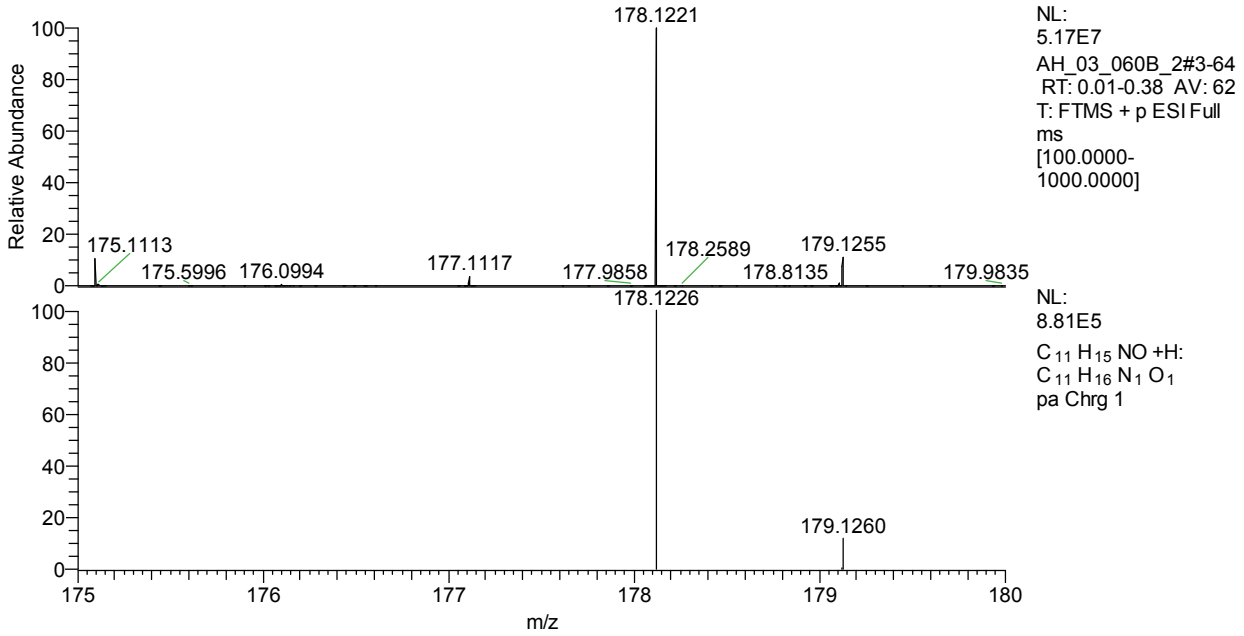


* Peaks due to residual starting material are indicated by asterisks.

iv). GC/EI-MS of 6:



v). HRAM MS of 6 in water (Top, experimental spectrum; bottom, calculated spectrum):



G). Summary of experimental and theoretical HRAM-MS data

Compound	Experimental *m*/*z*	Theoretical *m*/*z*	Δ (ppm)
1	150.0914	150.0913	0.67
2	206.1539	206.1539	0.05[a]
3	266.1364	266.1391	10.15
3[b]	266.1414	255.1391	8.64
4	130.1225	130.1226	0.77
5	102.0914	102.0913	0.98
6	178.1221	178.1226	2.81

[a] Error calculated using the fifth decimal place of the *m*/*z* values.

[b] Sample injected in THF with added acetic acid.

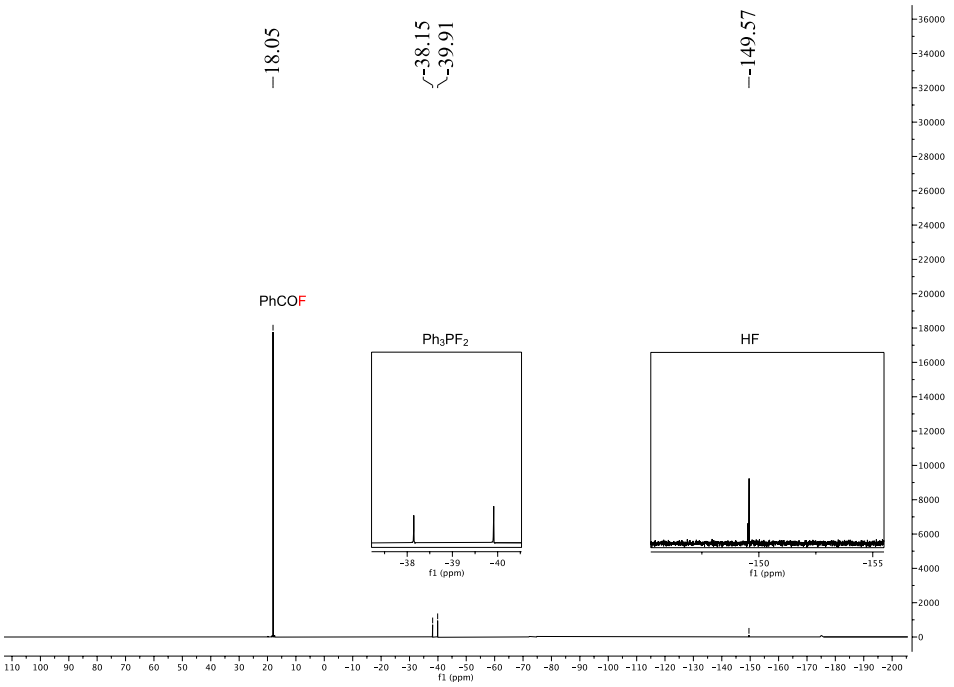
H). Experimental procedure and spectral data for the reaction:

i). Experimental procedure:

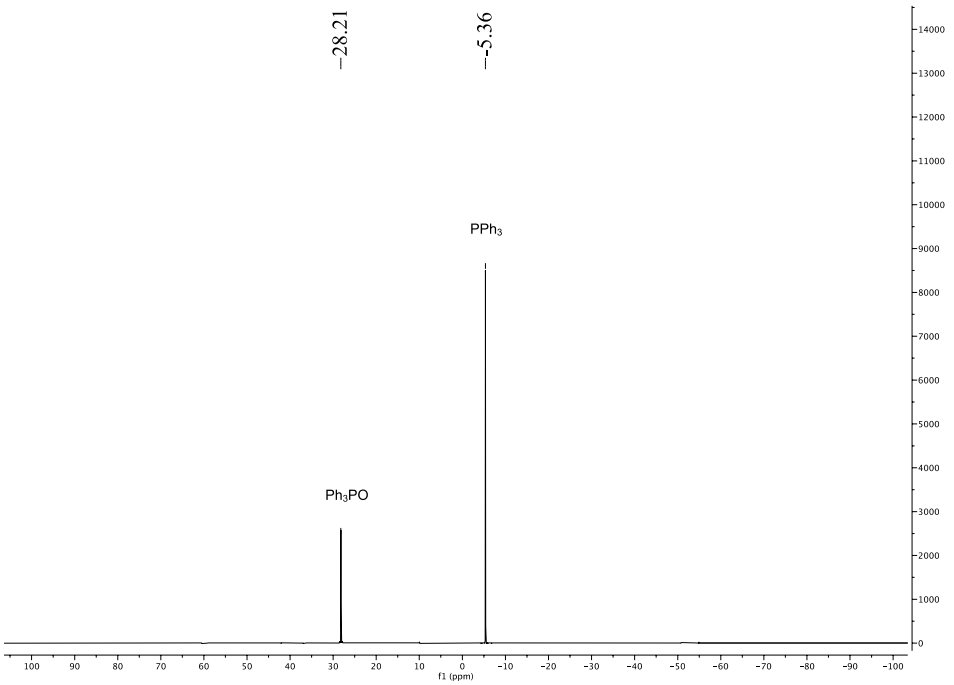
Note: *Hydrogen fluoride (HF) is formed in this reaction. This is a toxic, poisonous, and corrosive compound and needs to be handled with extreme care.*

In a screw-cap vial equipped with a stir bar on the benchtop, benzoic acid (0.200 g, 1.64 mmol, 1 equiv.) was dissolved in benzene (10 mL). To this was added triphenylphosphine (1.29 g, 4.91 mmol, 3 equiv.). The vial was immersed in an ice bath and *N*-bromosuccinimide (NBS, 0.612 g, 3.44 mmol, 2.1 equiv.) was slowly added to the reaction mixture. After the addition of NBS was complete the ice bath was removed and the reaction mixture was stirred for 15 min. Tetra-*n*-butylammonium fluoride (TBAF, 1.28 g, 4.91 mmol, 3 equiv.) was added to the reaction mixture and the reaction mixture was stirred for a further 2 h. An aliquot of the reaction mixture was removed and was analyzed by ^{19}F and ^{31}P NMR spectroscopy in C_6D_6. To the reaction mixture was then added *N,N*-Dimethyltriphenylgermylamine (Ph_3GeNMe_2, 0.617 g, 1.77 mmol, 1.1 equiv.) in benzene (10 mL) and the reaction mixture was stirred for 18 h. An aliquot of the reaction mixture was removed and was analyzed by ^{19}F NMR spectroscopy in C_6D_6. The vial was then opened, the reaction mixture was diluted was benzene (10 mL) and the solution was washed with aqueous sodium bicarbonate (3 x 10 mL) followed by distilled water (3 x 10 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. The benzene solution was passed through a silica column and after all of the benzene was extruded, the column was washed with chloroform (25 mL). The chloroform was removed *in vacuo* to yield *N,N*-Dimethylbenzamide (**1**, 0.060 g, 50 %).

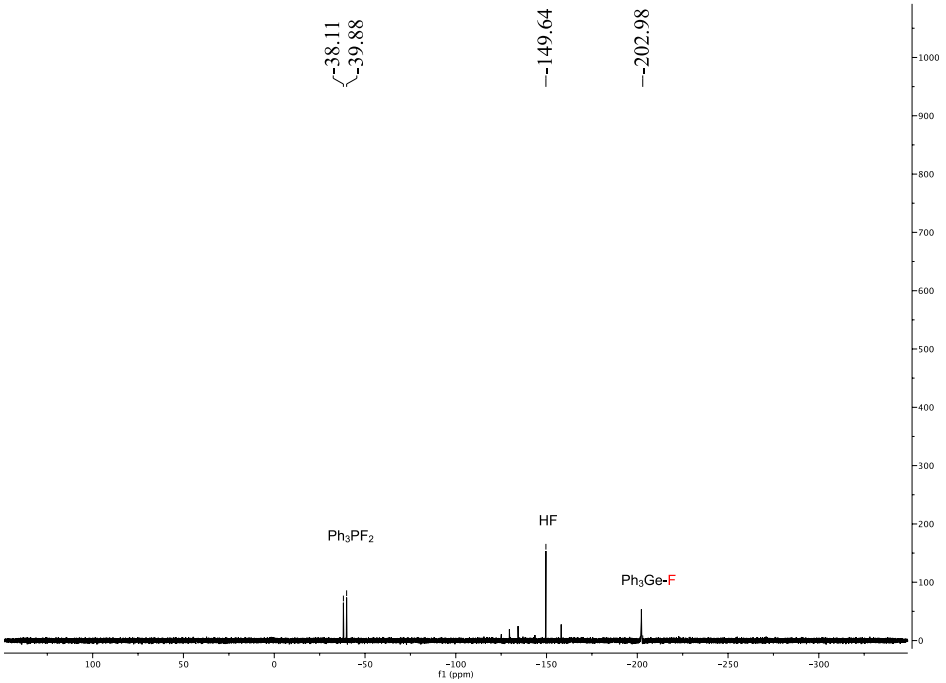
ii). ^{19}F NMR spectrum of the reaction mixture after the addition of PPh_3/NBS and TBAF



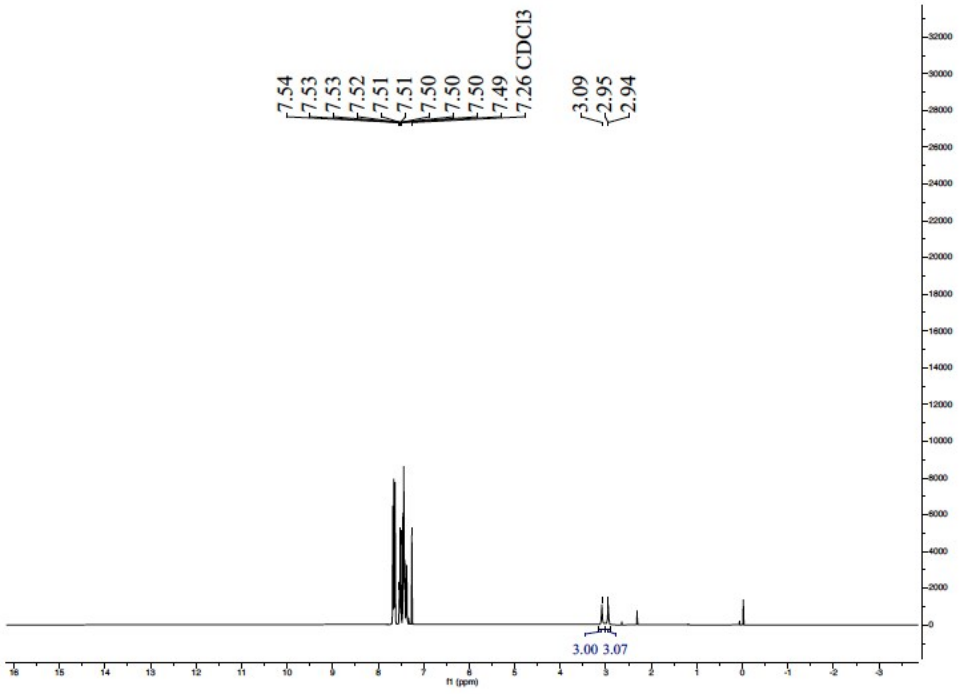
iii). ^{31}P NMR spectrum of the reaction mixture after the addition of PPh_3/NBS and TBAF



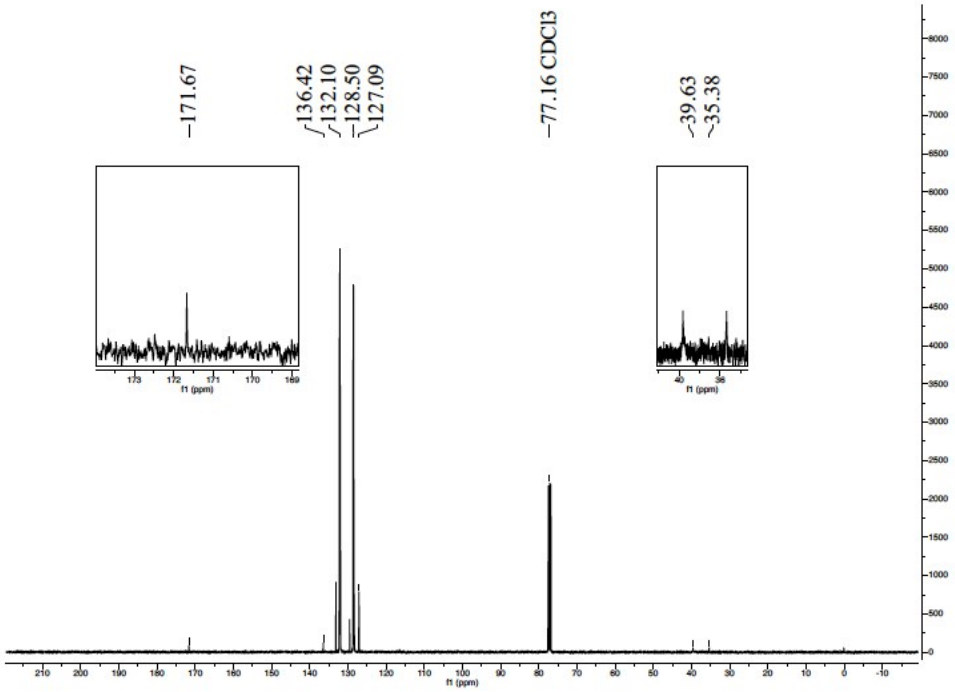
iv). ^{19}F NMR spectrum of the mixture after the addition of Ph_3GeNMe_2 to the reaction mixture



v). ^{1}H NMR spectrum of the isolated *N,N*-Dimethylbenzamide Product:



vi). ^{13}C NMR spectrum of the isolated *N,N*-Dimethylbenzamide Product:

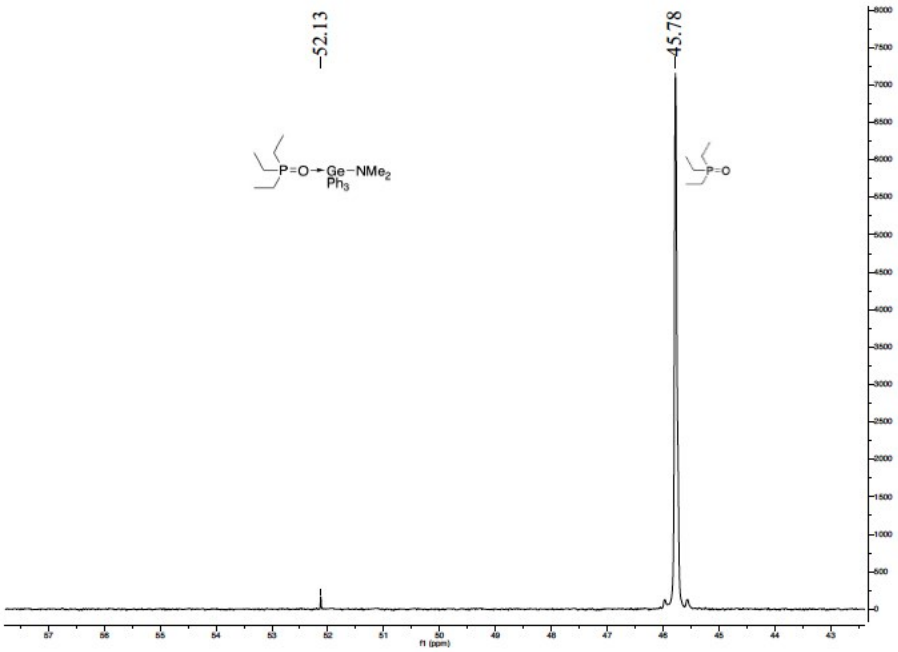


I). Determination of the Lewis acidity of Ph_3GeNMe_2 using the Guttman-Beckett method

i). Experimental procedure

A sample of Ph_3GeNMe_2 (0.100 g, 0.287 mmol, 1 equiv.) and $Et_3P{=}O$ (0.058 g, 0.43 mmol, 1.5 equiv.) was dissolved in C_6D_6 and the ^{31}P NMR spectrum of the mixture was recorded.

ii). ^{31}P NMR of the mixture of Ph_3GeNMe_2 and $Et_3P{=}O$



4). DFT Calculations: Wiberg Bond Indices

Gaussian 09 was used for geometry optimizations, frequency calculations, and NBO analysis.[12, 13] Geometries were fully optimized at B3LYP theoretical level using the triple-zeta basis set cc-pVTZ. To identify the nature of the stationary points of the optimized geometries, vibrational frequency calculations were performed and the local minima of the geometries were confirmed by zero imaginary frequencies. In addition to B3LYP, Grimm's dispersion correction (DFT-D3) was included.[14] Wiberg bond indices were calculated by using the keyword *BNDIDX* in NBO analysis.[15]

Table S1. Wiberg Bond Indices (WBI), occupancy on nitrogen, and percent p-character of the nitrogen lone pair in germylamines.

Germylamine	WBI	Occupancy (N/Ge)	N L.P. % p-character
Ph_3GeNMe_2	0.673	79.3/20.7	93.7
$Ph_3GeNPr^i_2$	0.649	80.2/19.8	98.1
$Ph_3GeN(SiMe_3)_2$	0.617	85.0/15.0	99.7
Ph_3GeNH_2	0.751	77.6/22.4	82.3

5). Kinetic Analysis Procedure and Plots

i). Experimental Procedure

In a screw-cap NMR tube, a sample of Ph_3GeNMe_2 (0.280 g) was dissolved in C_6D_6 (5.00 mL) to provide a 0.161 M solution. A sample of benzoyl fluoride (0.100 g) was dissolved in C_6D_6 (5.00 mL) to provide a 0.161 M solution. A sample of fluorobenzene (0.0770 g) was dissolved in C_6D_6 (5.00 mL) to provide a 0.161 M solution as an internal standard. An equimolar amount of the benzoyl fluoride solution (99 µL,16 µmol) and fluorobenzene solution (99 µL, 16 µmol) were combined and the initial concentration of benzoyl fluoride was measured using ^{19}F NMR spectroscopy. Subsequently an equimolar amount of Ph_3GeNMe_2 solution (99 µL, 16 µmol) was added to the NMR tube and the ^{19}F NMR spectrum was recorded. Successive spectra were recorded every 140 seconds for the duration of the experiment to determine the concentration of benzoyl fluoride remaining.

ii). Linear fit analysis plots:

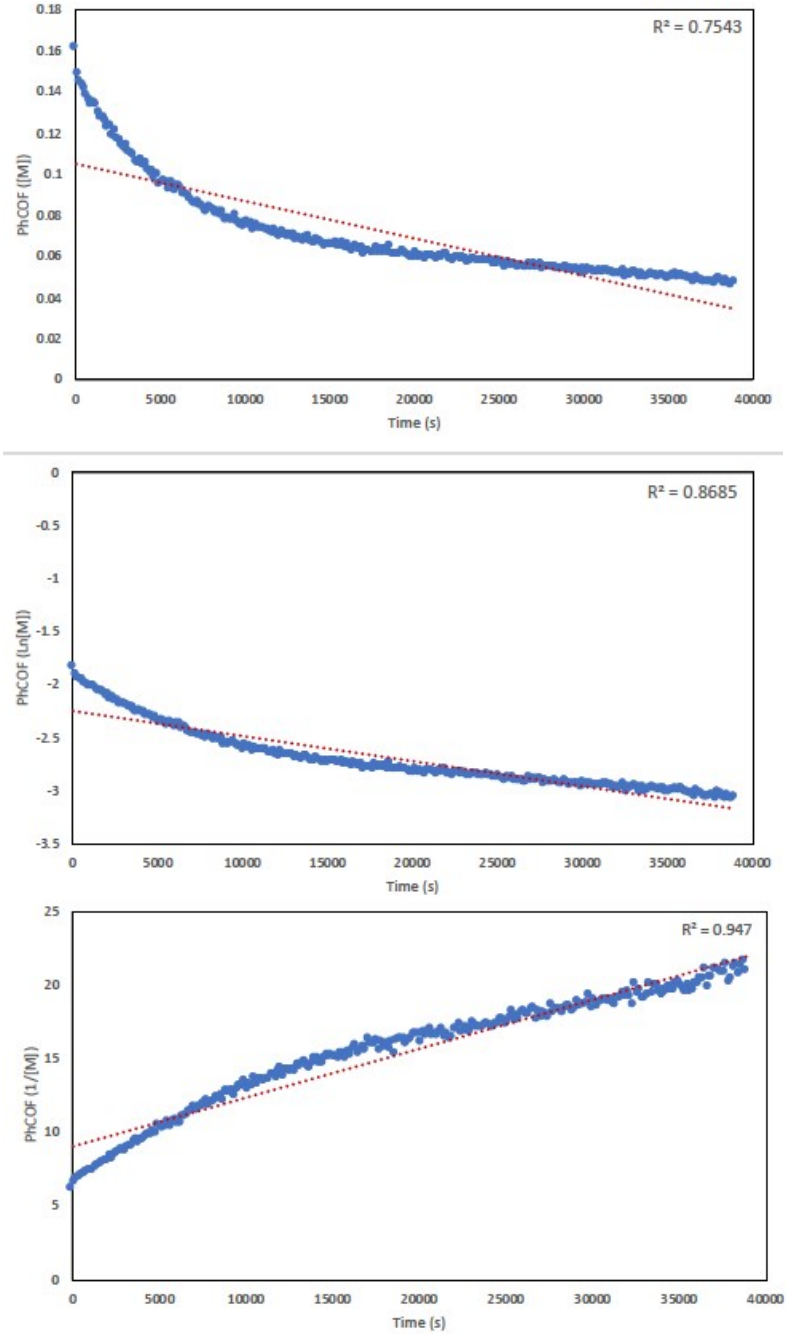
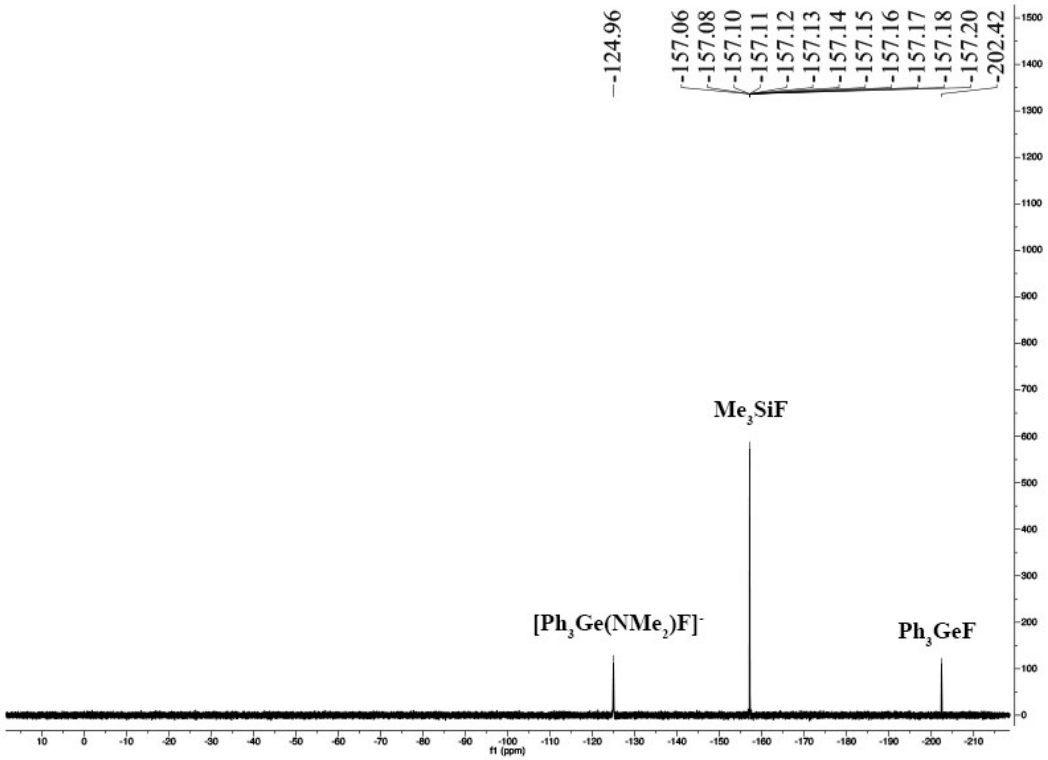


Figure SI-1. Kinetics analysis plots and linear fit analysis of [PhCOF] versus time (top), ln[PhCOF] versus time (middle), and 1/[PhCOF] versus time (bottom).

6). Experimental data for the reaction

i). Experimental procedure

In a screw-cap NMR tube, Ph_3GeNMe_2 (0.0317 g, 0.114 mmol) was combined with $[(Me_2N)_3S][Me_3SiF_2]$ (0.0040 g, 0.115 mmol) in benzene-d_6. The reaction was kept at room temperature for 15 minutes and then the ^{19}F NMR spectra were recorded.



7). Experimental data for the reaction

i). Experimental procedure

In a screw-cap NMR tube, benzoyl fluoride (0.014 g, 0.11 mmol) was combined with $HN(SiMe_3)_2$ (0.019 g, 0.12 mmol) in benzene-d_6. The reaction was heated in an oil bath at 75 ºC for 18 h and then the ^1H and ^{19}F NMR spectra were recorded and no reaction was observed.

8). FIA Calculations

	Electronic Energy (Def2-TZVPP/ D3(0)) (Hartree)	Thermal Correction to Enthalpy (Hartree)	Enthalpy @ 298.15 K & 1 atm (Hartree)	FIA (kJ/mol)
COF_2	-313.049	0.019	-313.031	
$[COF_2]^-$	-412.987	0.021	-412.966	
GeH_4	-2079.377	0.034	-2079.343	111
$GeMe_4$	-2236.661	0.158	-2236.503	107
$GePh_4$	-3003.630	0.384	-3003.246	188
$GeCl_4$	-3917.994	0.014	-3917.980	314
GeF_4	-2476.603	0.017	-2476.586	353
Ph_3GeNMe_2	-2906.559	0.377	-2906.181	210
$Ph_3GeN^iPr_2$	-3063.829	0.498	-3063.331	202
Ph_3GeNH_2	-2827.953	0.319	-2827.635	206
Ph_3GeNPh_2	-3290.068	0.489	-3289.579	217
$Ph_3GeN(SiMe_3)_2$	-3645.377	0.538	-3644.839	225

9). IRC Calculation of the TS

Summary of reaction path following

Reaction Coordinate	Energy	Step
-1	-0.00002	-0.00092
Transition State	0.00000	0.00000
+1	-0.00028	0.01693

10). Cartesian Coordinates and Energies of Calculated Structures

Ph_3GeNH_2			
Electronic energy (B3LYP/cc-pVTZ) = -2828.3266201 Hartree Thermal correction to enthalpy = 0.316581 Hartree Thermal correction to Gibbs free energy = 0.247609 Hartree			
N	0.01700	0.51500	2.49800
Ge	0.00600	0.10400	0.68600
C	-1.61200	0.95900	-0.00500
C	-2.21700	2.00000	0.70500
C	-3.35700	2.62800	0.21200
C	-3.90400	2.22500	-1.00200
C	-3.30900	1.19200	-1.72100
C	-2.17300	0.56400	-1.22300
C	1.67500	0.85800	-0.00300
C	2.33400	1.86700	0.70500
C	3.51000	2.42600	0.21500
C	4.03900	1.98600	-0.99400
C	3.39100	0.98500	-1.71000
C	2.21800	0.42500	-1.21500
C	-0.05700	-1.81000	0.23800
C	-1.28300	-2.47000	0.10400
C	-1.33400	-3.83200	-0.17600
C	-0.15600	-4.55700	-0.32700
C	1.07100	-3.91400	-0.19700
C	1.11800	-2.55200	0.08300
H	-0.81400	0.21500	2.99300
H	0.82400	0.16000	2.99600
H	-1.78800	2.31900	1.64700
H	-3.81600	3.43100	0.77300
H	-4.78900	2.71400	-1.38700
H	-3.73200	0.87600	-2.66600
H	-1.72400	-0.24600	-1.78500
H	1.91900	2.21400	1.64400
H	4.01200	3.20600	0.77500
H	4.95300	2.42200	-1.37600
H	3.80000	0.64000	-2.65100
H	1.72600	-0.36000	-1.77600
H	-2.20600	-1.91400	0.20900
H	-2.29200	-4.32700	-0.27800

H	-0.19400	-5.61500	-0.54700
H	1.99100	-4.47300	-0.31600
H	2.07900	-2.06100	0.17300

$[Ph_3Ge(F)\text{-}NH_2]^-$			
Electronic energy (M06-2X/Def2-TZVPP/D3(0)) = -2927.890 Hartree Thermal correction to enthalpy = 0.321 Hartree			
Ge	0.11200	-0.28300	0.99700
N	-0.01300	0.32400	2.76200
H	0.32100	1.26700	2.90200
H	0.44200	-0.30800	3.40500
C	1.85400	-0.35900	0.01500
C	2.62700	0.78100	-0.20500
C	3.84700	0.71700	-0.87000
C	4.31100	-0.50100	-1.35200
C	3.55400	-1.64900	-1.15000
C	2.34700	-1.57500	-0.46300
H	1.77500	-2.47500	-0.27100
H	3.91000	-2.60300	-1.52100
H	5.25500	-0.55500	-1.88100
H	4.43100	1.61800	-1.02000
H	2.25800	1.74000	0.13900
C	-1.40700	-1.17900	0.03700
C	-1.37700	-2.55700	-0.20600
C	-2.38900	-3.19400	-0.91500
C	-3.47700	-2.46900	-1.38600
C	-3.53600	-1.10300	-1.14500
C	-2.50800	-0.47000	-0.45300
H	-2.56800	0.59900	-0.29500
H	-4.38000	-0.52400	-1.50100
H	-4.27100	-2.96400	-1.93300
H	-2.33300	-4.26200	-1.09500
H	-0.55000	-3.13300	0.18700
C	-0.39300	1.60400	0.24600
C	-0.18600	1.88300	-1.10900
C	-0.62700	3.05900	-1.70300
C	-1.30200	4.00900	-0.94200
C	-1.53000	3.76000	0.40500
C	-1.08200	2.57200	0.98000
H	-1.30300	2.38000	2.02500
H	-2.06500	4.48700	1.00500
H	-1.65100	4.92900	-1.39600
H	-0.44900	3.23700	-2.75700

H	0.33200	1.14900	-1.71900
F	0.55300	-1.97400	1.75500

$Ph_3GeN^iPr_2$

Electronic energy (B3LYP/cc-pVTZ) = -3064.3020135 Hartree
Thermal correction to enthalpy = 0.493556 Hartree
Thermal correction to Gibbs free energy = 0.408673 Hartree

C	-2.62700	-0.17700	-2.67800	H	-2.50700	-3.50800	2.78500
C	-1.13400	-0.53200	-2.61000	H	-4.60600	-2.19600	2.82600
N	-0.33900	0.34800	-1.74100	H	-4.71400	-0.00900	1.66700
Ge	0.07000	-0.08400	0.01700	H	-2.74000	0.85300	0.47400
C	1.60200	-1.31200	0.04000	H	0.76000	2.09500	-1.67000
C	2.32800	-1.54500	-1.12900	H	-0.86300	1.69500	-4.21000
C	3.46700	-2.34400	-1.11700	H	0.84200	1.26100	-4.00900
C	3.89800	-2.92200	0.07300	H	0.32700	2.95100	-3.86400
C	3.19200	-2.69000	1.24900	H	-2.21900	2.50500	-2.14000
C	2.05700	-1.88500	1.23200	H	-0.98700	3.74100	-1.86200
C	0.67000	1.54000	0.94600	H	-1.39800	2.60600	-0.57500
C	-0.15400	2.22500	1.84100	H	-1.45200	-2.21900	-1.26900
C	0.29700	3.36900	2.49300	H	0.06000	-2.30500	-2.18500
C	1.58300	3.84400	2.25900	H	-1.48800	-2.61900	-2.98300
C	2.42000	3.16500	1.37800				
C	1.96600	2.02000	0.73300				
C	-1.48200	-0.82100	0.96600				
C	-1.43900	-2.05500	1.62000				
C	-2.55700	-2.54800	2.28700				
C	-3.73700	-1.81200	2.30900				
C	-3.79600	-0.58300	1.65900				
C	-2.67700	-0.09600	0.99300				
C	-0.16200	1.75500	-2.14500				
C	0.04800	1.91800	-3.65100				
C	-1.26600	2.70500	-1.65300				
C	-0.98600	-2.00700	-2.23200				
H	-2.78600	0.80900	-3.11000				
H	-3.06500	-0.19600	-1.67900				
H	-3.15500	-0.90400	-3.30100				
H	-0.73200	-0.43400	-3.62300				
H	1.99000	-1.09300	-2.05300				
H	4.01800	-2.51400	-2.03300				
H	4.78200	-3.54600	0.08500				
H	3.52800	-3.13100	2.17900				
H	1.52900	-1.69800	2.15900				
H	-1.15400	1.86100	2.03900				

H	-0.35500	3.88800	3.18500
H	1.93400	4.73300	2.76500
H	3.42500	3.52300	1.20000
H	2.63000	1.49000	0.06100

$[Ph_3Ge(F)\text{-}\ N^iPr_2]^-$							
Electronic energy (M06-2X/Def2-TZVPP/D3(0)) = -3163.763 Hartree Thermal correction to enthalpy = 0.499 Hartree							
Ge	-0.06900	-0.23400	-0.25700	H	-4.04000	0.28500	-3.45200
N	0.20600	-1.63000	0.98100	H	-1.81900	-0.51900	-2.72900
C	1.35800	-2.48500	0.72100	C	0.19800	1.26300	1.17000
C	2.10800	-2.74500	2.02800	C	0.04500	2.60500	0.80800
H	2.99200	-3.36700	1.86000	C	0.38400	3.64600	1.66300
H	2.41300	-1.79500	2.47100	C	0.89700	3.36500	2.92600
H	1.45700	-3.26300	2.73900	C	1.06400	2.04200	3.31100
C	1.05200	-3.80500	0.01200	C	0.71900	1.01200	2.43800
H	1.98000	-4.35700	-0.15700	H	0.87100	-0.02100	2.72800
H	0.39500	-4.42600	0.62900	H	1.47000	1.81300	4.29000
H	0.56400	-3.60000	-0.93900	H	1.16600	4.17100	3.59800
H	2.03400	-1.92600	0.06600	H	0.25500	4.67500	1.34800
C	-0.94900	-2.28800	1.56800	H	-0.34700	2.83900	-0.17900
H	-0.58800	-3.14400	2.15100	F	-0.26700	-1.59300	-1.61500
C	-1.65700	-1.34000	2.53300				
H	-0.99200	-1.04100	3.34400				
H	-1.96300	-0.43700	2.00200				
H	-2.55200	-1.81100	2.94800				
C	-1.96700	-2.81700	0.54800				
H	-1.48200	-3.41500	-0.21900				
H	-2.73500	-3.41000	1.05700				
H	-2.45400	-1.98000	0.04300				
C	1.56500	0.34400	-1.25700				
C	2.64700	0.94300	-0.60700				
C	3.79300	1.32000	-1.29800				
C	3.86900	1.13300	-2.67200				
C	2.80000	0.55100	-3.34100				
C	1.67100	0.14900	-2.63700				
H	0.85800	-0.34500	-3.15300				
H	2.84900	0.40000	-4.41400				
H	4.75500	1.43600	-3.21700				
H	4.62200	1.77000	-0.76500				

H	2.59300	1.12500	0.46100
C	-1.88900	0.41800	-0.81000
C	-2.40900	0.10300	-2.07000
C	-3.66700	0.54100	-2.46700
C	-4.45100	1.29400	-1.60300
C	-3.95900	1.61300	-0.34500
C	-2.69100	1.18700	0.03600
H	-2.31800	1.46600	1.01300
H	-4.56000	2.19800	0.34200
H	-5.43600	1.62700	-1.90600

Ph_3GeNMe_2

Electronic energy (B3LYP/cc-pVTZ) = -2906.9678599 Hartree
Thermal correction to enthalpy = 0.376362 Hartree
Thermal correction to Gibbs free energy = 0.299628 Hartree

C	0.70100	0.79100	3.05700	H	0.06600	-1.86600	3.29100
N	-0.20600	-0.00800	2.25600	H	-1.37500	-1.75200	2.28000
Ge	-0.05000	-0.01400	0.41400				
C	1.40800	-1.16800	-0.21600				
C	2.02100	-2.08800	0.63500				
C	3.05700	-2.89800	0.18300				
C	3.49500	-2.80000	-1.13200				
C	2.89700	-1.88400	-1.99100				
C	1.86500	-1.07400	-1.53400				
C	-1.77900	-0.62400	-0.26000				
C	-1.88500	-1.51100	-1.33300				
C	-3.13100	-1.90300	-1.80900				
C	-4.29000	-1.41500	-1.21700				
C	-4.19900	-0.53600	-0.14300				
C	-2.95200	-0.14600	0.33100				
C	0.34200	1.81000	-0.18100				
C	-0.67900	2.69500	-0.53300				
C	-0.38700	3.99200	-0.94100				
C	0.93300	4.42300	-1.00300				
C	1.96000	3.55100	-0.65900				
C	1.66500	2.25500	-0.25400				
C	-0.72100	-1.18100	2.93800				
H	0.93600	1.72600	2.55000				
H	1.65300	0.28700	3.28700				
H	0.23100	1.04800	4.01200				

H	1.70100	-2.17800	1.66400
H	3.52200	-3.60500	0.85700
H	4.30000	-3.42900	-1.48500
H	3.23800	-1.79800	-3.01400
H	1.42500	-0.35400	-2.21300
H	-0.99600	-1.91300	-1.80100
H	-3.19700	-2.59300	-2.64000
H	-5.25900	-1.72100	-1.58700
H	-5.09700	-0.15900	0.32700
H	-2.89300	0.52500	1.17900
H	-1.71300	2.38000	-0.50300
H	-1.19000	4.66400	-1.21300
H	1.16000	5.43200	-1.32100
H	2.99000	3.87900	-0.70800
H	2.47900	1.58900	0.00200
H	-1.31000	-0.88900	3.81500

$[Ph_3Ge(F)\text{-}NMe_2]^-$

Electronic energy (M06-2X/Def2-TZVPP/D3(0)) = -3006.498 Hartree
Thermal correction to enthalpy = 0.381 Hartree

C	-0.69200	-0.67900	-2.74700	H	-1.12100	-0.03900	-3.54000
N	0.08700	0.07200	-1.80400	F	-0.16100	-0.22100	2.08600
Ge	-0.02100	-0.08800	0.17700				
C	1.30000	-1.59900	0.30500				
C	1.64200	-2.35700	-0.81600				
C	2.55800	-3.40200	-0.74300				
C	3.17400	-3.70300	0.46300				
C	2.85400	-2.95900	1.59100				
C	1.92300	-1.93000	1.51200				
H	1.65200	-1.37500	2.40000				
H	3.32800	-3.18600	2.54000				
H	3.89400	-4.51100	0.52400				
H	2.79200	-3.97800	-1.63200				
H	1.18100	-2.12800	-1.76800				
C	0.60400	1.79200	0.46100				
C	1.28400	2.14400	1.62800				
C	1.69600	3.45000	1.86300				
C	1.41000	4.44800	0.94000				
C	0.71800	4.12400	-0.21900				
C	0.33200	2.80900	-0.45500				
H	-0.18200	2.55600	-1.37600				

H	0.48300	4.89600	-0.94400	
H	1.71900	5.47100	1.12500	
H	2.23100	3.69300	2.77400	
H	1.46900	1.37800	2.37000	
C	-1.99400	-0.37500	0.15600	
C	-2.82900	0.37000	-0.67700	
C	-4.21000	0.21700	-0.64800	
C	-4.78700	-0.71000	0.21000	
C	-3.97300	-1.46300	1.04800	
C	-2.59500	-1.28300	1.02900	
H	-1.96800	-1.83800	1.71600	
H	-4.41600	-2.18400	1.72600	
H	-5.86300	-0.84100	0.23000	
H	-4.83700	0.81600	-1.29900	
H	-2.38300	1.07600	-1.37000	
C	1.30100	0.53300	-2.41600	
H	1.10800	1.25700	-3.22900	
H	1.88900	-0.28800	-2.86800	
H	1.94900	1.02900	-1.69100	
H	-1.52300	-1.19500	-2.26300	
H	-0.09600	-1.44800	-3.27600	

Ph_3GeNPh_2

Electronic energy (B3LYP/cc-pVTZ) = -3290.6036593 Hartree
Thermal correction to enthalpy = 0.488011 Hartree
Thermal correction to Gibbs free energy = 0.396819 Hartree

C	-1.69700	-1.22000	-0.60200	H	2.86700	-0.71500	-4.22000
Ge	0.07100	-0.62800	0.00900	H	1.18700	0.19700	-2.67600
C	0.30900	-1.19400	1.87800	H	-1.17600	2.30300	1.98500
C	0.01100	-2.51000	2.24600	H	-3.39500	3.39700	1.97000
C	0.16100	-2.93500	3.56100	H	-4.64600	3.62800	-0.15500
C	0.60600	-2.04500	4.53200	H	-3.66200	2.76800	-2.25800
C	0.89700	-0.73200	4.18300	H	-1.43800	1.68400	-2.22900
C	0.75000	-0.31100	2.86600	H	2.58600	0.43500	0.55400
C	1.46200	-1.33200	-1.18600	H	4.59100	1.79700	0.63500
C	2.18600	-2.47800	-0.85600	H	4.50000	4.23000	0.13300
C	3.14100	-2.99100	-1.72800	H	2.31400	5.24800	-0.46600
C	3.38500	-2.36100	-2.94200	H	0.29200	3.88800	-0.57000
C	2.67400	-1.21600	-3.28100	H	-2.68800	-0.79400	1.26200
C	1.72000	-0.70600	-2.40800	H	-4.90300	-1.51600	0.49000
N	0.10200	1.25800	-0.09600	H	-5.20200	-2.36800	-1.81500
C	-1.16500	1.92400	-0.12100	H	-3.25600	-2.49700	-3.34100
C	-1.72500	2.41300	1.05900	H	-1.03600	-1.77500	-2.57400
C	-2.97000	3.02600	1.04700				
C	-3.67300	3.15600	-0.14600				
C	-3.12000	2.67300	-1.32600				
C	-1.87100	2.06500	-1.31400				
C	1.26300	2.04400	-0.02200				
C	2.50600	1.48600	0.32100				
C	3.65200	2.26500	0.36900				
C	3.60500	3.62500	0.08900				
C	2.38000	4.19100	-0.24300				
C	1.22700	3.42100	-0.30300				
C	-2.80200	-1.16400	0.25200				
C	-4.05700	-1.57200	-0.18200				
C	-4.22500	-2.05000	-1.47700				
C	-3.13300	-2.12000	-2.33400				
C	-1.87800	-1.70900	-1.89700				
H	-0.35600	-3.21100	1.50600				
H	-0.07400	-3.95700	3.82800				
H	0.72100	-2.37300	5.55700				
H	1.23900	-0.03400	4.93600				

H	0.98300	0.71400	2.61100
H	2.01800	-2.97400	0.09200
H	3.69600	-3.88000	-1.45600
H	4.13000	-2.75800	-3.61900

$[Ph_3Ge(F)- NPh_2]^-$							
Electronic energy (M06-2X/Def2-TZVPP/D3(0)) = -3390.010 Hartree Thermal correction to enthalpy = 0.493 Hartree							
Ge	0.28800	-0.50600	-0.41100	H	-4.50800	0.23800	-2.29100
C	-1.16500	-1.86500	-0.25300	H	-5.71700	1.35300	-0.43700
C	-2.10100	-1.81000	0.78000	H	-4.42400	2.48100	1.35500
C	-3.15100	-2.71600	0.85300	H	-1.95500	2.47900	1.28700
C	-3.27000	-3.72000	-0.09800	C	0.32100	2.46800	-0.54100
C	-2.34400	-3.79700	-1.13000	C	1.71800	2.42000	-0.35500
C	-1.31300	-2.86800	-1.21200	C	2.48500	3.56900	-0.34900
H	-0.62100	-2.90300	-2.04400	C	1.91100	4.82300	-0.52700
H	-2.43300	-4.57500	-1.88000	C	0.53800	4.88700	-0.72600
H	-4.08300	-4.43400	-0.04000	C	-0.24600	3.74500	-0.73700
H	-3.87700	-2.63700	1.65400	H	-1.30800	3.83400	-0.91500
H	-2.01600	-1.03800	1.53700	H	0.06000	5.84800	-0.88500
C	0.53400	-0.33200	1.65200	H	2.51600	5.72000	-0.51900
C	0.78300	-1.51500	2.35900	H	3.55500	3.47900	-0.20000
C	0.92900	-1.54000	3.73800	H	2.20500	1.46500	-0.21600
C	0.82900	-0.35900	4.46700	F	0.04600	-0.58100	-2.28300
C	0.58300	0.82900	3.79600				
C	0.43700	0.83400	2.40900				
H	0.25300	1.78200	1.91600				
H	0.50500	1.75800	4.35000				
H	0.94100	-0.36900	5.54500				
H	1.11800	-2.47800	4.24800				
H	0.86300	-2.45100	1.81100				
C	2.18300	-1.11200	-0.74400				
C	3.19900	-0.94500	0.20000				
C	4.49400	-1.39200	-0.03200				
C	4.80400	-2.03900	-1.22000				
C	3.81000	-2.21900	-2.17300				
C	2.52200	-1.75200	-1.94000				
H	1.76200	-1.86300	-2.70200				
H	4.04100	-2.71700	-3.10700				

H	5.81100	-2.39600	-1.40300
H	5.26000	-1.23800	0.71900
H	2.98100	-0.45100	1.14000
N	-0.42200	1.31400	-0.54800
C	-1.83300	1.38100	-0.54800
C	-2.52300	2.00200	0.49700
C	-3.90900	2.00100	0.53100
C	-4.63400	1.36700	-0.47100
C	-3.95600	0.74400	-1.50900
C	-2.56900	0.75500	-1.55600
H	-2.02300	0.25600	-2.34700

$Ph_3GeN(SiMe_3)_2$

Electronic energy (B3LYP/cc-pVTZ) = -3645.9211497 Hartree
Thermal correction to enthalpy = 0.534600 Hartree
Thermal correction to Gibbs free energy = 0.435890 Hartree

C	-2.88600	-1.06600	0.83000	H	1.83900	-2.30900	1.80800
Si	-2.63600	0.65600	0.10000	H	2.09800	-2.61600	4.23400
N	-0.94500	0.97600	-0.28800	H	0.92700	-1.10800	5.81100
Si	-0.42100	2.59800	-0.73000	H	-0.50800	0.71200	4.93800
C	0.31000	3.45300	0.78600	H	-0.78600	1.00200	2.50300
C	0.84100	2.62500	-2.13300	H	-0.92400	-0.82800	-2.62600
C	-1.87100	3.62600	-1.37900	H	-1.67600	-2.79000	-3.91800
Ge	0.30200	-0.37500	0.04700	H	-1.51100	-5.05800	-2.93500
C	0.47900	-0.64700	1.97900	H	-0.57600	-5.34800	-0.66100
C	1.30300	-1.65600	2.48600	H	0.18100	-3.39100	0.62500
C	1.46100	-1.82700	3.85800	H	2.65200	1.12800	1.19200
C	0.80400	-0.97900	4.74400	H	4.87500	1.79000	0.35700
C	-0.00400	0.04200	4.25300	H	5.59600	1.11300	-1.91400
C	-0.16300	0.20400	2.88000	H	4.09100	-0.24600	-3.33200
C	-0.29600	-1.96900	-0.91800	H	1.86100	-0.89200	-2.50200
C	-0.82800	-1.81900	-2.20100	H	-3.35100	0.05500	-2.19800
C	-1.26200	-2.92300	-2.92700	H	-3.74200	1.75200	-1.88500
C	-1.17000	-4.19700	-2.37500	H	-4.74500	0.47100	-1.19700
C	-0.64300	-4.36000	-1.09700	H	-2.91200	1.57100	2.40200
C	-0.20800	-3.25200	-0.37600	H	-4.35200	1.88100	1.43500
C	2.08700	0.09500	-0.60600	H	-2.92400	2.89900	1.24500
C	2.95800	0.83700	0.19500				
C	4.21400	1.20700	-0.27200				
C	4.62000	0.82500	-1.54700				

C	3.77300	0.06200	-2.34500
C	2.51500	-0.30100	-1.87400
C	-3.71800	0.75600	-1.44300
C	-3.25800	1.87500	1.41100
H	-2.76800	-1.85600	0.08900
H	-3.91000	-1.11200	1.21500
H	-2.21200	-1.27400	1.66200
H	1.14600	2.87700	1.18800
H	-0.43800	3.55100	1.57700
H	0.67900	4.45300	0.54300
H	1.85900	2.41600	-1.81000
H	0.82400	3.62300	-2.58400
H	0.58300	1.90600	-2.91400
H	-2.75000	3.64200	-0.73700
H	-2.18000	3.27300	-2.36500
H	-1.52200	4.65700	-1.49500

$[Ph_3Ge(F)\text{-}N(SiMe_3)_2]^-$

Electronic energy (M06-2X/Def2-TZVPP/D3(0)) = -3745.318 Hartree
Thermal correction to enthalpy = 0.537 Hartree

C	-3.08200	-0.65000	0.23000	C	4.87100	0.39000	-0.88100
Si	-1.85600	-0.31600	1.62700	C	4.09700	1.51200	-1.15300
N	-0.22000	-0.06400	1.14700	C	2.71200	1.41700	-1.15500
Si	0.97800	-0.01800	2.37200	H	2.11700	2.29800	-1.37500
C	1.74200	-1.71200	2.73000	H	4.57600	2.46200	-1.36000
H	2.27100	-2.10800	1.86100	H	5.95200	0.46200	-0.87200
H	0.97000	-2.43300	3.01600	H	4.84500	-1.71000	-0.43700
H	2.45900	-1.64000	3.55200	H	2.38900	-1.87000	-0.45400
C	2.41400	1.18000	2.11600	C	-2.64400	1.15900	2.51700
H	3.21600	0.77900	1.49600	H	-2.84500	1.95400	1.79500
H	2.82900	1.41300	3.10100	H	-2.03300	1.57800	3.31600
H	2.08300	2.11700	1.66200	H	-3.60200	0.85200	2.94800
C	0.31700	0.56900	4.05800	C	-2.05300	-1.82600	2.75900
H	-0.58400	0.07000	4.41300	H	-1.81700	-2.73500	2.19900
H	0.11400	1.64300	4.03000	H	-3.09000	-1.90500	3.09700
H	1.10600	0.40600	4.79800	H	-1.41300	-1.80100	3.64200
Ge	0.10300	0.09000	-0.93300	H	-3.00200	0.06300	-0.59300
C	-0.54100	-1.77500	-1.23600	H	-4.08200	-0.54100	0.66100
C	-1.17300	-2.12400	-2.43100	H	-2.99500	-1.65700	-0.17900

C	-1.64300	-3.41300	-2.64800	F	0.21400	0.25700	-2.81900
C	-1.45600	-4.39800	-1.68600				
C	-0.79400	-4.08100	-0.50900				
C	-0.35300	-2.78100	-0.28700				
H	0.12600	-2.53700	0.65400				
H	-0.63100	-4.84200	0.24600				
H	-1.81900	-5.40500	-1.85600				
H	-2.15200	-3.65200	-3.57500				
H	-1.28700	-1.37000	-3.19800				
C	-0.88500	1.82800	-0.97800				
C	-0.82600	2.73900	0.07600				
C	-1.46500	3.97300	0.00900				
C	-2.21100	4.30900	-1.11100				
C	-2.28900	3.41400	-2.17000				
C	-1.61600	2.20000	-2.11000				
H	-1.63800	1.52900	-2.95800				
H	-2.86500	3.66800	-3.05200				
H	-2.72500	5.26200	-1.16100				
H	-1.39200	4.66400	0.84100				
H	-0.28600	2.47000	0.97600				
C	2.07100	0.21200	-0.87300				
C	2.86200	-0.91000	-0.63600				
C	4.24900	-0.82600	-0.63300				

I_1_trans

Electronic energy (B3LYP/cc-pVTZ) = -3006.9232602 Hartree
Thermal correction to enthalpy = 0.376228 Hartree
Thermal correction to Gibbs free energy = 0.300258 Hartree

Ge	0.01300	0.00000	-0.15500	H	-5.87300	0.01400	-0.30200
N	-0.05200	0.00000	1.88500	H	-4.62700	-2.13200	-0.28900
C	-0.64200	1.17300	2.49200	H	-2.16600	-2.13500	-0.26300
H	-0.23500	2.08600	2.05400	F	-0.01500	-0.00100	-2.09900
H	-0.43700	1.20000	3.57600				
H	-1.74400	1.21300	2.37900				
C	-0.64800	-1.17000	2.49100				
H	-0.24700	-2.08500	2.05200				
H	-1.75000	-1.20400	2.37800				
H	-0.44300	-1.19900	3.57500				
C	1.06600	1.69000	-0.22200				
C	1.99100	1.99800	0.78000				
C	2.77100	3.15000	0.71500				
C	2.62600	4.03100	-0.35200				
C	1.70700	3.74100	-1.35700				
C	0.94700	2.57600	-1.29700				
H	0.26900	2.32200	-2.10000				
H	1.59200	4.41800	-2.19600				
H	3.22600	4.93200	-0.40300				
H	3.48700	3.36300	1.50100				
H	2.07600	1.32700	1.62500				
C	1.05800	-1.69500	-0.22200				
C	0.93300	-2.58100	-1.29600				
C	1.68800	-3.75000	-1.35500				
C	2.60600	-4.04300	-0.35100				
C	2.75700	-3.16200	0.71500				
C	1.98300	-2.00700	0.77900				
H	2.07200	-1.33500	1.62400				
H	3.47400	-3.37700	1.50000				
H	3.20200	-4.94700	-0.40200				
H	1.56900	-4.42700	-2.19400				
H	0.25600	-2.32500	-2.09800				
C	-1.96900	0.00500	-0.26400				
C	-2.69600	-1.18900	-0.26800				
C	-4.08800	-1.19100	-0.28300				

C	-4.78900	0.01100	-0.29000
C	-4.08300	1.21000	-0.28100
C	-2.69000	1.20200	-0.26600
H	-2.15700	2.14500	-0.26000
H	-4.61700	2.15400	-0.28600

I_1_cis

Electronic energy (B3LYP/cc-pVTZ) = -3006.8512808 Hartree
Thermal correction to enthalpy = 0.377136 Hartree
Thermal correction to Gibbs free energy = 0.300880 Hartree

Ge	-0.02300	-0.38800	0.57000	H	-4.74600	0.80900	-1.05300
N	-0.00500	0.11300	2.40300	H	-5.20700	-1.38800	-2.11200
C	0.44000	-0.85000	3.38900	H	-3.47500	-3.16300	-2.04300
H	-0.32000	-1.61400	3.61900	H	-1.33200	-2.75300	-0.87600
H	0.69300	-0.32500	4.32300				
H	1.32400	-1.37700	3.03100				
C	-1.18800	0.80800	2.85900				
H	-1.50000	1.55400	2.12600				
H	-0.98200	1.33500	3.80500				
H	-2.04500	0.13400	3.04300				
F	-0.15100	-2.25800	1.12300				
C	0.07500	1.62200	-0.05300				
C	0.56600	2.64800	0.76300				
C	0.75000	3.94700	0.29000				
C	0.45000	4.25700	-1.03300				
C	-0.03400	3.25500	-1.87000				
C	-0.21600	1.96500	-1.37900				
H	-0.59800	1.20200	-2.04800				
H	-0.27000	3.48000	-2.90500				
H	0.59400	5.26400	-1.40800				
H	1.13200	4.71700	0.95200				
H	0.81600	2.40800	1.78900				
C	1.74100	-0.87400	-0.27800				
C	2.69200	0.10000	-0.60300				
C	3.91100	-0.23600	-1.18800				
C	4.20300	-1.56200	-1.48300				
C	3.27100	-2.54800	-1.17300				
C	2.06300	-2.20700	-0.57000				
H	1.35600	-2.97500	-0.29300				
H	3.48700	-3.58700	-1.39400				

H	5.14700	-1.82600	-1.94700
H	4.62900	0.54400	-1.41800
H	2.48000	1.14000	-0.39900
C	-1.77500	-0.72500	-0.36800
C	-2.06500	-1.96300	-0.95100
C	-3.28100	-2.19800	-1.58800
C	-4.25500	-1.20400	-1.62700
C	-3.99500	0.02800	-1.03500
C	-2.76300	0.26200	-0.42700
H	-2.56200	1.23600	-0.00100

I_2			
Electronic energy (B3LYP/cc-pVTZ) = -2772.0387109 Hartree Thermal correction to enthalpy = 0.290462 Hartree Thermal correction to Gibbs free energy = 0.227236 Hartree			
Ge	-0.00100	0.00000	-0.00200
C	0.64900	-1.78300	-0.00100
C	-0.16300	-2.83200	-0.46700
C	0.31800	-4.13200	-0.46800
C	1.60300	-4.39800	0.00300
C	2.41400	-3.36600	0.47200
C	1.94500	-2.06100	0.46600
H	2.57600	-1.26400	0.83600
H	3.40700	-3.58200	0.84000
H	1.97300	-5.41300	0.00500
H	-0.30200	-4.93700	-0.83500
H	-1.15800	-2.62900	-0.83900
C	1.22000	1.45400	-0.00200
C	0.81500	2.71500	0.46800
C	1.71300	3.77200	0.47400
C	3.01000	3.58400	0.00200
C	3.41900	2.34000	-0.47200
C	2.53300	1.27400	-0.47000
H	2.85300	0.31000	-0.84300
H	4.42600	2.20400	-0.84000
H	3.70600	4.41200	0.00400
H	1.40500	4.74000	0.84500
H	-0.18900	2.86400	0.84100
C	-1.87000	0.33000	0.00000
C	-2.76000	-0.65300	0.46700

C	-4.12400	-0.40600	0.47100
C	-4.61100	0.81200	0.00100
C	-3.73800	1.79100	-0.47000
C	-2.37100	1.55800	-0.46700
H	-1.69700	2.31800	-0.83900
H	-4.12400	2.73100	-0.83800
H	-5.67600	1.00000	0.00200
H	-4.80800	-1.15800	0.84000
H	-2.38500	-1.59800	0.83800

Ph_3GeF			
Electronic energy (B3LYP/cc-pVTZ) = -2872.2539408 Hartree Thermal correction to enthalpy = 0.292980 Hartree Thermal correction to Gibbs free energy = 0.225926 Hartree			
Ge	0.00000	0.00000	0.61500
F	0.00000	0.00000	2.38000
C	0.00000	1.87000	0.08000
C	-0.99300	2.74000	0.54300
C	-1.00400	4.07300	0.15100
C	-0.02200	4.55300	-0.71200
C	0.97000	3.69800	-1.18000
C	0.98000	2.36300	-0.78500
H	1.75700	1.70300	-1.14900
H	1.73500	4.06900	-1.84900
H	-0.03100	5.59100	-1.01700
H	-1.77500	4.73800	0.51800
H	-1.75800	2.37600	1.21700
C	1.61900	-0.93500	0.08000
C	1.55700	-2.03000	-0.78500
C	2.71800	-2.68900	-1.18000
C	3.95400	-2.25700	-0.71200
C	4.02900	-1.16700	0.15100
C	2.86900	-0.51000	0.54300
H	2.93600	0.33500	1.21700
H	4.99100	-0.83200	0.51800
H	4.85700	-2.76900	-1.01700
H	2.65600	-3.53700	-1.84900
H	0.59600	-2.37400	-1.14900
C	-1.61900	-0.93500	0.08000
C	-2.53700	-0.33300	-0.78500
C	-3.68700	-1.00900	-1.18000
C	-3.93200	-2.29600	-0.71200
C	-3.02500	-2.90600	0.15100
C	-1.87600	-2.23000	0.54300
H	-1.17800	-2.71000	1.21700
H	-3.21600	-3.90600	0.51800
H	-4.82600	-2.82200	-1.01700
H	-4.39100	-0.53200	-1.84900
H	-2.35400	0.67000	-1.14900

PhCOF			
Electronic energy (B3LYP/cc-pVTZ) = -445.011398 Hartree Thermal correction to enthalpy = 0.110357 Hartree Thermal correction to Gibbs free energy = 0.070515 Hartree			
C	-1.70400	0.13900	0.00000
F	-2.30500	-1.08500	0.00000
C	-0.23200	0.04000	0.00000
C	0.50100	1.23100	0.00000
C	1.88700	1.18900	0.00000
C	2.54500	-0.03900	0.00000
C	1.81800	-1.22500	0.00000
C	0.43000	-1.19000	0.00000
H	-0.14300	-2.10500	0.00000
H	2.33200	-2.17600	0.00000
H	3.62700	-0.07100	0.00000
H	2.45500	2.10900	0.00000
H	-0.03100	2.17100	0.00000
O	-2.37000	1.12100	0.00000

$PhCONMe_2$			
Electronic energy (B3LYP/cc-pVTZ) = -479.7379706 Hartree Thermal correction to enthalpy = 0.194639 Hartree Thermal correction to Gibbs free energy =0.146513 Hartree			
C	3.35300	0.04000	-0.17300
N	1.96200	-0.31000	0.07000
C	1.75900	-1.49600	0.88500
H	0.72100	-1.59000	1.18100
H	2.05400	-2.39900	0.34400
H	2.36900	-1.43400	1.79200
C	1.00100	0.62900	-0.20600
C	-0.44600	0.23400	-0.08300
C	-1.32000	1.12900	0.53400
C	-2.67800	0.85200	0.60000
C	-3.18300	-0.30800	0.02100
C	-2.32200	-1.19100	-0.62100
C	-0.95900	-0.92500	-0.66600
H	-0.29400	-1.61100	-1.17500
H	-2.71100	-2.08400	-1.09100
H	-4.24300	-0.51800	0.06100
H	-3.34600	1.54600	1.09200

H	-0.92400	2.04600	0.94800
O	1.28600	1.75700	-0.58500
H	3.85000	0.36000	0.74800
H	3.88200	-0.83100	-0.56400
H	3.39600	0.85200	-0.89000

TS

Electronic energy (B3LYP/cc-pVTZ) = -3351.9491717 Hartree
Thermal correction to enthalpy = 0.485718 Hartree
Thermal correction to Gibbs free energy = 0.401086 Hartree

$\underline{Ph_3GeNMe_2}$

Ge	-0.658	0.019	0.051
N	0.677	-0.318	-1.321
C	1.261	0.937	-1.917
H	0.501	1.425	-2.537
H	2.124	0.668	-2.532
H	1.576	1.616	-1.133
C	0.149	-1.19	-2.431
H	0.072	-2.199	-2.03
H	0.863	-1.195	-3.26
H	-0.818	-0.818	-2.776
C	-2.258	0.589	-0.966
C	-2.288	1.18	-2.233
C	-3.481	1.617	-2.816
C	-4.688	1.454	-2.137
C	-4.688	0.861	-0.871
C	-3.49	0.44	-0.298
H	-3.506	-0.015	0.687
H	-5.618	0.727	-0.33
H	-5.618	1.787	-2.584
H	-3.462	2.084	-3.795
H	-1.362	1.331	-2.783
C	-1.316	-1.607	0.873
C	-2.235	-2.415	0.197
C	-2.703	-3.604	0.756
C	-2.272	-3.989	2.027
C	-1.365	-3.185	2.723
C	-0.877	-2.019	2.137
H	-0.136	-1.43	2.657
H	-1.022	-3.479	3.708
H	-1.55	2.88	-0.12
H	-1.077	4.946	1.138
H	0.454	4.89	3.098
H	1.558	2.753	3.733
H	1.15	0.71	2.386

$\underline{PhCOF}$

F	1.235	-0.633	0.986
C	1.846	-1.293	-0.452
C	3.213	-0.688	-0.463
C	4.171	-1.369	-1.217
C	5.457	-0.847	-1.352
C	5.786	0.359	-0.728
C	4.836	1.021	0.057
C	3.55	0.5	0.194
H	2.836	0.964	0.865
H	5.104	1.93	0.581
H	6.785	0.767	-0.829
H	6.198	-1.377	-1.939
H	3.884	-2.307	-1.677
O	1.648	-2.493	-0.63

H	-2.636	-4.91	2.469	
H	-3.407	-4.221	0.208	
H	-2.607	-2.097	-0.771	
C	-0.27	1.629	1.072	
C	0.622	1.626	2.158	
C	0.874	2.785	2.892	
C	0.258	3.986	2.532	
C	-0.603	4.017	1.433	
C	-0.866	2.847	0.718	

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