SUPPORTING INFORMATION

Hydrogermylation of Alkynes via Metal-Ligand Cooperative Catalysis

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I. General Remarks

All reactions were performed in oven-dried glassware and using standard Schlenk techniques under an argon atmosphere unless otherwise stated. Dry solvents were obtained from a PureSolv solvent purification system and degassed by the freeze-pump-thaw method (three cycles times). Deuterated solvents for NMR spectroscopic analyses were purchased from Eurisotop, dried over activated 3 Å molecular sieves powder and degassed by the freeze-pump-thaw method.

NMR experiments were performed in deuterated solvents. ^{1}H, ^{13}C, ^{19}F, ^{31}P and ^{29}Si NMR spectra were recorded on Avance 300 MHz, Avance II 300 MHz, Avance 400 MHz, Avance III HD 400 MHz, Avance 500 MHz and Avance III HD 500 MHz Bruker spectrometers. All spectra were recorded at ambient temperature (298 K). Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual protium in the solvents (^{1}H) or the solvent carbon (^{13}C) as internal standards. Multiplicity of signals is indicated using the following abbreviations: s (singlet), br (broad), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplets), dhept (doublet of heptet), t (triplet), td (triplet of doublet), q (quadruplet), and m (multiplet). When necessary, NOESY, NOESY ZQF selective analyses were used to determine the regio- and stereochemistry of the obtained products.

Flash column chromatography was performed using Sigma-Aldrich Silica gel 60 – 200 µm or on an automated Interchim puriFlash system using pre-packed Interchim 30 µm silica gel cartridges.

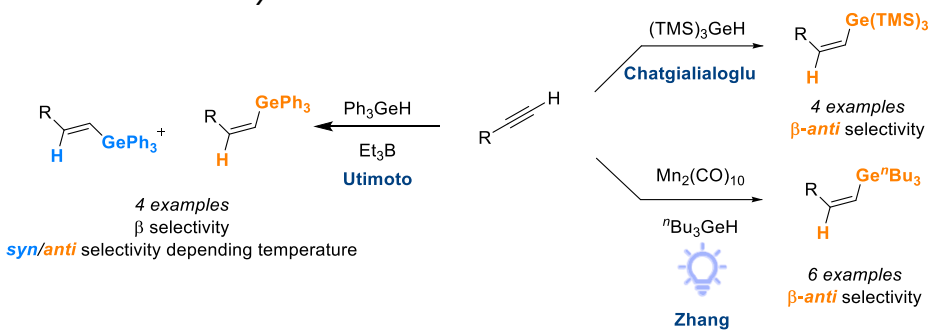
GC analyses were performed on a GC Perkin Elmer Clarus 500 with a flame ionization detector (FID) using a SGE BPX5 column (30 m x 0.32 mm x 0.25 mm) composed of 5% phenylmethylsiloxane in a 2 mL/min flow.

High-resolution mass spectra (HRMS) were recorded using either electrospray ionisation (ESI) or desorption chemical ionisation (DCI) using a Waters GCT Premier or Sciex QTRAP 4500 AB or Thermo Fisher Scientific DSQ II spectrometers.

Chart S1. Main precedents of catalytic alkyne hydrogermylation reactions. Ajouter les refs dans le Chart.

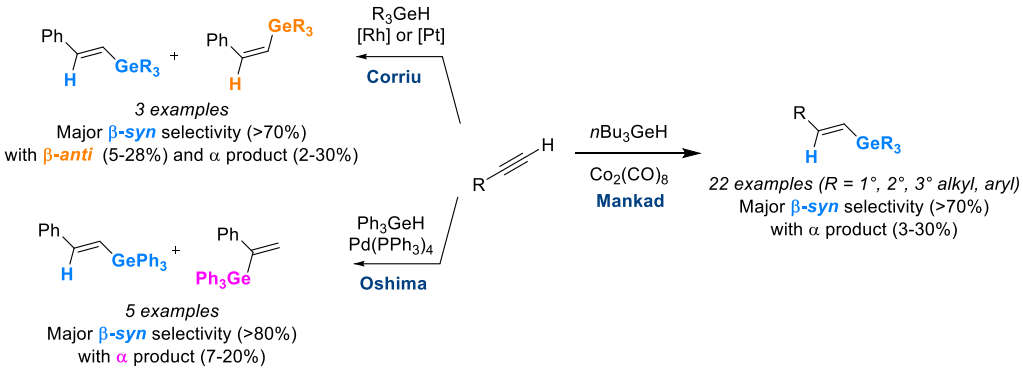
Radical hydrogermylations[1]

Terminal alkynes

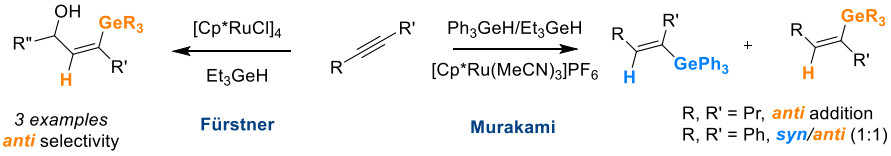


Transition Metal catalyzed hydrogermylations

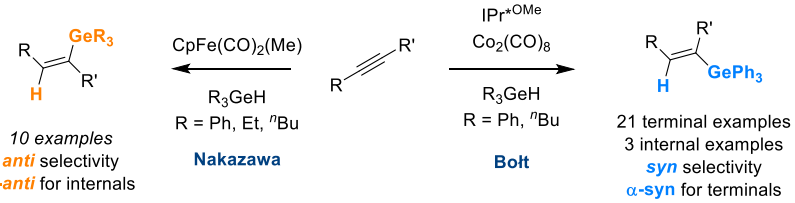
Terminal alkynes[2]



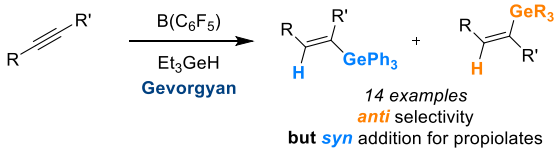
Internal alkynes[3]



Terminal and internal alkynes[4]

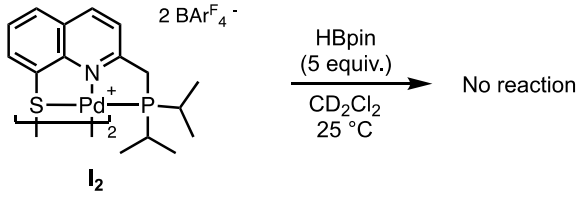


Lewis-Acid catalyzed hydrogermylations[5]



II. Activation of E-H bond (E= B, Sn & Ge) across the Pd-S bond

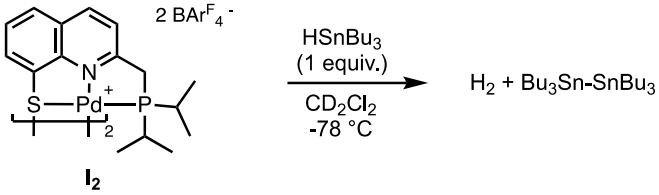
Test activation of Pinacolborane:



I_2

A J-young NMR tube was charged with **I_2** (11 mg, 0.01 mmol, 1.0 equivalent), HBpin (6.4 µL, 0.05 mmol, 5.0 equivalent) and 0.7 mL of CD_2Cl_2. The reaction was monitored by NMR. After 48 h, no reaction occurs and **I_2** was detected as the only species by ^{31}P NMR analysis.

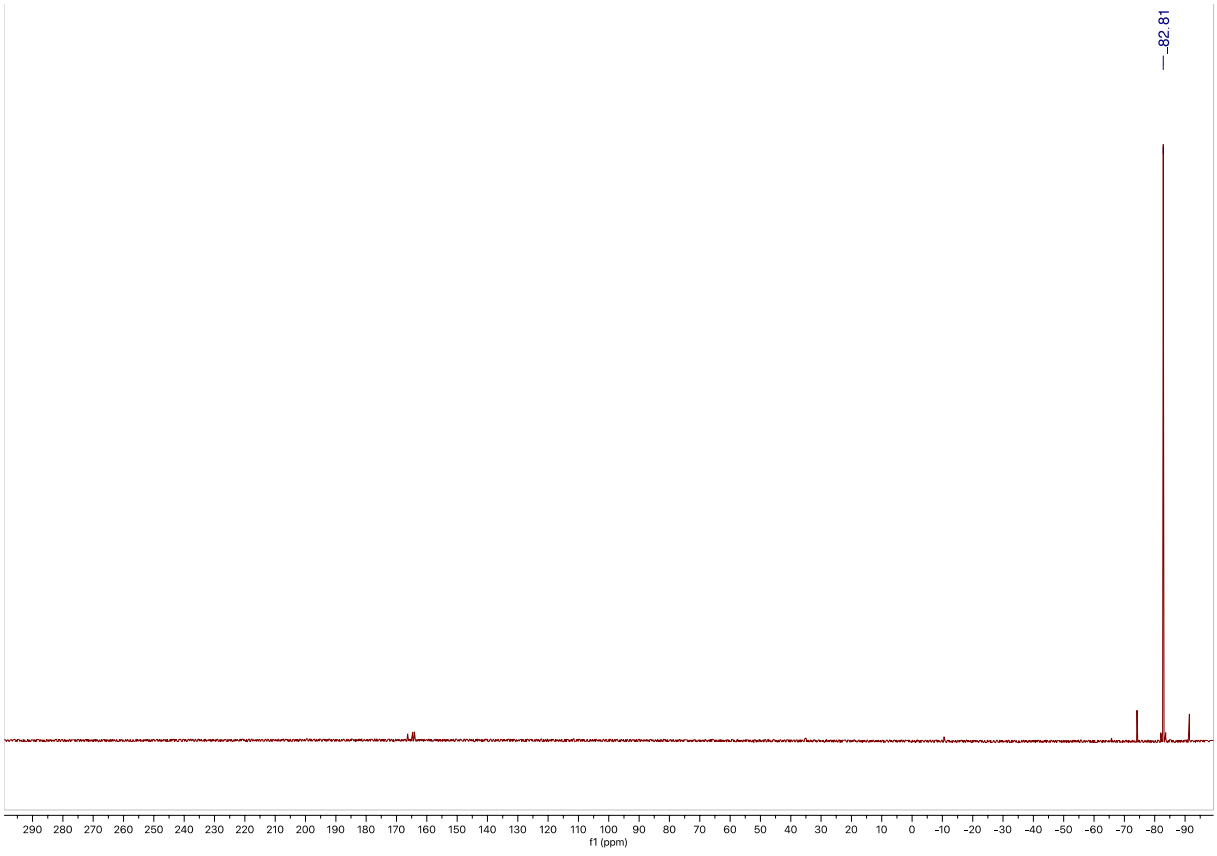
Test activation of tributyltin hydride:



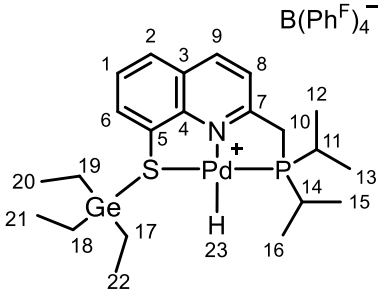
I_2

A J-young NMR tube was charged with **I_2** (11 mg, 0.01 mmol, 1.0 equivalent), $HSnBu_3$ (2.8 µL, 0.01 mmol, 1.0 equivalent) and 0.7 mL of CD_2Cl_2. An instantaneous gas evolution (H_2), even at low temperature (–78 °C). The reaction was monitored by NMR. The dehydrogenative coupling product $Bu_3SnSnBu_3$ was detected as a singlet at δ –83 ppm in ^{119}Sn NMR spectroscopy.

Figure S1: ^{119}Sn NMR spectroscopy of mixture of $HSnBu_3$ and I_2



Activation of Et_3Ge-H:



A J-young NMR tube was charged with **I_2** (20 mg, 0.018 mmol, 1.0 equivalent), Et_3GeH (16.2 µL, 0.093 mmol, 5.0 equivalent) and 1 mL of CD_2Cl_2. The reaction was monitored by NMR. After <5 min the product **II** was detected as the only species by ^{31}P NMR analysis and characterized spectroscopically in presence of excess Et_3GeH.

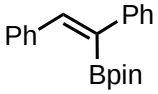
^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.50 (d, J = 8.5 Hz, 1H, H_9), 8.03 (d, J = 7.4 Hz, 1H, H_6), 8.00 (d, J = 8.2 Hz, 1H, H_2), 7.77 (d, J = 8.5 Hz, 1H, H_8), 7.75 – 7.68 (m, 1H, H_1), 3.99 (d, $J_{H\text{-}P}$ = 9.8 Hz, 2H, H_{10}), 2.49 – 2.32 (m, 2H, $H_{14,11}$), 1.32 (dd, $J_{H\text{-}P}$ = 19.5, $J_{H\text{-}H}$ =7.0 Hz, 6H, $H_{12,13,15,16}$), 1.26 – 1.17 (m, 12H, $H_{12,13,15,16}$; $H_{17\text{-}19}$), 1.11 – 1.09 (m, 9H, $H_{20\text{-}22}$), -12.62 (d, $J_{H\text{-}P}$ = 4.9 Hz, 1H, H_{23}).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 162.4 (d, $J_{C\text{-}P}$ = 4.1 Hz, C_7), 148.5 (d, $J_{C\text{-}F}$ = 240.0 Hz, C_{BPhF}), 147.0 (d, $J_{C\text{-}P}$ = 2.2 Hz, C_4), 141.1 (C_9), 138.4 (d, $J_{C\text{-}P}$ = 2.7 Hz, C_6), 138.2 (d, $J_{C\text{-}F}$ =245 Hz, C_{BPhF}), 135.9 (d, $J_{C\text{-}F}$ = 246 Hz, C_{BPhF}), 133.4 (d, $J_{C\text{-}P}$ = 1.4 Hz, C_5), 129.5 (C_3), 129.4 (C_2), 129.1 (C_1), 121.7 (d, $J_{C\text{-}P}$ = 10.5 Hz, C_8), 38.5 (d, $J_{C\text{-}P}$ = 23.0 Hz, C_{10}), 25.2 (d, $J_{C\text{-}P}$ = 28.0 Hz, $C_{11,14}$), 19.1 (d, $J_{C\text{-}P}$ = 4.2 Hz, $C_{16,12}$), 18.2 ($C_{15,13}$), 10.7 ($C_{17,\,18,\,19}$), 8.69 ($C_{20,\,21,\,22}$)

^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ 74.8 (s).

III. Preliminary catalytic results

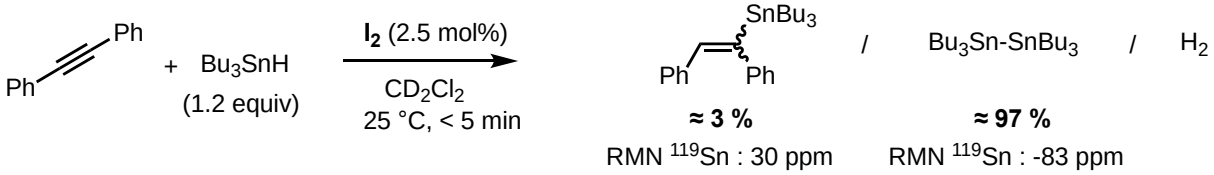
Hydroboration of diphenylacetylene: (E)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane - CAS [1391743-16-0]



In an J-Young NMR tube, diphenylacetylene (35.6 mg, 0.20 mmol, 1.0 equiv), pinacolborane (49 µL, 0.34 mmol, 1.7 equiv) and 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) were dissolved in CD_2Cl_2 (0.6 mL). After shaking, 5 mol% of catalyst **I_2** was added (11 mg, 0.01 mmol, 2.5 mol%). The mixture was placed at 70 °C for 4 h. (*E*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*Anti*-isomer, 72%) along with the *syn*-isomer (28%) was formed with quantitative yield as estimated by ^{1}H NMR analysis. The mixture was purified by column chromatography using 100% pentane, 75% yield was obtained (46 mg). Spectroscopic data in accordance with the literature.[6] For minor isomer, a detailed ^{1}H NMR analysis could not be provided. However diagnostic signals are listed below.

^{1}H NMR (300 MHz, C_6D_6) δ 7.87 (s, 1H, H_{vinyl}), 7.44 – 7.32 (m, 4H, H_{arom}), 7.21 – 7.19 (m, 2H, H_{arom}), 7.03 – 7.01 (m, 2H, H_{arom}), 6.90 – 6.87 (m, 2H, H_{arom}), 1.08 (s, 12H, 4xCH_3).
For *Syn*-isomer in CD_2Cl_2: CH_{vinyl} signals at 7.29 ppm (s)

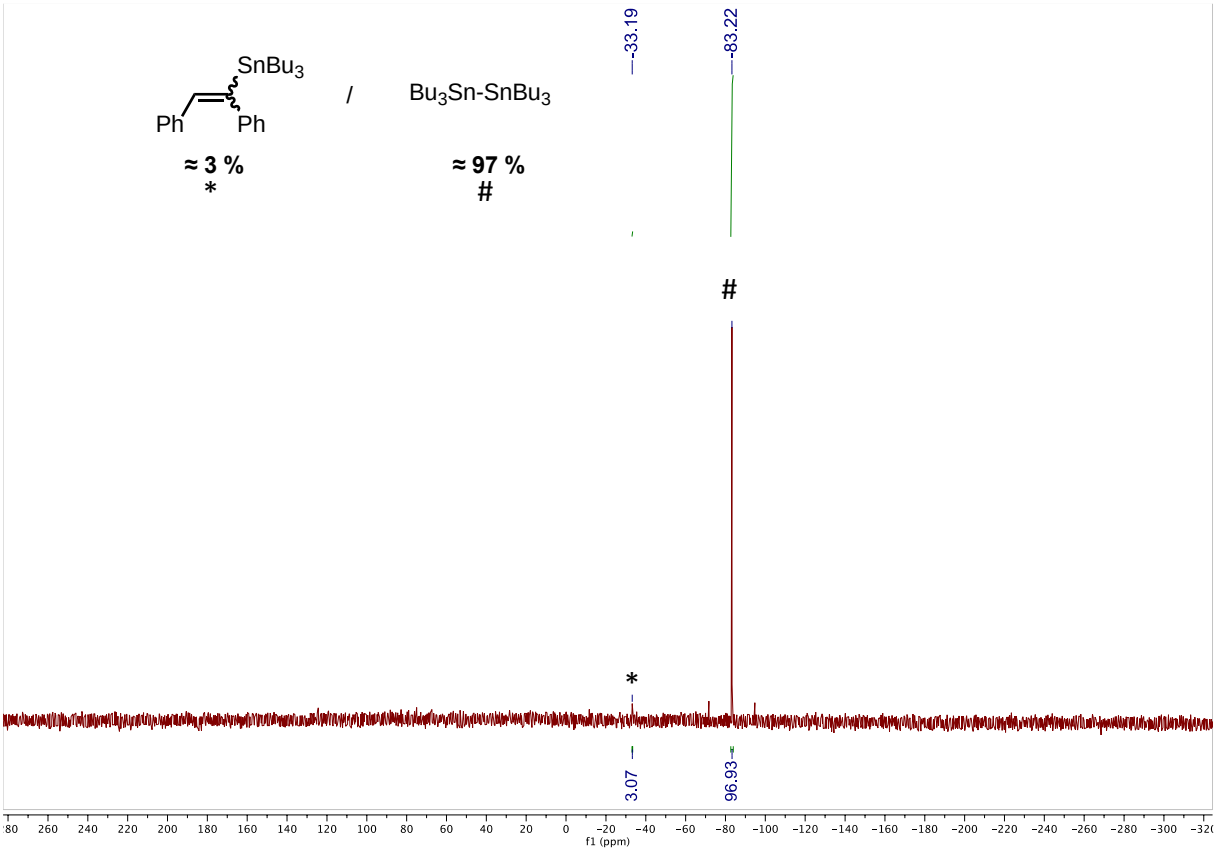
Hydrostannylation of diphenylacetylene:



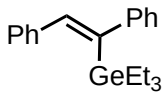
In an J-Young NMR tube, diphenylacetylene (35.6 mg, 0.20 mmol, 1.0 equiv), tributyltin hydride (65 µL, 0.24 mmol, 1.2 equiv) and 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol,

0.5 equiv) were dissolved in CD_2Cl_2 (0.6 mL). After shaking, 2.5 mol% of catalyst **I_2** was added (11 mg, 0.01 mmol, 5 mol%). An instantaneous gas evolution (H_2), even at low temperature (–78 °C). The reaction was monitored by NMR. The dehydrogenative coupling product $Bu_3SnSnBu_3$ was detected as a singlet at δ –83 ppm and only traces of hydrostannylation product was detected at δ 30 ppm in ^{119}Sn NMR spectroscopy.

Figure S2: ^{119}Sn NMR spectroscopy of hydrostannylation of diphenylacetylene



Hydrogermylation of diphenylacetylene: (E)-(1,2-diphenylvinyl)triethylgermane 2a - CAS [869795-36-8]

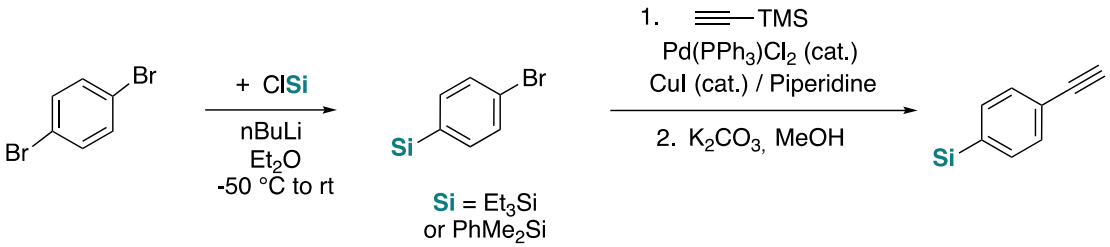


In an J-Young NMR tube, diphenylacetylene (35.6 mg, 0.20 mmol, 1.0 equiv), triethylgermane (39 µL, 0.24 mmol, 1.2 equiv) and 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) were dissolved in CD_2Cl_2 (0.6 mL). After shaking, 2.5 mol% of complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) was added. The mixture was placed at 25 °C for 5 h. **2a** (*Anti*-isomer, 55%) along with the *syn*-isomer (45%) was formed with quantitative yield as estimated by ^{1}H NMR analysis. Isolated as mixture by column chromatography using 100% pentane, 96% yield was obtained (65.4 mg). Spectroscopic data in accordance with the literature.[5] For minor product, a detailed ^{1}H NMR analysis could not be provided, diagnostic signals however are listed below.

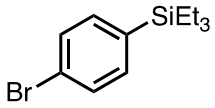
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 5H, H_{arom} & H_{vinyl}), 7.30 – 7.25 (m, 2H, H_{arom}), 7.22 – 7.14 (m, 2H, H_{arom}), 7.12 – 7.05 (m, 2H, H_{arom}), 0.99 (t, J = 7.9 Hz, 9H, $GeCH_2C\underline{H}_3$), 0.74 (q, J = 7.9 Hz, 6H, $GeCH_2$).

For *Syn*-isomer in CD_2Cl_2: CH_{vinyl} signals at 6.75 ppm (s)

IV. Synthesis of precursors



(4-bromophenyl)triethylsilane - CAS [18036-95-8]:



(4-bromophenyl)triethylsilane has been synthesized on the basis of a previously reported procedure.[7] Under nitrogen, 8.7 mL of 2.5 M *n*-BuLi (in hexane, 14.0 mmol, 1.1 equiv.) was slowly added to a 15 mL dry ether solution of 1,4-dibromobenzene (3.0 g, 12.7 mmol, 1.0 equiv.) at -50 °C, and the mixture was then stirred at -50 °C for 1 h. Next, 2.15 mL of chlorotriethylsilane (12.7 mmol, 1.0 equiv.) was slowly added to the above mixture and stirring was continued overnight at room temperature. Water was then added to the reaction mixture, and the organic layer was collected. The aqueous phase is extracted with ethyl acetate (2x) and combined organic phases were dried over Na_2SO_4, the solvent was removed under reduced pressure. (4-bromophenyl)triethylsilane was obtained after purification by flash chromatography (pentane), 67% yield was obtained (2.3 g). Spectroscopic data are in accordance with the literature.[7]

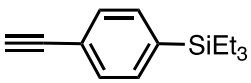
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H, H_{arom}), 7.36-7.33 (m, 2H, H_{arom}), 0.95 (t, J=7.3 Hz, 9H, 3x$SiCH_2$-$C\underline{H}_3$), 0.79 (q, J=7.8 Hz, 6H, 3x$SiCH_2$).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 136.4 (C_{arom}), 135.9 (CH_{arom}), 134.3 (C_{arom}), 130.9 (CH_{arom}), 7.6 ($SiCH_2$-$\underline{C}H_3$), 3.5 ($SiCH_2$).

^{29}Si{^{1}H} DEPT 9H NMR (99 MHz, $CDCl_3$) δ 2.5 (s).

HRMS (DCl-CH_4) calculated for [$C_{12}H_{19}SiBr$] M^+: 270.0439, found 270.0442.

(4-ethynylphenyl)triethylsilane - CAS [16116-94-2]:



(4-ethynylphenyl)triethylsilane has been synthesized on the basis of a previously reported procedure.[7] Under nitrogen, a mixture of dry (4-bromophenyl)triethylsilane (2.1 g, 7.92 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (139 mg, 0.20 mmol, 2.5 mol%), CuI (60 mg, 0.32 mmol, 4 mol%), and 15 mL of dry piperidine was stirred at 0 °C for 10 min. Then trimethylsilylacetylene (1.64 mL, 11.9 mmol, 1.5 equiv.) was added to the mixture and stirred at 80 °C for 18 h. After cooling to room temperature, the solvent was removed under vacuum.

A methanol (20 mL) solution of K_2CO_3 (3.3 g, 23.8 mmol) was added to the mixture and stirring was continued at room temperature for 2 h. The methanol was then removed under vacuum, and the organic product was extracted with hexane and then filtered through a Celite pad, the solvent was removed under reduced pressure. (4-ethynylphenyl)triethylsilane was obtained after purification by flash chromatography (pentane), 60% yield was obtained (1.0 g). Spectroscopic data are in accordance with the literature.[7]

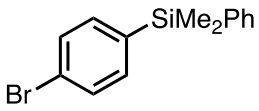
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.41 (m, 4H, H_{arom}), 3.08 (s, 1H, ≡CH), 0.95 (t, *J* = 7.3 Hz, 9H, 3x$SiCH_2$-$C\underline{H}_3$), 0.79 (q, *J* = 7.8 Hz, 6H, 3x$SiCH_2$).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 139.1 (C_{arom}), 134.2 (CH_{arom}), 131.3 (CH_{arom}), 122.4 (C_{arom}), 84.0 (-C≡CH), 77.6 (-C≡CH), 7.5 ($SiCH_2$-CH_3), 3.4 ($SiCH_2$).

$^{29}Si\{^1H\}$ DEPT 9H NMR (99 MHz, $CDCl_3$) δ 2.4 (s).

HRMS (DCl-CH_4) calculated for [$C_{14}H_{21}Si$] M^+: 217.1413, found 217.1402.

(4-bromophenyl)dimethyl(phenyl)silane - CAS [18407-37-9]:



(4-bromophenyl)dimethyl(phenyl)silane has been synthesized on the basis of a previously reported procedure.[7] Under nitrogen, 8.3 mL of 2.5 M n-BuLi (in hexane, 13.3 mmol, 1.1 equiv.) was slowly added to a 15 mL dry ether solution of 1,4-dibromobenzene (2.85 g, 12.1 mmol, 1.0 equiv.) at -50 °C, and the mixture was then stirred at -50 °C for 1 h. Next, 2.03 mL of chlorodimethylphenylsilane (12.1 mmol, 1.0 equiv.) was slowly added to the above mixture and stirring was continued overnight at room temperature. Water was then added to the reaction mixture, and the organic layer was collected. The aqueous phase is extracted with ethyl acetate (2x) and combined organic phases were dried over Na_2SO_4, the solvent was removed under reduced pressure. (4-bromophenyl)dimethyl(phenyl)silane was obtained after purification by flash chromatography (pentane), 78% yield was obtained (2.75 g). Spectroscopic data are in accordance with the literature.[8]

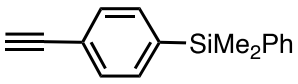
^1H NMR (300 MHz, $CDCl_3$) δ 7.52-7.48 (m, 4H, H_{arom}), 7.40-7.37 (m, 5H, H_{arom}), 0.56 (s, 6H, 2x$SiCH_3$).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 137.7 (C_{arom}), 137.3 (C_{arom}), 135.9 (CH_{arom}), 134.2 (CH_{arom}), 131.1 (CH_{arom}), 129.5 (CH_{arom}), 128.1 (CH_{arom}), 124.1 (C_{arom}), -2.2 (2x$SiCH_3$).

$^{29}Si\{^1H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$) δ -7.5 (s).

HRMS (DCl-CH_4) calculated for [$C_{14}H_{15}SiBr$] M^+: 290.0126, found 290.0126.

(4-ethynylphenyl)dimethyl(phenyl)silane - CAS [2359689-24-8]:



(4-ethynylphenyl)dimethyl(phenyl)silane has been synthesized on the basis of a previously reported procedure.[7] Under nitrogen, a mixture of dry (4-bromophenyl)dimethyl(phenyl)silane (2.0 g, 6.87 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (119 mg, 0.17 mmol, 2.5 mol%), CuI (51.4 mg, 0.27 mmol, 4 mol%), and 15 mL of dry piperidine was stirred at 0 °C for 10 min. Then trimethylsilylacetylene (1.4 mL, 10.3 mmol, 1.5 equiv.) was added to the mixture and stirred at 80 °C for 18 h. After cooling to room temperature, the solvent was removed under vacuum. A methanol (20 mL) solution of K_2CO_3 (2.8 g, 20.6 mmol) was added to the mixture and stirring was continued at room temperature for 2 h. The methanol was then removed under vacuum, and the organic product was extracted with hexane and then filtered through a Celite pad, the solvent was removed under reduced pressure. (4-ethynylphenyl)dimethyl(phenyl)silane was obtained after purification by flash chromatography (pentane), 84% yield was obtained (1.36 g). Spectroscopic data are in accordance with the literature.[9]

^1H NMR (300 MHz, $CDCl_3$) δ 7.52-7.48 (m, 6H, H_{arom}), 7.34-7.38 (m, 3H, H_{arom}), 3.10 (s, 1H, ≡CH), 0.56 (s, 6H, 2x$SiCH_3$).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 139.7 (C_{arom}), 137.8 (C_{arom}), 134.3 (CH_{arom}), 134.2 (CH_{arom}), 131.4 (CH_{arom}), 129.4 (CH_{arom}), 128.0 (CH_{arom}), 122.8 (C_{arom}), 83.9 (-C≡CH), 77.8 (-C≡CH), -2.4 (2x$SiCH_3$).

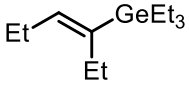
$^{29}Si\{^1H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$) δ -7.7 (s).

HRMS (DCl-CH_4) calculated for [$C_{16}H_{16}Si$] M^+: 236.1021, found 236.1022.

V. Catalytic Hydrogermylation

General procedure **A** for hydrogermylation:
In an J-Young NMR tube, the alkyne (0.2 mmol), the germane (0.24 mmol, 1.2 equiv or 0.60 mmol, 3.0 equiv) and the internal standard (1,2,4,5-tetramethylbenzene) were dissolved in CD_2Cl_2 (0.6 mL). After shaking, 2.5 mol% of catalyst was added. The tube was placed at 25 °C for the indicated time (reaction monitored by ^1H NMR).

(E)-triethyl(hex-3-en-3-yl)germane 2b:



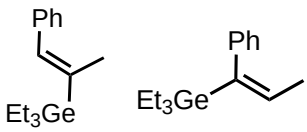
Using the general procedure **A**, hex-3-yne (22 µL, 0.20 mmol, 1.0 equiv), triethylgermane (97 µL, 0.60 mmol, 3.0 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25 °C for 5 h. **2b** (β-*syn*, 84%) along with the β-*anti* (16%) isomer was formed with 57% yield as estimated by ^1H NMR analysis. Isolated by column chromatography using 100% pentane, 53% combined yield of isomers was obtained (19 mg). Stereochemistry was determined according to data obtained for hydrosilylation of hex-1-yne.[10] For minor product, a detailed ^1H NMR analysis could not be provided, diagnostic signals however are listed below.

^1H NMR (300 MHz, $CDCl_3$) δ 5.48 ppm (tt, J = 6.8, 1.0 Hz, 1H, C-$\underline{H}_{vinyl}$), 2.20 – 2.06 ppm (m, 4H, 2x$C\underline{H}_2$-C_{vinyl}), 1.02 (t, J = 7.9 Hz, 9H, Ge-CH_2-$C\underline{H}_3$), 0.97 (t, J = 7.6 Hz, 3H, CH_2-$C\underline{H}_3$), 0.92 (t, J = 7.6 Hz, 9H, CH_2-$C\underline{H}_3$), 0.77 (q, J = 7.9 Hz, 6H, Ge-$C\underline{H}_2$-CH_3).
For β-*anti*: CH_{vinyl} signal at 5.90 ppm (tt, J = 7.3, 1.4 Hz, 1H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 140.4 ($\underline{C}H_{vinyl}$), 24.0 ($\underline{C}H_2$-CH_3), 21.4 ($\underline{C}H_2$-CH_3), 14.8 (CH_2-$\underline{C}H_3$), 14.7 (CH_2-$\underline{C}H_3$), 9.1 (Ge-CH_2-$\underline{C}H_3$), 4.2 (Ge-$\underline{C}H_2$-CH_3).

HRMS (DCl-CH_4) calculated for [$C_{10}H_{21}Ge$] MH^+-C_2H_6: 215.0855, found 215.0871.

(E)-triethyl(1-phenylprop-1-en-2-yl)germane 2c & (E)-triethyl(1-phenylprop-1-en-1-yl)germane 2c':



Using the general procedure **A**, prop-1-yn-1-ylbenzene (23.2 mg, 0.20 mmol, 1.0 equiv), triethylgermane (39 µL, 0.24 mmol, 1.2 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25°C for 1 h. (E)-triethyl(1-phenylprop-1-en-2-yl)germane **2c** (β-*syn*, 42%) and (E)-triethyl(1-phenylprop-1-en-1-yl)germane **2c'** (α-*syn*, 42%) were formed along with β-*anti* (14%) and α-*anti* (2%) isomer as estimated by ^1H NMR. Isolated by column chromatography using 100% pentane, 88% combined yield of isomers was obtained (48.9 mg). Spectroscopic data in accordance with the literature.[5,11] Stereochemistry was confirmed by NOESY 2D. For minor products, a detailed ^1H NMR analysis could not be provided, diagnostic signals however are listed below.

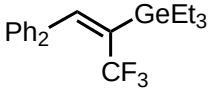
^1H NMR (500 MHz, $CDCl_3$) δ
β-*syn:* 7.31-7.29 (m, 3H, H_{arom}), 6.96-6.94 (m, 2H, H_{arom}), 6.59 (q, J = 1.9 Hz, 1H, H_{vinyl}), 2.02 (d, J = 1.9 Hz, 3H, CH_3), 1.08 (t, J = 7.8Hz, 9H, $GeCH_2C\underline{H}_3$), 0.89 (q, J = 7.8 Hz, 6H, $GeCH_2$).

β-*anti:* CH_{vinyl} signal at 7.21 ppm (stacked with H_{arom}) and 2.01 ppm (d, *J* = 1.9 Hz, 3H, CH_3).
α-*syn:* 7.36-7.33 (m, 3H, H_{arom}), 7.23-7.18 (m, 2H, H_{arom}), 5.90 (q, *J* = 6.5 Hz, 1H, H_{vinyl}), 1.61 (d, *J* = 6.5 Hz, 3H, CH_3), 0.99 (t, *J* = 7.8 Hz, 9H, $GeCH_2C\underline{H_3}$), 0.77 (q, *J* = 7.8 Hz, 6H, $GeCH_2$).
α-*anti:* CH_{vinyl} signal at 6.20 ppm (q, *J* = 7.1 Hz, 1H, H_{vinyl}) and 1.88 ppm (d, *J* = 7.1 Hz, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) *δ*
β-*syn:* 143.6 (C_{vinyl}), 138.4 (C_{arom}), 136.5 ($\underline{C}H_{vinyl}$), 18.5 (CH_3), 9.1 ($Ge-CH_2-\underline{C}H_3$), 3.7 ($Ge-\underline{C}H_2-CH_3$).
α-*syn:* 143.4 (C_{vinyl}), 140.3 (C_{arom}), 134.1 ($\underline{C}H_{vinyl}$), 15.9 (CH_3), 8.9 ($Ge-CH_2-\underline{C}H_3$), 4.1 ($Ge-\underline{C}H_2-CH_3$).

HRMS (DCl-CH_4) calculated for $[C_{15}H_{23}Ge]$ $[M-H]^+$: 273.1042, found 273.1038

(E)-(1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoroprop-1-en-2-yl)triethylgermane 2d:



Using the general procedure **A**, 4-(3,3,3-trifluoroprop-1-yn-1-yl)-1,1'-biphenyl (49,2mg, 0.20 mmol, 1.0 equiv), triethylgermane (39 µL, 0.24 mmol, 1.2 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 70°C for 3 h. **2d** (β-*syn*, 39%) was formed along with the β-*anti* (38%) and α-*syn* (21%) isomer as estimated by ^1H NMR. The mixture was purified by preparative TLC using 100% pentane, 99% combined yield was obtained (80 mg). Stereochemistry was confirmed by NOESY 2D. For minor products, a detailed ^1H NMR analysis could not be provided, diagnostic signals however are listed below.

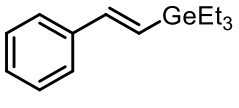
^1H NMR (500 MHz, $CDCl_3$) *δ* 7.64-7.58 (m, 6H, H_{arom}), 7.50-7.40 (m, 8H, H_{arom}), 7.03 (s, 1H, H_{vinyl}), 1.15 (t, *J* = 7.7Hz, 9H, $GeCH_2C\underline{H_3}$), 1.04 (q, *J* = 7.7 Hz, 6H, $GeCH_2$).
β-*anti:* CH_{vinyl} signal at 7.96 ppm (q, *J* = 2.6 Hz, 1H).
α-*syn:* CH_{vinyl} signal at 5.95 ppm (q, *J* = 7.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) *δ* 146.2 (q, *J* = 6.4 Hz, CH_{vinyl}), 141.3 (C_{arom}), 140.8 (C_{arom}), 139.1 (C_{arom}), 136.1 (C_{arom}), 129.4 (q, *J* = 2.8 Hz, CH_{arom}), 128.9 (CH_{arom}), 128.6 (CH_{arom}), 127.7 (CH_{arom}), 127.2 (CH_{arom}), 126.9 (CH_{arom}), 8.8 ($GeCH_2\underline{C}H_3$), 5.9 ($GeCH_2$).

^{19}F NMR (471 MHz, $CDCl_3$) *δ* -52.7 (broad s).
β-*anti:* -59.2 (d, *J* =2.6 Hz).
α-*syn:* -56.8 (d, *J* =7.9 Hz).

HRMS (DCl-CH_4) calculated for $[C_{21}H_{24}F_3Ge]$ M^+: 405.1229, found 405.1231.

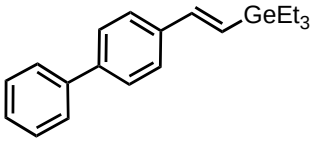
(E)-triethyl(styryl)germane 2e - CAS [19319-12-1]:



Using the general procedure **A**, phenylacetylene (22 µL, 0.20 mmol, 1.0 equiv), triethylgermane (39 µL, 0.24 mmol, 1.2 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25 °C for 10 min. (E)-triethyl(styryl)germane (β-*syn,* 32%) was formed along with the β-anti isomer (68%) in a quantitative yield as estimated by ^1H NMR. After 6 h, 100% of (*E*)-triethyl(styryl)germane was obtained. Isolated by column chromatography using 100% pentane, **2e** was obtained (90% yield, 47.3 mg). Spectroscopic data in accordance with literature.[5,12] For minor product, a detailed ^1H NMR analysis could not be provided, diagnostic signals however are listed below.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.48 – 7.45 (m, 2H, H_{arom}), 7.37 – 7.25 (m, 3H, H_{arom}), 6.88 (d, *J* = 19.0 Hz, 1H, Ph-H_{vinyl}), 6.67 (d, *J* = 19.0 Hz, 1H, Ge-H_{vinyl}), 1.12 (t, *J* = 7.8 Hz, 9H, 3xCH_3), 0.92 (q, *J* = 7.8 Hz, 6H, 3xCH_2).
For β-*anti* in CD_2Cl_2: CH_{vinyl} signals at 7.50 ppm (d, *J* = 14.1 Hz, 1H) and 5.97 ppm (d, *J* = 14.1 Hz, 1H).

(E)-(2-([1,1'-biphenyl]-4-yl)vinyl)triethylgermane 2f:



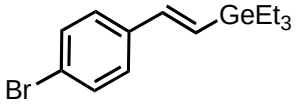
Using the general procedure **A**, 4-ethynylbiphenyl (35.6 mg, 0.20 mmol, 1.0 equiv), triethylgermane (49 µL, 0.24 mmol, 1.5 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25°C for 1 h. (*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)triethylgermane (β-*syn,* 40%) along with the β-anti isomer (60%) was formed with 90% as estimated by ^{1}H NMR analysis. After 26 h, 100% of (*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)triethylgermane (β-*syn)* is obtained. Isolated by column chromatography using 100% pentane, **2f** was obtained (89% yield, 60.5 mg). For minor product, a detailed ^{1}H NMR analysis could not be provided, diagnostic signals however are listed below.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 4H, H_{arom}), 7.56 – 7.44 (m, 4H, H_{arom}), 7.40 – 7.34 (m, 1H, H_{arom}), 6.92 (d, *J* = 19.0 Hz, 1H, Ph-Ph-H_{vinyl}), 6.71 (d, *J* = 19.0 Hz, 1H, Ge-H_{vinyl}), 1.42 (t, *J* = 7.8 Hz, 9H, 3xCH_3), 0.94 (q, *J* = 7.8 Hz, 6H, 3xCH_2).
For β-*anti* in CD_2Cl_2 *:* CH_{vinyl} signal at 6.02 ppm (d, *J* = 14.1 Hz, 1H)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.9 (CH_{vinyl}), 140.9 (C_{arom}), 140.5 (C_{arom}), 137.6 (C_{arom}), 128.9 (CH_{arom}), 128.2 (CH_{vinyl}), 127.4 (CH_{arom}), 127.3 (CH_{arom}), 127.1 (CH_{arom}), 126.7 (CH_{arom}), 9.1 ($GeCH_2\underline{C}H_3$), 4.6 ($GeCH_2$).

HRMS (DCl-CH_4) calculated for [$C_{20}H_{26}Ge$] M^+: 336.1277, found 336.1291.

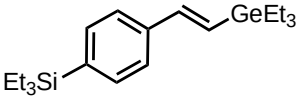
(E)-(4-bromostyryl)triethylgermane 2g – CAS [2660285-24-3]:



Using the general procedure **A**, 1-ethynyl-4-bromobenzene (36 mg, 0.20 mmol, 1.0 equiv), dimethylphenylsilane (37 µL, 0.24 mmol, 1.2 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25°C for 24 h. **2g** (β-*syn*, 80%) was formed along with the product resulting from dehalogenation (20%) with quantitative yield as estimated by ^{1}H NMR. For β-*syn* isomer, spectroscopic data are in accordance with the literature.[13] For minor product, a detailed ^{1}H NMR analysis could not be provided; diagnostic signals however are listed below.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 19.0 Hz, 1H), 6.64 (d, *J* = 19.0 Hz, 1H), 1.09 (t, *J* = 7.9 Hz, 9H), 0.92 (q, *J* = 7.9 Hz, 6H).
Dehalogenated product β-*syn* (same than **2e**): 6.87 (d, *J* = 19.0 Hz, 1H, H_{vinyl}) & 6.65 (d, *J* = 19.0 Hz, 1H, H_{vinyl}).

(E)-triethyl(4-(2-(triethylgermyl)vinyl)phenyl)silane 2h:



Using the general procedure **A**, (4-ethynylphenyl)triethylsilane (400 mg, 1.85 mmol, 1.0 equiv), triethylgermane (359 µL, 2.22 mmol, 1.2 equiv) and **I_2** (100 mg, 0.01 mmol, 2.5 mol%) were dissolved in DCM (8 mL). The mixture was placed at 25°C for 48 h, ((*E*)-triethyl(4-(2-(triethylgermyl)vinyl)phenyl)silane (β-*syn,* 36%) along with the β-anti isomer (64%) was

formed with quantitative yield as estimated by ^{1}H NMR analysis. After 48 h, 100% of (*E*)-triethyl(4-(2-(triethylgermyl)vinyl)phenyl)silane (β-*syn)* is obtained. Isolated by column chromatography using 100% pentane, **2h** was obtained (65% yield, 458 mg). For minor product, a detailed ^{1}H NMR analysis could not be provided, diagnostic signals however are listed below.

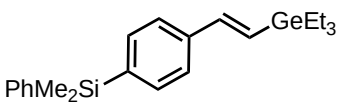
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.42 (m, 4H, H_{arom}), 6.85 (d, *J* = 19.0 Hz, 1H, H_{vinyl}), 6.68 (d, *J* = 19.0 Hz, 1H, H_{vinyl}), 1.10 (t, *J* = 7.8 Hz, 9H, 3x$GeCH_2\underline{CH_3}$), 0.99 (t, *J* = 7.8 Hz, 9H, 3x $SiCH_2\underline{CH_3}$), 0.90 (q, *J* = 7.8 Hz, 6H, 3x$GeCH_2$), 0.81 (q, *J* = 7.8 Hz, 6H, 3x$SiCH_2$).
For β-*anti* in CD_2Cl_2 : CH_{vinyl} signal at 5.96 ppm (d, *J* = 14.1 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.6 (CH_{vinyl}), 134.6 (C_{arom}), 128.2 (CH_{vinyl}), 125.5 (C_{arom}), 9.1 ($GeCH_2\underline{C}H_3$), 7.5 ($SiCH_2$-$\underline{C}H_3$), 4.6 ($GeCH_2$), 3.5 ($SiCH_2$).

^{29}Si{^{1}H} DEPT 6H NMR (99 MHz, $CDCl_3$) δ 1.8 ppm(s).

HRMS (DCl-CH_4) calculated for [$C_{20}H_{36}GeSi$] M^+: 374.1829, found 374.1843.

(E)-dimethyl(phenyl)(4-(2-(triethylgermyl)vinyl)phenyl)silane 2i:



Using the general procedure **A**, (4-ethynylphenyl)dimethyl(phenyl)silane (47.3 mg, 0.20 mmol, 1.0 equiv), triethylgermane (39 µL, 0.24 mmol, 1.2 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25°C for 1 h, ((*E*)-dimethyl(phenyl)(4-(2-(triethylgermyl)vinyl)phenyl)silane (β-*syn,* 36%) along with the β-anti isomer (64%) was formed with quantitative yield as estimated by ^{1}H NMR analysis. After 48 h, 100% of (*E*)-dimethyl(phenyl)(4-(2-(triethylgermyl)vinyl)phenyl)silane (β-*syn)* is obtained. Isolated by column chromatography using 100% pentane, **2i** was obtained (94% yield, 74 mg). For minor product, a detailed ^{1}H NMR analysis could not be provided, diagnostic signals however are listed below.

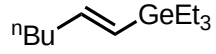
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 4H, H_{arom}), 7.44 – 7.39 (m, 2H, H_{arom}), 7.39 – 7.34 (m, 3H, H_{arom}), 6.83 (d, *J* = 19.0 Hz, 1H, H_{vinyl}), 6.66 (d, *J* = 19.0 Hz, 1H, H_{vinyl}), 1.08 (t, *J* = 7.8 Hz, 9H, 3xCH_3), 0.88 (q, *J* = 7.8 Hz, 6H, 3xCH_2), 0.56 (s, 6H, 2x$SiCH_3$).
For β-*anti* in CD_2Cl_2: CH_{vinyl} signal at 6.02 ppm (d, *J* = 14.2 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.4 (CH_{vinyl}), 139.2 (C_{arom}), 138.4 (C_{arom}), 137.7 (C_{arom}), 134.6 (CH_{arom}), 134.5 (CH_{arom}), 129.2 (CH_{arom}), 128.7 (CH_{arom}), 127.9 (CH_{arom}), 125.7 (CH_{vinyl}), 9.1 ($GeCH_2\underline{C}H_3$), 5.5 ($GeCH_2$), -2.2 ($SiCH_3$).

^{29}Si{^{1}H} DEPT 6H NMR (99 MHz, $CDCl_3$) δ -8.1 ppm(s).

HRMS (DCl-CH_4) calculated for [$C_{22}H_{32}GeSi$] M^+: 398.1485, found 398.1490.

(E)-triethyl(hex-1-en-1-yl)germane 2j – [CAS 876955-82-7]:



Using the general procedure **A**, hex-1-yne (23 µL, 0.20 mmol, 1.0 equiv), triethylgermane (97 µL, 0.60 mmol, 3 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.5 equiv) and complex **I_2** (11 mg, 0.01 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25 °C for 3 h. **2j** (β-*syn*, 73%) was formed along with the β-*anti* isomer (22%) and the product resulting from chain walking (5%) with 85% yield as estimated by ^{1}H NMR. Isolated by column chromatography using 100% pentane, 74%

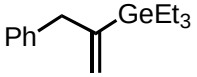
combined yield of isomers was obtained (36 mg). Stereochemistry was determined according to data obtained for hydrosilylation of hex-1-yne.[10]For minor product, a detailed ^{1}H NMR analysis could not be provided, diagnostic signals however are listed below.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92 (dt, *J* = 18.4, 6.2 Hz, 1H, *n*Bu-C$\underline{H}_{vinyl}$), 5.66 (dt, *J* = 18.4, 1.4 Hz, 1H, -Ge-C$\underline{H}_{vinyl}$), 2.12 (m, 2H, =CH-C$\underline{H}_2$-CH_2), 1.44-1.29 (m, 4H, =CH-CH_2-C$\underline{H}_2$-C$\underline{H}_2$), 1.01 (t, *J* = 7.7 Hz, 9H, Ge-CH_2-C$\underline{H}_3$), 0.90 (t, *J* = 6.2 Hz, 3H, -CH_2-CH_2-C$\underline{H}_3$), 0.75 (q, *J* = 6.2 Hz, 6H, Ge-C$\underline{H}_2$-CH_3).
For β-*anti*: CH_{vinyl} signal at 6.37 ppm (dt, *J* = 12.8, 7.2 Hz, 1H) and 5.53 ppm (dt, *J* = 12.8, 1.3 Hz, 1H).
Chain-walking : CH_{vinyl} signals at 5.48 – 5.21 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.9 (*n*BuCH_{vinyl}), 126.2 (GeCH_{vinyl}), 36.7 (=CH$\underline{C}H_2CH_2$), 31.3 (=CH$CH_2\underline{C}H_2CH_2$), 22.4 (=CH$CH_2CH_2\underline{C}H_2$), 14.1 ($CH_2CH_2\underline{C}H_3$), 9.1 (Ge$CH_2\underline{C}H_3$), 4.5 (GeCH_2).

HRMS (DCl-CH_4) calculated for [$C_{10}H_{21}Ge$] MH^+-C_2H_6: 215.0855, found 215.0867.

Triethyl(3-phenylprop-1-en-2-yl)germane 2c" - CAS [35552-91-1]:

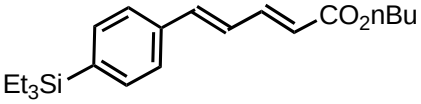


Using the general procedure **A**, propa-1,2-dien-1-ylbenzene (20 mg, 0.17 mmol, 1.0 equiv), triethylgermane (33 µL, 0.21 mmol, 1.2 equiv), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.10 mmol, 0.59 equiv) and complex **I_2** (9mg, 0.0085 mmol, 2.5 mol%) were dissolved in CD_2Cl_2 (0.6 mL). The mixture was placed at 25°C for 28 h. **2c"** (52%), (*E*)-triethyl(1-phenylprop-1-en-2-yl)germane (38%) and (*Z*)-triethyl(1-phenylprop-1-en-2-yl)germane (10%) were formed as estimated by ^{1}H NMR. Spectroscopic data in accordance with the literature.[14] For minor product, a detailed ^{1}H NMR analysis could not be provided, diagnostic signals however are listed below.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.25-7.17 (m, 5H, H_{arom}), 5.54 (dt, *J* = 2.8 & 1.6 Hz, 1H, H_{vinyl}), 5.29 (dt, *J* = 2.8 & 1.2 Hz, 1H, H_{vinyl}), 3.52 (s, 2H, CH_2), 0.98 (t, *J* = 7.9 Hz, 9H, Ge$CH_2C\underline{H}_3$), 0.73 (q, *J* = 7.9 Hz, 6H, GeCH_2).
(*E*)-triethyl(1-phenylprop-1-en-2-yl)germane **2c**: CH_3 signal at 2.02 (d, *J* = 1.9 Hz, 3H, CH_3).
(*Z*)-triethyl(1-phenylprop-1-en-2-yl)germane **2c'**: CH_3 signal at 2.01 (d, *J* = 1.9 Hz, 3H, CH_3).

1. C-C coupling of vinylgermane

Butyl (2E,4E)-5-(4-(triethylsilyl)phenyl)penta-2,4-dienoate 3:



Butyl (2E,4E)-5-(4-(triethylsilyl)phenyl)penta-2,4-dienoate **3** has been synthesized on the basis of a previously reported procedure.[15] Under air, ((E)-triethyl(4-(2-(triethylgermyl)vinyl)phenyl)silane **2h** (100 mg, 0.26 mmol, 1.0 equiv.) and butyl acrylate (502 mg, 0.79 mmol, 3 equiv.) were dissolved in cyclohexane (0.25M). $Pd^{(II)}(OAc)_2$ (10 mol%) and $PhI(TFA)_2$ (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. Then the mixture was filtered through a plug of silica rinsing with diethyl ether. The resulting solution was concentrated under reduced pressure. **3** was obtained after purification by flash chromatography (100% pentane), 47% yield was obtained (43 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H, H_{arom}), 7.45-7.37 (m, 3H, $H_{arom/vinyl}$), 6.90 (m, 2H, 2xH_{vinyl}), 6.00 (d, *J* = 15.3 Hz, 1H, H_{vinyl}), 4.18 (t, *J* = 6.6 Hz, 2H, OCH_2), 1.70-1.65 (m, 2H,

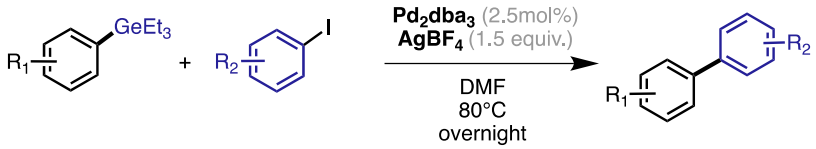
$OCH_2\underline{CH_2}CH_2CH_3$), 1.46-1.41 (m, 2H, $OCH_2CH_2\underline{CH_2}CH_3$), 0.95 (m, 12H, $OCH_2CH_2CH_2\underline{CH_3}$ & $3xSiCH_2\text{-}C\underline{H_3}$), 0.79 (q, *J* = 7.8 Hz, 6H, $3xSiCH_2$).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.3 (C=O), 144.7 (CH), 140.6 (CH), 139.3 (C_{arom}), 136.4 (C_{arom}), 134.8 (CH), 129.0 (CH), 128.2 (CH), 126.5 (CH), 126.5 (CH), 121.5 (CH), 64.4 ($O\underline{C}H_2CH_2CH_2CH_3$), 30.9 ($OCH_2\underline{C}H_2CH_2CH_3$), 19.4 ($OCH_2CH_2\underline{C}H_2CH_3$), 14.5 ($OCH_2CH_2CH_2\underline{C}H_3$),7.5 ($SiCH_2\text{-}\underline{C}H_3$), 3.4 ($SiCH_2$).

$^{29}Si\{^1H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$) δ 2.1 (s).

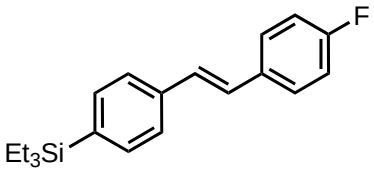
HRMS (DCl-CH_4) calculated for $[C_{21}H_{32}O_2Si]$ M^+: 344.2172, found 344.2158.

General procedure **B** for C-C coupling of germane:[16]



Arylgermane (1.0 equiv.), aryliodide (1.5 equiv.), $AgBF_4$ (1.5 equiv.) and Pd_2dba_3 (2.5 mol%) were added to a reaction vial, dissolved in DMF (0.3 M) and stirred at 80 °C for 16 h. The reaction was quenched by addition of aqueous solution of NH_4Cl (sat.), the organic phase was separated, and the aqueous phase was extracted with DCM (3x). The combined organic phases were dried with $MgSO_4$, the solvent was removed under reduced pressure and the crude product mixture was purified by silica column chromatography.

(E)-triethyl(4-(4-fluorostyryl)phenyl)silane 4a:



According to the general procedure **B**, cross coupling was performed using ((E)-triethyl(4-(2-(triethylgermyl)vinyl)phenyl)silane **2h** (157 mg, 0.41 mmol, 1.0 equiv.) and 1-fluoro-4-iodotoluene (138 mg, 0.62 mmol, 1.5 equiv.). **4a** was obtained after purification by flash chromatography (100% pentane), 69% yield was obtained (90 mg).

^1H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 5H, $H_{arom\ or\ vinyl}$), 7.23-7.00 (m, 5H, $H_{arom\ or\ vinyl}$), 0.97 (t, J=7.8 Hz, 9H, $3xSiCH_2\text{-}C\underline{H_3}$), 0.80 (q, J=7.8 Hz, 6H, $3xSiCH_2$).

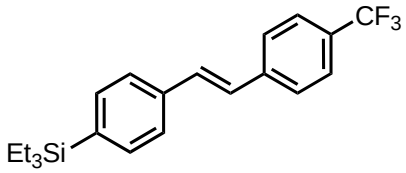
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.5 (C_{arom}), 137.6 (C_{arom}), 137.3 (C_{arom}), 134.8 (CH), 133.7 (C), 128.7 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 127.7 (CH), 125.8 (CH), 120.5 (CH), 115.8 (CH), 115.7 (CH), 7.6 ($SiCH_2\text{-}\underline{C}H_3$), 3.5 ($SiCH_2$).

$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$) δ -114.2 (s).

$^{29}Si\{^1H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$) δ 2.6 (s).

HRMS (DCl-CH_4) calculated for $[C_{20}H_{25}FSi]$ M^+: 312.1710, found 312.1703.

(E)-triethyl(4-(4-(trifluoromethyl)styryl)phenyl)silane 4b:



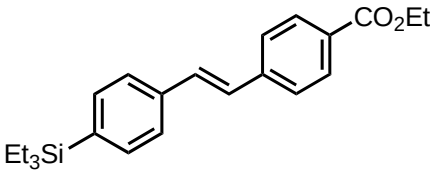
According to the general procedure **B**, cross coupling was performed using ((E)-triethyl(4-(2-(triethylgermyl)vinyl)phenyl)silane **2h** (117 mg, 0.31 mmol, 1.0 equiv.) and 1-iodo-4-(trifluoromethyl)benzene (126 mg,

0.46 mmol, 1.5 equiv.). **4b** was obtained after purification by flash chromatography (pentane), 60% yield was obtained (67 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 4H, H_{arom}), 7.51 (s, 4H, H_{arom}), 7.18 (d, *J* = 16.4 Hz, 1H, H_{vinyl}), 7.16 (d, *J* = 16.4 Hz, 1H, H_{vinyl}), 0.98 (t, *J* = 7.8 Hz, 9H, 3x$SiCH_2$-$C\underline{H_3}$), 0.81 (q, *J* = 7.8 Hz, 6H, 3x$SiCH_2$).

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ -62.5 (s).

Ethyl (E)-4-(4-(triethylsilyl)styryl)benzoate 4c:



According to the general procedure **B**, cross coupling was performed using ((E)-triethyl(4-(2-(triethylgermyl)vinyl)phenyl)silane **2h** (458 mg, 1.21 mmol, 1.0 equiv.) and ethyl 4-iodobenzoate (502 mg, 1.82 mmol, 1.5 equiv.). **4c** was obtained after purification by flash chromatography (pentane), 69% yield was obtained (304 mg).

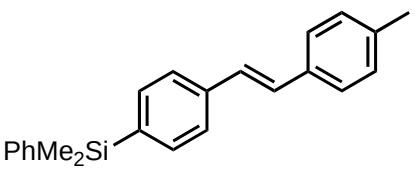
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.01 (m, 2H, H_{arom}), 7.58 – 7.55 (m, 2H, H_{arom}), 7.51 (s, 4H, $H_{arom/vinyl}$), 7.21 (d, *J* = 16.0 Hz, 1H, H_{vinyl}), 7.16 (d, *J* = 16.0 Hz, 1H, H_{vinyl}), 4.39 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.41 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H_3}$), 0.98 (t, *J* = 7.8 Hz, 9H, 3x$SiCH_2$-$C\underline{H_3}$), 0.81 (q, *J* =7.8 Hz, 6H, 3x$SiCH_2$).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.6 (C=O), 141.9 (C_{arom}), 138.1 (C_{arom}), 137.8 (CH), 137.2 (C_{arom}), 134.8 (CH), 134.3 (CH), 131.4 (CH), 131.2 (CH), 130.1 (CH), 129.4 (C_{arom}), 128.9 (CH), 127.9 (CH), 126.4 (CH), 126.1 (CH), 61.1 (OCH_2), 14.5 ($OCH_2\underline{C}H_3$), 7.6 ($SiCH_2$-$\underline{C}H_3$), 3.5 ($SiCH_2$).

^{29}Si{^{1}H} DEPT 6H NMR (99 MHz, $CDCl_3$) δ 2.0 (s).

HRMS (DCl-CH_4) calculated for [$C_{23}H_{30}O_2Si$] M^+: 366.2015, found 366.2015.

(E)-dimethyl(4-(4-methylstyryl)phenyl)(phenyl)silane 4d:



According to the general procedure **B**, cross coupling was performed using (*E*)-dimethyl(phenyl)(4-(2-(triethylgermyl)vinyl)phenyl)silane **2i** (200 mg, 0.50 mmol, 1.0 equiv.) and 4-iodotoluene (166 mg, 0.75 mmol, 1.5 equiv.). **4d** was obtained after purification by flash chromatography (pentane), 52% yield was obtained (85 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.35 (m, 11H, $H_{arom\ or\ vinyl}$), 7.17 (d, *J* = 8.0 Hz, 2H, H_{arom}), 7.17 (d, *J* = 8.0 Hz, 2H, H_{arom}), 2.37 (s, 3H, CH_3), 0.57 (s, 6H, 2x$SiCH_3$).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 138.4 (C_{arom}), 138.4 (C_{arom}), 137.8 (C_{arom}), 137.5 (C_{arom}), 134.7 (CH), 134.6 (C_{arom}), 134.3 (CH), 129.5 (CH), 129.3 (CH), 129.2 (CH), 127.9 (CH), 127.8 (CH), 126.6 (CH), 125.9 (CH), 21.4 (CH_3), -2.2 (2x$SiCH_3$).

^{29}Si{^{1}H} DEPT 6H NMR (99 MHz, $CDCl_3$) δ -8.2 (s).

HRMS (DCl-CH_4) calculated for [$C_{23}H_{24}Si$] M^+: 328.1647, found 328.1655.

VI. Computational details

All calculations were performed on the real systems using the Gaussian 16 package[17] and the B3PW91 hybrid functional[18] with D3 dispersion correction of Grimme with Becke–Johnson damping (DFT-D3*(*BJ)).*[19]* All stationary points involved were fully optimized in solvent (DCM: Dichloromethane) by means of SMD model.[20]

The palladium and tin atoms were described with the relativistic electron core potential SDD and associated basis set,[21] augmented by a set of f-orbital polarization function for Pd (f:1.472) and d polarization function for Sn (d: 0.180).[22] The 6-31G** basis set was employed for all other atoms. Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS), corresponding to the expected process, and all of them positive for *minima*. The connectivity of the transition states and their adjacent *minima* was confirmed by intrinsic reaction coordinate (IRC) calculations.[23]

Intrinsic Bond Orbitals (IBO) analysis was also performed in order to analyze the evolution of the main orbitals along the pathway. The calculations of wave functions have been made with version 7.4.2 of Turbomole1989[24] at RI-B3LYP(D3)/def2-TZVP level of theory on the geometry optimized in solvent with Gaussian 16, at B3PW91-D3(BJ)/SDD+f(Au), SDD+d(Sn), 6-31G**(other atoms) level of theory. Orbital visualizations were produced with IboView (v20150427),[25] a program developed to analyze molecular electronic structure, based on Intrinsic Atomic Orbitals (IAOs).

To analyze the bonding situation in the adducts coming from the interaction between (P,N,S)Pd+ and H-GeEt3 (η^1 or η^2 coordination mode), Energy Decomposition Analysis (EDA)[26] was performed with Amsterdam Density Functional 2021.102 program package[27] at ZORA-B3LYP-D3(BJ)/TZ2P level of theory on the geometries optimized from Gaussian 16 at SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Au), SDD+d(Sn), 6-31G** (other atoms) level. This analysis is based on the EDA method of Morokuma and the ETS partitioning scheme of Ziegler and Rauk. The interaction energy term $\Delta E_{int}(\zeta)$ is decomposed into different chemically meaningful contributions: (i) electrostatic interaction energy between the reagents (ΔV_{elstat}), (ii) Pauli repulsion which account for destabilizing interactions between occupied orbitals of each fragment (ΔE_{Pauli}), (iii) stabilizing orbital interactions (ΔE_{orb}) and iv) dispersion energy (ΔE_{disp}).

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp}$$

The main orbital interaction contributions to the total ΔE_{orb} term can be visualized and quantified by means of the Natural Orbital for Chemical Valence (NOCV)[28] extension of the EDA method. The EDA-NOCV approach is a powerful tool to quantitatively analyze chemical bonds, combining the extended transition state (ETS) method for energy decomposition analysis combined with the natural orbitals for chemical valence (NOCV) theory. Within this methodology, the ΔE_{orb} term is decomposed into the contributions from different natural orbitals of chemical valence (NOCV) eigenvalues (λ_i) as follows:

$$\Delta E_{orb} = \sum_{k} \Delta E_{orb}^{k} = \sum_{k=1}^{M/2} v_k [-F_{-k,-k}^{TS} + F_{k,k}^{TS}]$$

where the terms $F^{TS}_{k,k}$ are the diagonal Kohn-Sham matrix elements corresponding to NOCVs. The components ΔE^{k}_{orb} provide energetic estimation of $\Delta\rho^k$ and allow to characterize the importance of a particular electron flow channel for the bonding between considered molecular fragments.

In addition, Wiberg Bond indexes (WBI) were also computed using Natural Bond Orbital[29] analyses (NBO, 6.0 version).[30] The Natural Localized Molecular Orbitals (NLMO) associated to the σ_{PdH}, σ_{EH} and d(Pd) were also analyzed.

Table S1. Coordination energies of H–EEt3 (E: Si, Ge, Sn) or H-BPin to the (P,N,S)Pd+ fragment to give the corresponding σ-complexes (global minima), computed at SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd), SDD+d(Sn), 6-31G** (other atoms). Gibbs Free energy values, ΔG in kcal/mol.

	$\Delta G_{coordination}$
H-SiEt$_3$	-26.1
H-GeEt$_3$	-42.4
H-SnEt$_3$	-36.4
H-BPin	-17.9

Scheme S1. Splitting of the (PdS) dimer by [E]–H, computed at SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd), SDD+d(Sn), 6-31G** (other atoms) and formation of the E–H activation product. Gibbs free energies (ΔG) in kcal/mol.

With HEEt$_3$

[(P,N,S)Pd]$_2^{2+}$ ⟶ **2 x (P,N,S)Pd$^+$** ΔG +71.3 kcal/mol

½ **[(P,N,S)Pd]$_2^{2+}$** ⟶ **(P,N,S)Pd$^+$** ΔG +35.7 kcal/mol

(P,N,S)Pd$^+$ + HEEt$_3$ ⟶ **(P,N,S-EEt$_3$)Pd(H)$^+$**
E: Si ΔG –34.4 kcal/mol
E: Ge ΔG –48.2 kcal/mol
E: Sn ΔG –35.8 kcal/mol

½ **[(P,N,S)Pd]$_2^{2+}$ + HEEt$_3$** ⟶ **(P,N,S-EEt$_3$)Pd(H)$^+$**
E: Si ΔG 1.3 kcal/mol
E: Ge ΔG –12.5 kcal/mol
E: Sn ΔG –0.1 kcal/mol

With HBPin

[(P,N,S)Pd]$_2^{2+}$ ⟶ **2 x (P,N,S)Pd$^+$** ΔG +71.3 kcal/mol

½ **[(P,N,S)Pd]$_2^{2+}$** ⟶ **(P,N,S)Pd$^+$** ΔG +35.7 kcal/mol

(P,N,S)Pd$^+$ + HBPin ⟶ **(P,N,S-BPin)Pd(H)$^+$** ΔG –28.8 kcal/mol

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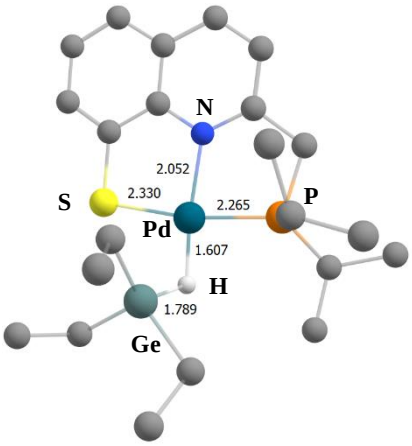
½ **[(P,N,S)Pd]$_2^{2+}$ + HBPin** ⟶ **(P,N,S-BPin)Pd(H)$^+$** ΔG 6.9 kcal/mol

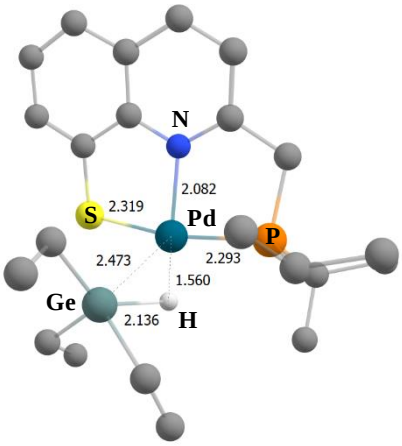
Figure S3. H–$GeEt_3$ and H–$SnEt_3$ σ-complexes computed at SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd), SDD+d(Sn), 6-31G** (H, C, N, P, S, Ge). Relative stability, ΔG in kcal/mol. Main hydrogen atoms have been omitted for clarity. Main bond lengths in Å and bond angles in °.

Ge σ-complex, form 1



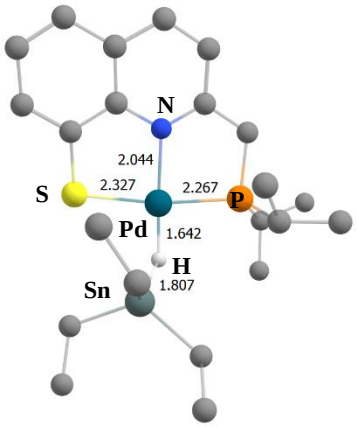
PdHGe 98.56°; Pd…Ge 2.576 Å
ΔG 2.4 kcal/mol

Ge σ-complex, form 2



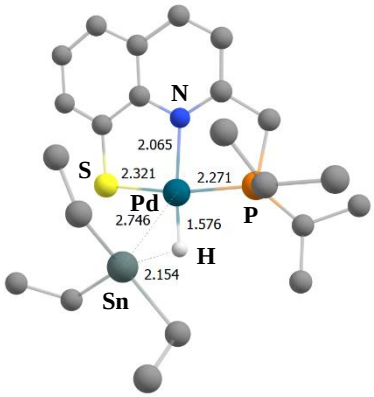
PdHGe 82.39°
ΔG 0 kcal/mol

Sn σ-complex, form 1



PdHSn 108.42°; Pd…Ge 2.799 Å
ΔG 4.2 kcal/mol

Sn σ-complex, form 2



PdHSn 93.50°
ΔG 0 kcal/mol

Two adducts close in energy were found on the Potential Energy Surface (PES). The forms 2 were found 2.4 (Ge)/4.2 (Sn) kcal/mol lower in energy than the forms 1. They display slightly shorter Pd…E contacts, suggesting slight shift towards side-on η^2-coordination compared to forms 1.

Table S2. Energy Decomposition Analysis (EDA) energies (ΔE_{Pauli}, ΔE_{elstat}, ΔE_{orb}, ΔE_{disp}, ΔE_{int} in kcal/mol) for the σ-complexes associated to the activation of the Ge–H bond of H–$GeEt_3$ by the (P,N,S)Pd^+ fragment, as computed at ZORA-B3LYP-D3(BJ)/TZ2P level of theory.

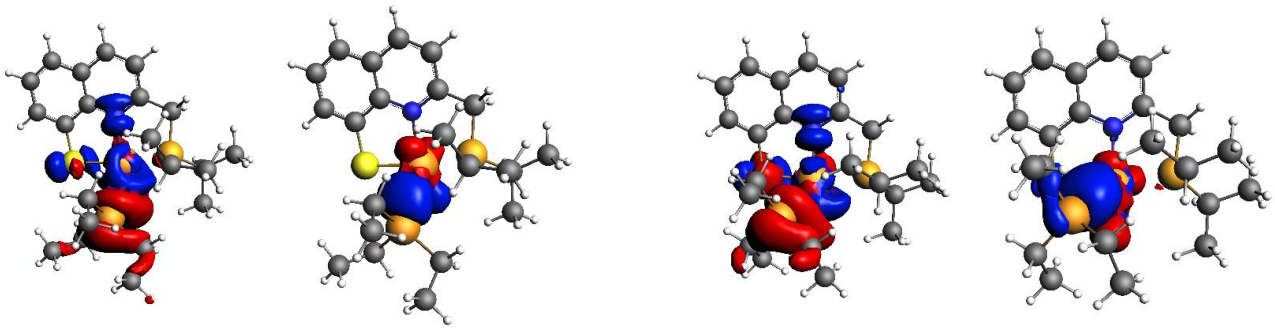
	[&]Ge-H σ-complex, form 1	[&]Ge-H σ-complex, form 2
ΔE_{Pauli}	161.3	249.8
ΔE_{Elstat}	-131.0 (58.8 %)[a]	-210.3 (62.7 %)[a]
ΔE_{Orb}	-71.8 (32.2 %)[a]	-103.2 (30.8 %)[a]
ΔE_{Orb1}	-41.3 (57.6 %)[b] **Donation Pd→Ge**	-59.53 (57.7 %)[b] **Donation Pd→Ge**
ΔE_{Orb2}	-14.8 (20.6 %)[b] **Back-Donation Ge→Pd**	-24.3 (23.5 %)[b] %[b] **Back-Donation Ge→Pd**
$\Delta E_{dispersion}$	-20.0 (9.0 %)[a]	-21.9 (6.5 %)[a]
ΔE_{int}	-61.5	-85.7

[&]Fragmentation: (P,N,S)Pd^+ and H–$GeEt_3$. Values into brackets (%) correspond to: [a]the contribution of each term to the total attractive interaction. [b]Contribution of each term to the total orbital energy.

To analyze the bonding situation between the (P,N,S)Pd^+ and H–$GeEt_3$ fragments in the two σ-complexes localized on the PES, the EDA-NOCV approach was used. The main stabilizing contribution to the ΔE_{int} term comes from the electrostatic term (ΔE_{elstat}), which accounts for approximatively 60% of the total attractive interaction energy. The orbital interactions between the two fragments contribute also significantly (~ 30 %) to the total bonding. Two main interactions are involved in the ΔE_{orb} term, the donation from the σ_{GeH} orbital of $HGeEt_3$ to the metal center and the back-donation from a d(Pd) orbital to the σ^*_{GeH} orbital (see plot of the NOCV, Figure S2). The σ-donation term is approximatively three times larger than the back-donation. Nevertheless, the back-donation term is not negligible.

Figure S4. σ-Complexes associated to the activation of the Ge–H bond. Plot of the contours of deformation densities contributions ($\Delta\rho_{orb}$) of the main pairwise orbital interactions between H–$GeEt_3$ and (P,N,S)Pd^+ fragments and associated orbital interaction energies contributions (ΔE_{orb}, in kcal/mol), computed at ZORA-B3LYP-D3(BJ)/TZ2P level of theory. The charge flow is red → blue ($\Delta\rho < 0$ in red and $\Delta\rho > 0$ in blue). The contour value for density is 0.001 a.u.

σ-complex, form 1 **σ-complex, form 2**



ΔEorb1 (ρ) **Donation** –41.3 | ΔEorb2 (ρ) **Back-Donation** –14.8 | ΔEorb1 (ρ) **Donation** –59.5 | ΔEorb2 (ρ) **Back-Donation** –24.3

Table S3. Wiberg Bond Indexes (WBI) and main NLMO from Natural Bond Orbital analysis (NBO) for the σ-complexes associated to the activation of the E–H bond of (P,N,S)Pd^{+}-$HEEt_3$ (E: Si, Ge, Sn) and (P,N,S)Pd^{+}-HBPin, computed at B3PW91-D3(BJ)/SDD+f(Pd), SDD+d(Sn), 6-31G**(H, C, N, P, S, Si, Ge, B) level of theory.

	WBI	**NLMO[b]**
SiH σ-complex	Si-H 0.4297 (0.9080)[a] Pd-H 0.3565 Pd-Si 0.2194	Pd-H 31.3 % Pd, 46.4 % H, 20.1 % Si d(Pd) 95.6 % Pd, 2.6 % Si, 0.7 % H
GeH σ-complex form 1	Ge-H 0.4394 (0.9036)[a] Pd-H 0.3480 Pd-Ge 0.2136	Pd-H 33.1 % Pd, 44.1 % H, 20.2 % Ge d(Pd) 95.7 % Pd, 2.3 % Ge, 0.9 % H
GeH σ-complex form 2	Ge-H 0.2460 (0.9036)[a] Pd-H 0.4750 Pd-Ge 0.2942	Pd-H 33.1 % Pd, 41.9 % H, 14.6 % Ge d(Pd) 92.6 % Pd, 4.7 % Ge, 1.1 % H
SnH σ-complex form 1	Sn-H 0.4164 (0.8579)[a] Pd-H 0.3437 Pd-Sn 0.1563	Pd-H 28.6 % Pd, 52.0 % H, 16.9 % Sn d(Pd) 97 % Pd, 1.5 % Sn, 0.4 % H
SnH σ-complex form 2	Sn-H 0.2737 (0.8579)[a] Pd-H 0.4561 Pd-Sn 0.2249	Pd-H 38 % Pd, 45.7 % H, 13.2 % Sn d(Pd) 94.8 % Pd, 3.3 % Sn, 0.7 % H
BH σ-complex	B-H 0.6164 (0.9628)[a] Pd-H 0.2306 Pd-B 0.2260	B-H 12.9 % Pd, 47.3 % H, 34.7 % B d(Pd) 96 % Pd, 1.9 % Si, 0.7 % H

[a] into brackets WBI of E–H bond in $H–EEt_3$ (E: Si, Ge, Sn) and HBPin.
[b] Contribution of mains atoms (in %) in the NLMO.

The Wiberg Bond indexes (WBI) confirm the conclusions of the EDA analysis. In all the complexes the E–H bond is weakened compared to that in the Et_3E-H or HBPin substrates and an interaction is observed between Pd and E (E : Si, Ge, Sn, B).

Figure S5. Reaction profile (ΔG in kcal/mol) computed in solvent for the Pd/S cooperative activation of $Et_3Si–H$ with selected Intrinsic Bond Orbitals (IBOs). For clarity, the hydrogen atoms are omitted, except that at Si/Pd. Optimizations performed at the SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd),6-31G** (other atoms) level of theory. Main distances are in Å. For the IBOs, the fractions of electrons in the doubly occupied orbitals assigned to each atom are given.

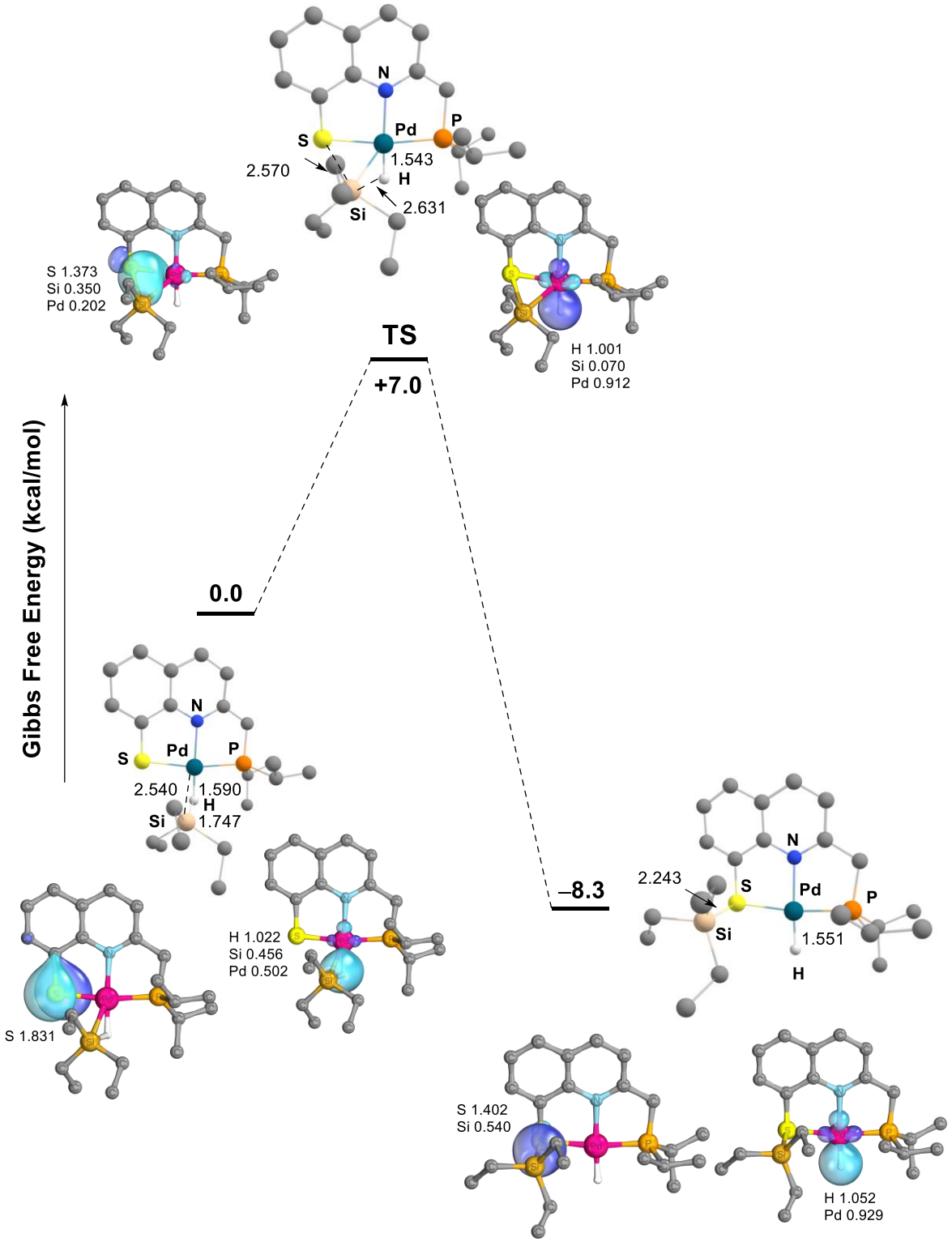


Figure S6. Reaction profile (ΔG in kcal/mol) computed in solvent for the Pd/S cooperative activation of $Et_3Ge–H$ with selected Intrinsic Bond Orbitals (IBOs). For clarity, the hydrogen atoms are omitted, except that at Ge/Pd. Optimizations performed at the SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd),6-31G** (other atoms) level of theory. Main distances are in Å. For the IBOs, the fractions of electrons in the doubly occupied orbitals assigned to each atom are given.

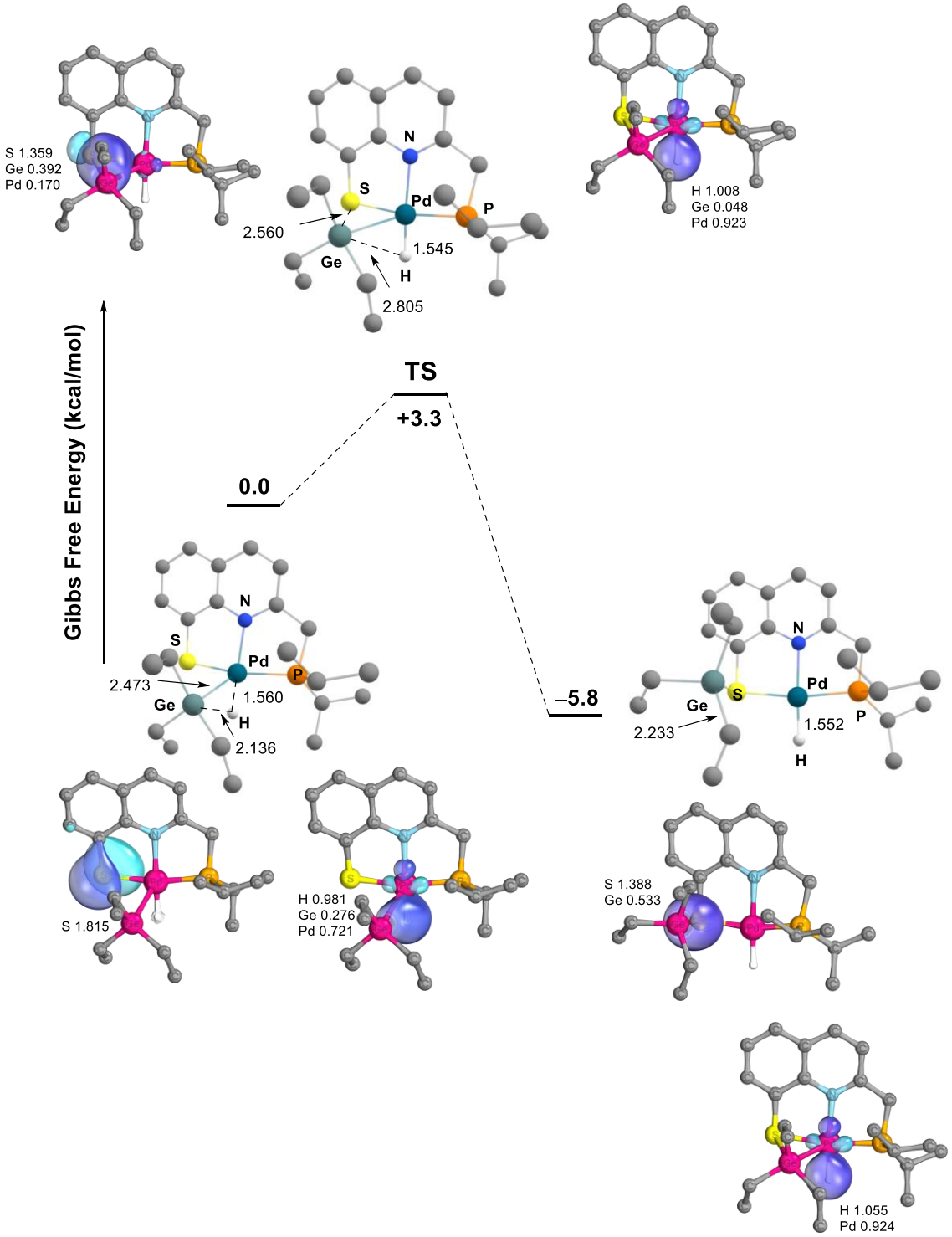


Figure S7. Reaction profile (ΔG in kcal/mol) computed in solvent for the Pd/S cooperative activation of $Et_3Sn–H$ with selected Intrinsic Bond Orbitals (IBOs). For clarity, the hydrogen atoms are omitted, except that at Sn/Pd. Optimizations performed at the SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd), SDD+d(Sn), 6-31G** (other atoms) level of theory. Main distances are in Å. For the IBOs, the fractions of electrons in the doubly occupied orbitals assigned to each atom are given.

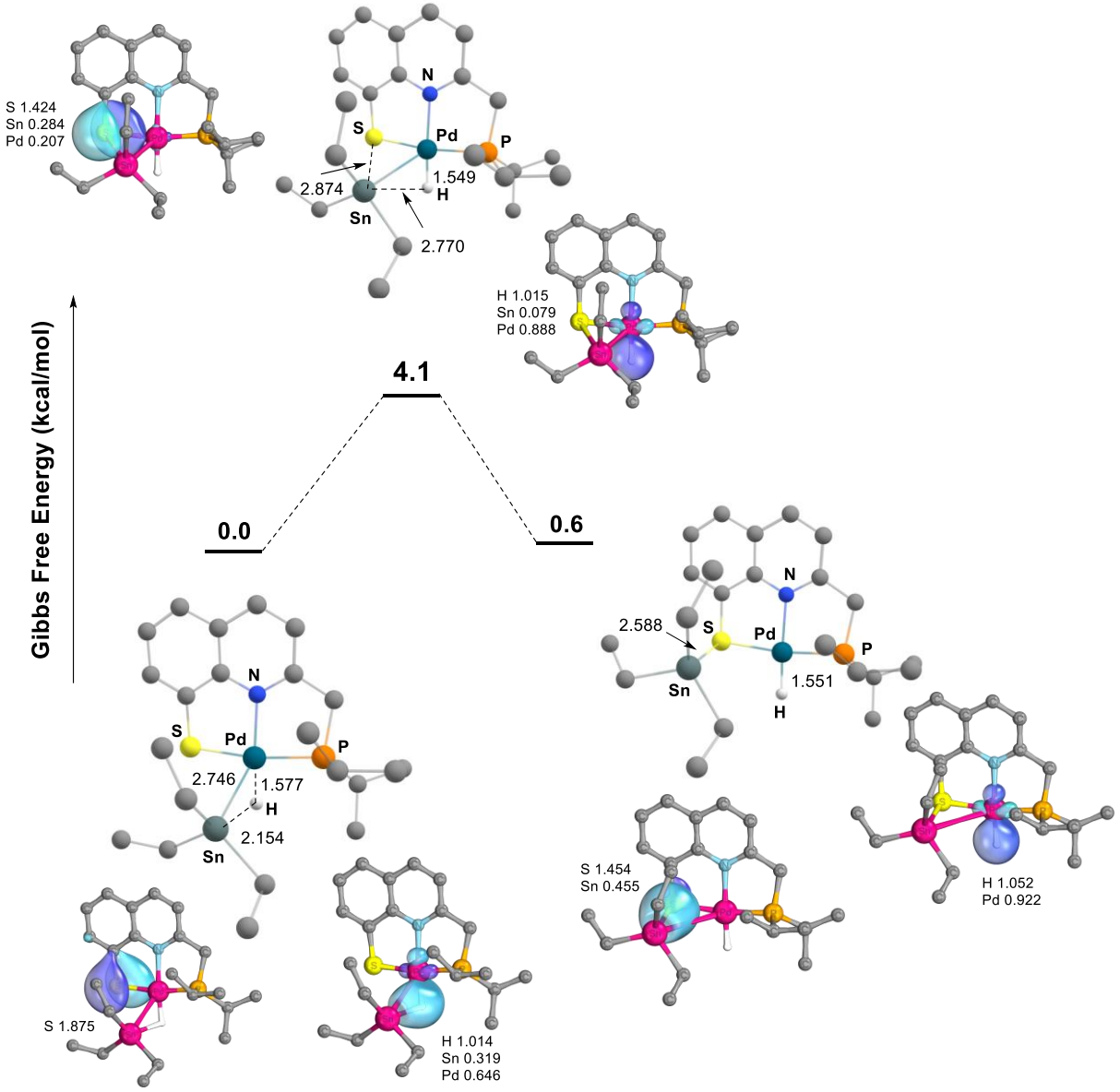
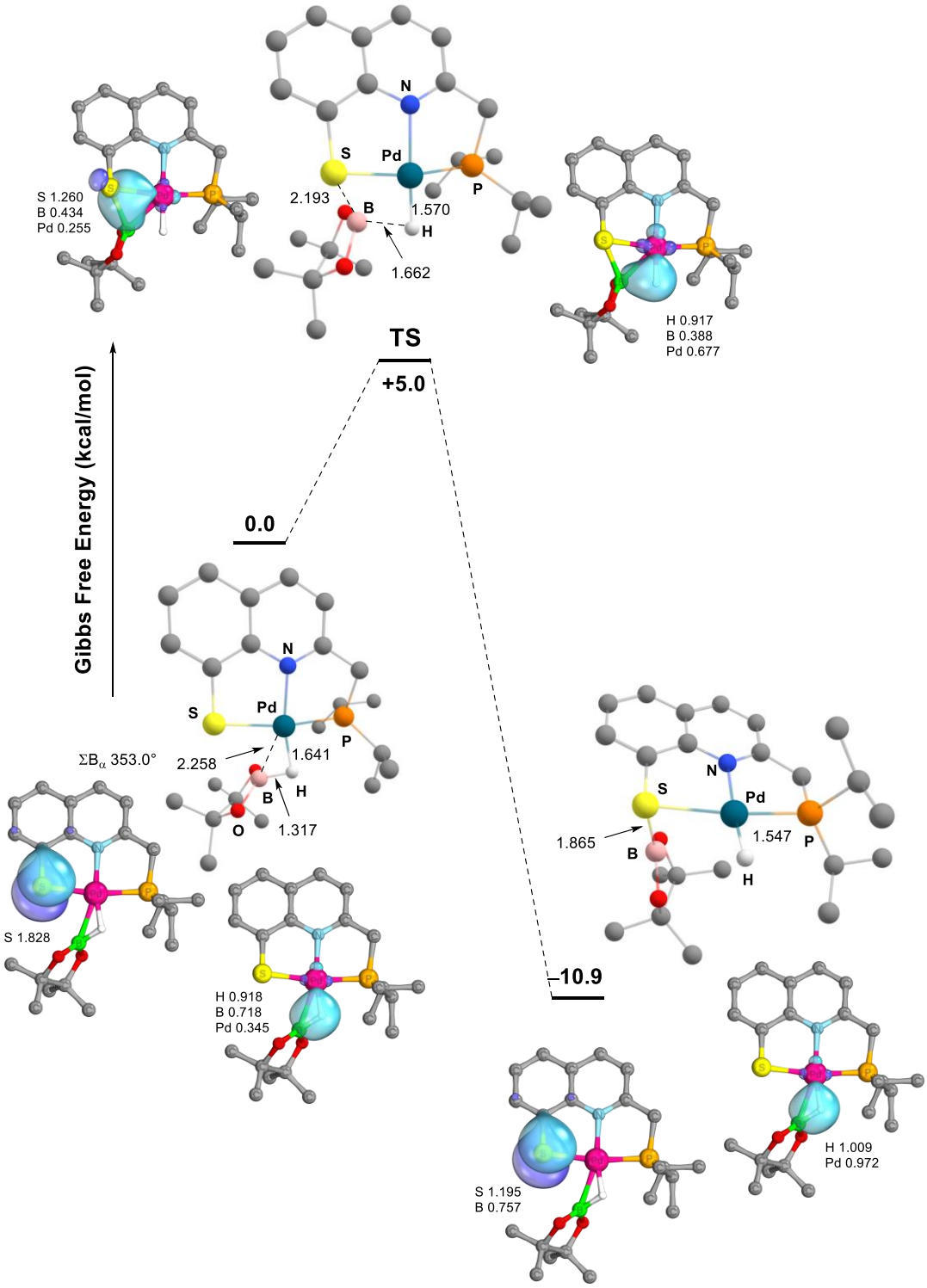


Figure S8. Reaction profile (ΔG in kcal/mol) computed in solvent for the Pd/S cooperative activation of PinB–H with selected Intrinsic Bond Orbitals (IBOs). For clarity, the hydrogen atoms are omitted, except that at B/Pd. Optimizations performed at the SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd),6-31G** (other atoms) level of theory. Main distances are in Å. For the IBOs, the fractions of electrons in the doubly occupied orbitals assigned to each atom are given.



Z-matrices and energies in au, in solvent at SMD(DCM)-B3PW91-D3(BJ) level

41

(S,N,P)Pd$^+$

C	-2.884407000	-0.896617000	0.063966000
C	-3.026302000	1.546538000	-0.238633000
C	-4.426491000	1.477846000	-0.058927000
C	-5.026236000	0.259391000	0.168148000
C	-2.349141000	2.757508000	-0.502792000
H	-5.006661000	2.393341000	-0.112138000
H	-6.101658000	0.197381000	0.302579000
C	-0.992295000	2.757341000	-0.701507000
C	-0.266452000	1.553190000	-0.619847000
H	-2.916616000	3.681767000	-0.555969000
H	-0.452097000	3.670409000	-0.923209000
S	-1.916560000	-2.361333000	0.117433000
Pd	0.145408000	-1.281135000	-0.028135000
C	1.202457000	1.533461000	-0.889719000
H	1.351895000	1.399836000	-1.969210000
H	1.675635000	2.477521000	-0.607776000
P	1.973757000	0.082316000	-0.069461000
C	2.484748000	0.602225000	1.625897000
H	2.844447000	-0.324626000	2.090202000
C	3.407146000	-0.457655000	-1.094237000
H	2.916751000	-0.971076000	-1.932228000
C	1.251462000	1.087771000	2.391003000
H	0.864334000	2.022372000	1.971991000
H	0.444804000	0.348110000	2.383093000
H	1.527368000	1.282265000	3.432027000
C	3.606270000	1.639195000	1.635690000
H	3.794753000	1.949808000	2.668881000
H	4.538329000	1.238513000	1.232977000
H	3.333518000	2.533189000	1.064969000
C	4.236152000	-1.476739000	-0.311656000
H	3.621372000	-2.297415000	0.073163000
H	4.997532000	-1.908082000	-0.968529000
H	4.748923000	-1.005830000	0.532474000
C	4.253120000	0.683154000	-1.660088000
H	4.787529000	1.225318000	-0.877561000
H	4.997838000	0.260064000	-2.342501000
H	3.654882000	1.399601000	-2.229357000
C	-4.263005000	-0.920887000	0.221516000
H	-4.758784000	-1.872449000	0.388383000
C	-2.255790000	0.352115000	-0.164989000
N	-0.885952000	0.398823000	-0.335431000

Sum of electronic and zero-point Energies= -1544.040184

Sum of electronic and thermal Free Energies= -1544.088936

23

SiHEt$_3$

H	-0.158875000	-0.018371000	-1.731605000
Si	-0.165103000	-0.226887000	-0.244145000
C	0.206067000	1.441079000	0.572603000
H	-0.742682000	1.983044000	0.682467000
H	0.557047000	1.248361000	1.595927000
C	-1.875907000	-0.853854000	0.262400000
H	-2.001787000	-1.868504000	-0.138989000
H	-1.888348000	-0.962222000	1.355970000
C	1.132556000	-1.533600000	0.185655000
H	0.879223000	-2.449347000	-0.365871000
H	1.013430000	-1.784971000	1.248913000
C	-3.034370000	0.037668000	-0.191613000
H	-2.953154000	1.048394000	0.223621000
H	-3.059025000	0.136332000	-1.282798000
H	-4.004500000	-0.365185000	0.122694000
C	1.212596000	2.319170000	-0.176640000
H	1.386905000	3.268742000	0.343532000
H	2.183382000	1.825267000	-0.287056000
H	0.856040000	2.558079000	-1.184683000
C	2.583575000	-1.135586000	-0.095536000
H	3.277603000	-1.955274000	0.125735000
H	2.730612000	-0.858331000	-1.145567000
H	2.888478000	-0.278857000	0.514522000

Sum of electronic and zero-point Energies= -527.516797

Sum of electronic and thermal Free Energies= -527.553959

64

(P,N,S)Pd$^+$…H-SiEt$_3$ (σ-complex)

C	2.817393000	1.404479000	-0.534554000
C	4.143432000	-0.474226000	0.365731000
C	5.276122000	0.368803000	0.434600000
C	5.171966000	1.680891000	0.029570000
C	4.168530000	-1.835550000	0.748227000
H	6.211831000	-0.034903000	0.807761000
H	6.036459000	2.335932000	0.078372000
C	3.040187000	-2.608447000	0.630022000
C	1.846385000	-2.033162000	0.148682000
H	5.093684000	-2.262365000	1.124409000
H	3.045335000	-3.659540000	0.894989000
C	0.632579000	-2.872345000	-0.090376000
H	0.749953000	-3.356603000	-1.068139000
H	0.551307000	-3.672975000	0.649446000
P	-0.913847000	-1.861058000	-0.171513000
C	-1.779957000	-2.098040000	1.438808000
H	-2.646749000	-1.433126000	1.374036000
C	-1.874021000	-2.509607000	-1.608808000
H	-1.243171000	-2.191009000	-2.450158000
C	-0.857036000	-1.601695000	2.553177000
H	0.017366000	-2.251846000	2.663211000
H	-0.502238000	-0.584250000	2.370702000
H	-1.398402000	-1.608156000	3.504245000
C	-2.270453000	-3.520792000	1.697772000
H	-2.661574000	-3.577374000	2.719273000
H	-3.075888000	-3.805033000	1.018986000
H	-1.466686000	-4.258822000	1.612053000
C	-3.217545000	-1.790916000	-1.711502000
H	-3.091420000	-0.706739000	-1.778276000
H	-3.741139000	-2.124011000	-2.613149000
H	-3.857268000	-2.016711000	-0.852484000
C	-2.025310000	-4.030037000	-1.671218000
H	-2.745399000	-4.398142000	-0.938148000
H	-2.397041000	-4.301263000	-2.664829000
H	-1.080007000	-4.558199000	-1.519701000
C	3.954331000	2.195493000	-0.456545000
H	3.903375000	3.230493000	-0.781084000
C	2.910483000	0.054312000	-0.106391000
N	1.790740000	-0.737669000	-0.168367000
Pd	0.007288000	0.189313000	-0.585100000
H	-1.392306000	0.790565000	-1.040360000
S	1.303603000	2.025929000	-1.195606000
Si	-1.662123000	1.893465000	0.287370000
C	-3.278877000	1.127869000	0.887293000
H	-3.639354000	0.396983000	0.156596000
H	-3.064178000	0.569623000	1.806237000
C	-0.537296000	2.380120000	1.727030000
H	0.182726000	3.103214000	1.328545000
H	0.055249000	1.519767000	2.055529000
C	-4.370402000	2.171726000	1.153878000
H	-4.650990000	2.700806000	0.237996000

H	-5.274427000	1.694258000	1.547949000
H	-4.053321000	2.922391000	1.883871000
C	-1.987299000	3.320376000	-0.890313000
H	-2.564923000	4.064721000	-0.325100000
H	-1.032370000	3.798493000	-1.135638000
C	-1.315251000	2.968762000	2.908591000
H	-1.881964000	3.860230000	2.620175000
H	-2.021235000	2.246957000	3.331402000
H	-0.628702000	3.263838000	3.709920000
C	-2.733077000	2.919731000	-2.163750000
H	-2.955826000	3.791455000	-2.788312000
H	-2.136150000	2.227457000	-2.768631000
H	-3.684515000	2.425160000	-1.938862000

Sum of electronic and zero-point Energies= -2071.619999

Sum of electronic and thermal Free Energies= -2071.684453

64

TS_HSiEt$_3$

C	2.713346000	-0.574933000	-0.765641000
C	2.619705000	-2.789469000	0.312874000
C	4.032749000	-2.797857000	0.379030000
C	4.748242000	-1.729342000	-0.113093000
C	1.804158000	-3.850029000	0.777203000
H	4.534894000	-3.654603000	0.817449000
H	5.832541000	-1.731761000	-0.065101000
C	0.436746000	-3.780782000	0.655036000
C	-0.152947000	-2.628924000	0.091206000
H	2.274804000	-4.722794000	1.220567000
H	-0.199348000	-4.593961000	0.985726000
C	-1.631859000	-2.515957000	-0.130039000
H	-1.862667000	-2.937026000	-1.117404000
H	-2.194301000	-3.095918000	0.606377000
P	-2.178647000	-0.742346000	-0.169200000
C	-2.616378000	-0.342474000	1.580565000
H	-2.783278000	0.739393000	1.574269000
C	-3.640718000	-0.643653000	-1.288488000
H	-3.171042000	-0.716299000	-2.278380000
C	-1.411367000	-0.658337000	2.470098000
H	-1.273465000	-1.739359000	2.575181000
H	-0.480096000	-0.236031000	2.082474000
H	-1.579927000	-0.248226000	3.470690000
C	-3.879348000	-1.034870000	2.087804000
H	-4.000442000	-0.811995000	3.153521000
H	-4.774543000	-0.682730000	1.571776000
H	-3.821016000	-2.122771000	1.983264000
C	-4.279059000	0.739465000	-1.158955000
H	-3.543694000	1.538701000	-1.296904000
H	-5.053031000	0.858090000	-1.923604000
H	-4.752045000	0.870091000	-0.180783000
C	-4.656382000	-1.777532000	-1.156459000
H	-5.195194000	-1.740549000	-0.208127000
H	-5.393574000	-1.682293000	-1.960879000
H	-4.193102000	-2.763364000	-1.251586000
C	4.093145000	-0.620159000	-0.688299000
H	4.679191000	0.206946000	-1.077138000
C	1.963309000	-1.662898000	-0.250482000
N	0.601575000	-1.606892000	-0.307130000
Pd	-0.249866000	0.189427000	-0.938365000
H	-0.968424000	1.450054000	-1.463642000
S	1.892042000	0.798289000	-1.547519000
Si	0.815615000	2.201363000	0.317985000
C	-0.841726000	2.657772000	1.147456000
H	-1.666262000	2.545088000	0.439566000
H	-1.016347000	1.938068000	1.952358000
C	2.002779000	1.524746000	1.617288000
H	3.018721000	1.584421000	1.210219000
H	1.793756000	0.454537000	1.742164000
C	-0.843232000	4.081732000	1.718118000
H	-0.803023000	4.833260000	0.924190000
H	-1.761337000	4.259236000	2.290735000
H	-0.000864000	4.266011000	2.391531000
C	1.407355000	3.738752000	-0.596206000
H	1.380081000	4.554899000	0.138268000
H	2.455538000	3.612107000	-0.884481000
C	1.924875000	2.226655000	2.975419000
H	2.169155000	3.291248000	2.898613000
H	0.927016000	2.145871000	3.417971000
H	2.633081000	1.779999000	3.682491000
C	0.552183000	4.107702000	-1.810132000
H	0.877504000	5.055039000	-2.253914000
H	0.612965000	3.342222000	-2.591326000
H	-0.504439000	4.214824000	-1.540718000

Sum of electronic and zero-point Energies= -2071.612517

Sum of electronic and thermal Free Energies= -2071.673317

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FP_(PNSSiEt$_3$)PdH$^+$

C	1.943776000	-1.457515000	-0.837558000
C	1.091193000	-3.415287000	0.366532000
C	2.377588000	-3.998671000	0.284764000
C	3.399258000	-3.334198000	-0.352878000
C	-0.006375000	-4.044702000	1.003469000
H	2.537031000	-4.977426000	0.726797000
H	4.384402000	-3.783108000	-0.425562000
C	-1.232284000	-3.429983000	1.032364000
C	-1.394198000	-2.164234000	0.424383000
H	0.136000000	-5.019454000	1.460908000
H	-2.085881000	-3.901879000	1.505757000
C	-2.746758000	-1.516878000	0.357342000
H	-3.327081000	-2.046582000	-0.408239000
H	-3.288423000	-1.647252000	1.299020000
P	-2.677876000	0.271380000	-0.145190000
C	-2.911453000	1.269642000	1.391240000
H	-2.827115000	2.304906000	1.038555000
C	-4.069014000	0.556853000	-1.329448000
H	-3.674723000	0.129874000	-2.260519000
C	-1.737798000	0.985635000	2.328610000
H	-1.725402000	-0.058784000	2.658987000
H	-0.785729000	1.199884000	1.835657000
H	-1.814864000	1.616953000	3.219525000
C	-4.262703000	1.082277000	2.074537000
H	-4.269806000	1.642720000	3.015695000
H	-5.083593000	1.457647000	1.460380000
H	-4.461055000	0.032893000	2.314535000
C	-4.260324000	2.060547000	-1.527564000
H	-3.318313000	2.562910000	-1.769037000
H	-4.957413000	2.233576000	-2.353397000
H	-4.681814000	2.526732000	-0.631357000
C	-5.380445000	-0.151753000	-0.991061000
H	-5.829763000	0.227786000	-0.071177000
H	-6.092773000	0.022890000	-1.804520000
H	-5.258163000	-1.233595000	-0.892895000
C	3.181897000	-2.060642000	-0.919918000
H	3.996931000	-1.546306000	-1.419110000
C	0.868241000	-2.134198000	-0.206463000
N	-0.365736000	-1.546157000	-0.151419000
Pd	-0.590201000	0.384373000	-0.919321000
H	-0.843165000	1.818582000	-1.453233000
S	1.694487000	0.197580000	-1.493255000

Si	2.523410000	1.325217000	0.258946000
C	1.768942000	3.038092000	0.095925000
H	1.719800000	3.294642000	-0.969952000
H	0.728653000	2.983129000	0.438981000
C	2.029183000	0.372600000	1.802638000
H	2.677128000	-0.509083000	1.878005000
H	1.008724000	-0.003832000	1.677614000
C	2.540623000	4.119361000	0.860966000
H	3.572037000	4.206060000	0.504688000
H	2.066556000	5.098607000	0.733202000
H	2.579265000	3.912374000	1.934730000
C	4.384494000	1.333093000	0.023061000
H	4.803531000	1.854386000	0.895591000
H	4.747292000	0.300043000	0.094589000
C	2.120646000	1.213442000	3.080653000
H	3.131233000	1.602806000	3.243605000
H	1.437774000	2.068181000	3.048596000
H	1.856309000	0.615143000	3.959420000
C	4.864015000	1.990664000	-1.271530000
H	5.957563000	1.997042000	-1.333760000
H	4.487756000	1.460689000	-2.153084000
H	4.524078000	3.028906000	-1.345978000

Sum of electronic and zero-point Energies= -2071.634727

Sum of electronic and thermal Free Energies= -2071.697670

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$GeHEt_3$

H	0.000014000	0.038792000	-1.652766000
Ge	-0.000053000	-0.232804000	-0.120911000
C	0.000024000	1.503923000	0.767166000
H	-0.878711000	1.551226000	1.420455000
H	0.878314000	1.550880000	1.421073000
C	-1.621132000	-1.225977000	0.281330000
H	-1.544381000	-2.217396000	-0.179483000
H	-1.658513000	-1.377604000	1.366879000
C	-2.861213000	-0.488513000	-0.218170000
H	-2.946259000	0.505042000	0.236991000
H	-2.814570000	-0.336327000	-1.302867000
H	-3.787234000	-1.032566000	0.003370000
C	1.620851000	-1.226244000	0.281423000
H	1.543870000	-2.217705000	-0.179264000
H	1.658179000	-1.377762000	1.366989000
C	0.000579000	2.656128000	-0.234566000
H	0.000651000	3.638003000	0.254379000
H	0.878413000	2.604570000	-0.888890000
H	-0.876906000	2.604947000	-0.889388000
C	2.861070000	-0.489081000	-0.218152000
H	3.787003000	-1.033224000	0.003539000
H	2.814510000	-0.337100000	-1.302881000
H	2.946230000	0.504549000	0.236827000

Sum of electronic and zero-point Energies= -2313.042222

Sum of electronic and thermal Free Energies= -2313.080688

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(P,N,S)Pd^+…H-$GeEt_3$ (σ-complex, form 2)

C	-2.934758000	-0.379011000	-0.752327000
C	-3.652596000	1.749868000	0.273310000
C	-4.975482000	1.255429000	0.346949000
C	-5.254487000	-0.013154000	-0.110888000
C	-3.274959000	3.038456000	0.719943000
H	-5.751548000	1.885425000	0.770071000
H	-6.266880000	-0.400935000	-0.053824000
C	-1.970958000	3.456754000	0.609508000
C	-1.003673000	2.584458000	0.068348000
H	-4.029912000	3.693972000	1.144395000
H	-1.667961000	4.447099000	0.930057000
C	0.412589000	3.018377000	-0.141833000
H	0.482280000	3.504616000	-1.123884000
H	0.714489000	3.759690000	0.601382000
P	1.584760000	1.582029000	-0.190292000
C	2.345383000	1.496018000	1.489236000
H	3.086999000	0.693252000	1.406108000
C	2.806066000	1.986875000	-1.511868000
H	2.158929000	1.988053000	-2.400172000
C	1.267054000	1.088106000	2.495257000
H	0.458868000	1.825116000	2.542844000
H	0.835209000	0.117756000	2.249477000
H	1.709847000	1.015504000	3.493611000
C	3.060419000	2.774071000	1.924063000
H	3.435004000	2.634409000	2.943589000
H	3.913172000	3.010138000	1.287641000
H	2.388936000	3.638171000	1.939184000
C	3.815719000	0.851050000	-1.653363000
H	3.314511000	-0.100437000	-1.847827000
H	4.488758000	1.060169000	-2.490694000
H	4.427352000	0.745009000	-0.751375000
C	3.479312000	3.355690000	-1.407276000
H	4.277494000	3.356729000	-0.661961000
H	3.933616000	3.596275000	-2.374021000
H	2.777710000	4.158038000	-1.162197000
C	-4.243045000	-0.826998000	-0.659735000
H	-4.493071000	-1.819682000	-1.022053000
C	-2.632283000	0.919421000	-0.264710000
N	-1.335888000	1.353646000	-0.318559000
Pd	0.110344000	-0.058219000	-0.818029000
H	1.228348000	-1.075123000	-1.203370000
S	-1.676535000	-1.365877000	-1.505951000
Ge	0.490455000	-2.104580000	0.516844000
C	2.272736000	-2.088151000	1.296472000
H	2.489369000	-1.149499000	1.803022000
H	2.191608000	-2.858199000	2.074643000
C	-0.920413000	-1.878108000	1.841541000
H	-1.734688000	-2.493660000	1.447526000
H	-1.265083000	-0.841165000	1.865924000
C	3.362062000	-2.472204000	0.306348000
H	3.344589000	-1.827504000	-0.577834000
H	4.361553000	-2.395568000	0.749929000
H	3.235561000	-3.501930000	-0.040660000
C	0.304575000	-3.792071000	-0.419045000
H	0.860884000	-4.497859000	0.210637000
H	-0.755133000	-4.053263000	-0.359901000
C	-0.466609000	-2.366923000	3.212966000
H	-0.210844000	-3.431997000	3.186924000
H	0.421681000	-1.825844000	3.554454000
H	-1.251349000	-2.234230000	3.966636000
C	0.816516000	-3.830574000	-1.852383000
H	0.752017000	-4.838998000	-2.277197000
H	0.232793000	-3.167302000	-2.499057000
H	1.859891000	-3.507817000	-1.915278000

Sum of electronic and zero-point Energies= -3857.175691

Sum of electronic and thermal Free Energies= -3857.237256

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(P,N,S)Pd^{+}…H-GeEt$_3$ (σ-complex, form 1)

C	-2.760165000	-1.702136000	-0.415436000
C	-4.331889000	0.011326000	0.417885000
C	-5.330888000	-0.979627000	0.552218000
C	-5.044618000	-2.282542000	0.210286000
C	-4.548776000	1.370960000	0.739960000
H	-6.310193000	-0.693713000	0.922593000
H	-5.805350000	-3.051018000	0.308222000
C	-3.543225000	2.290414000	0.575672000
C	-2.286023000	1.872869000	0.094894000
H	-5.521672000	1.677349000	1.113258000
H	-3.694764000	3.338618000	0.806457000
C	-1.193379000	2.866594000	-0.150248000
H	-1.356412000	3.324083000	-1.134726000
H	-1.218185000	3.676904000	0.582822000
P	0.459245000	2.046910000	-0.229449000
C	1.207290000	2.112713000	1.465447000
H	1.854436000	1.229519000	1.479346000
C	1.371484000	2.972906000	-1.535150000
H	0.733977000	2.763452000	-2.405916000
C	0.104190000	1.908935000	2.506895000
H	-0.513605000	2.806225000	2.606710000
H	-0.553843000	1.067846000	2.270749000
H	0.563999000	1.709553000	3.479578000
C	2.039024000	3.353551000	1.766131000
H	2.431141000	3.277421000	2.786048000
H	2.888600000	3.453694000	1.087640000
H	1.435806000	4.264421000	1.709039000
C	2.745114000	2.367021000	-1.797924000
H	2.668322000	1.302369000	-2.028972000
H	3.206720000	2.869724000	-2.653626000
H	3.411993000	2.488260000	-0.940067000
C	1.418253000	4.487548000	-1.330635000
H	2.116825000	4.769002000	-0.540990000
H	1.759413000	4.955388000	-2.260060000
H	0.437897000	4.908530000	-1.090620000
C	-3.771859000	-2.641485000	-0.272830000
H	-3.575977000	-3.674655000	-0.544288000
C	-3.042884000	-0.356551000	-0.059494000
N	-2.053229000	0.587487000	-0.188570000
Pd	-0.186193000	-0.064333000	-0.735833000
H	1.238540000	-0.418789000	-1.389458000
S	-1.175834000	-2.149991000	-1.047917000
Ge	1.929576000	-1.354375000	-0.030515000
C	3.663829000	-0.475100000	-0.045999000
H	3.862395000	-0.251612000	-1.097625000
H	3.646162000	0.469807000	0.502107000
C	1.130307000	-1.537490000	1.733018000
H	0.524260000	-2.445033000	1.677208000
H	0.445298000	-0.706208000	1.902846000
C	4.756323000	-1.406522000	0.479788000
H	4.794857000	-2.340674000	-0.089495000
H	5.740925000	-0.932968000	0.394668000
H	4.604121000	-1.667753000	1.529352000
C	2.185210000	-1.609377000	2.830193000
H	2.818110000	-2.494526000	2.717743000
H	2.838100000	-0.730569000	2.805120000
H	1.722159000	-1.654529000	3.822415000
C	2.135358000	-3.034245000	-0.981190000
H	1.310746000	-3.172185000	-1.685157000
H	3.050972000	-2.924665000	-1.571857000
C	2.231289000	-4.213990000	-0.019385000
H	3.038977000	-4.079684000	0.708124000
H	1.298989000	-4.331761000	0.541469000
H	2.418216000	-5.153340000	-0.552016000

Sum of electronic and zero-point Energies= -3857.170887

Sum of electronic and thermal Free Energies= -3857.233498

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TS_HGeEt$_3$

C	-2.487610000	1.032510000	-0.864075000
C	-2.078744000	3.219360000	0.193789000
C	-3.474505000	3.447346000	0.221990000
C	-4.334707000	2.497700000	-0.281838000
C	-1.122154000	4.145759000	0.674994000
H	-3.848093000	4.377698000	0.638236000
H	-5.406180000	2.669623000	-0.264954000
C	0.220413000	3.864894000	0.589198000
C	0.639069000	2.633202000	0.041052000
H	-1.463355000	5.084917000	1.100597000
H	0.965566000	4.573190000	0.932771000
C	2.087353000	2.302927000	-0.160355000
H	2.380296000	2.673214000	-1.151319000
H	2.722596000	2.808327000	0.571659000
P	2.374655000	0.469007000	-0.189458000
C	2.771713000	0.010588000	1.557545000
H	2.884982000	-1.079615000	1.529328000
C	3.811351000	0.151833000	-1.304247000
H	3.349858000	0.237002000	-2.296599000
C	1.581869000	0.365396000	2.451009000
H	1.399559000	1.444668000	2.471620000
H	0.665944000	-0.130589000	2.126412000
H	1.791270000	0.045940000	3.476736000
C	4.072900000	0.615175000	2.081184000
H	4.187056000	0.346259000	3.136784000
H	4.944734000	0.233993000	1.546457000
H	4.074722000	1.707577000	2.018527000
C	4.271972000	-1.292178000	-1.106759000
H	3.434058000	-1.993976000	-1.172902000
H	4.997490000	-1.556701000	-1.882127000
H	4.755988000	-1.423858000	-0.134070000
C	4.957171000	1.159178000	-1.223531000
H	5.487453000	1.109854000	-0.270730000
H	5.678093000	0.933517000	-2.016515000
H	4.614751000	2.186602000	-1.374019000
C	-3.844820000	1.291712000	-0.825125000
H	-4.541684000	0.561170000	-1.224660000
C	-1.590142000	1.998071000	-0.341789000
N	-0.252215000	1.734911000	-0.371709000
Pd	0.343654000	-0.175805000	-0.969505000
H	0.885345000	-1.543040000	-1.443219000
S	-1.873698000	-0.470943000	-1.590924000
Ge	-1.142788000	-1.788433000	0.479010000
C	0.404556000	-2.747661000	1.200840000
H	1.185253000	-2.063525000	1.521961000
H	-0.051833000	-3.176106000	2.103685000
C	-1.975404000	-0.643880000	1.807547000
H	-3.017018000	-0.548641000	1.487866000
H	-1.532383000	0.354643000	1.796295000
C	0.953490000	-3.857069000	0.321262000
H	1.245028000	-3.481861000	-0.666307000
H	1.840850000	-4.317924000	0.771206000
H	0.215719000	-4.649688000	0.169918000
C	-2.376940000	-3.193438000	-0.048090000
H	-2.281740000	-3.942535000	0.748561000
H	-3.374821000	-2.748734000	0.024186000
C	-1.885501000	-1.280814000	3.191786000
H	-2.369345000	-2.263760000	3.211391000
H	-0.843749000	-1.423771000	3.494678000
H	-2.372837000	-0.658289000	3.950682000

C	-2.164264000	-3.833069000	-1.415214000
H	-2.869383000	-4.655323000	-1.584139000
H	-2.316609000	-3.107681000	-2.220694000
H	-1.153997000	-4.235350000	-1.526816000

Sum of electronic and zero-point Energies= -3857.172205

Sum of electronic and thermal Free Energies= -3857.231922

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FP_(PNSGeEt$_3$)PdH$^+$

C	-1.886129000	1.321193000	-1.032496000
C	-1.149311000	3.377641000	0.081898000
C	-2.477465000	3.861298000	0.020448000
C	-3.467066000	3.092401000	-0.547286000
C	-0.087445000	4.101182000	0.677511000
H	-2.697973000	4.841753000	0.430962000
H	-4.487081000	3.459742000	-0.593188000
C	1.173267000	3.561573000	0.727491000
C	1.405637000	2.278952000	0.181620000
H	-0.286130000	5.083015000	1.097013000
H	1.997909000	4.101154000	1.179297000
C	2.783528000	1.683611000	0.167499000
H	3.326184000	2.127600000	-0.676984000
H	3.338353000	1.952961000	1.070766000
P	2.771608000	-0.151639000	-0.119896000
C	2.909669000	-0.974651000	1.529478000
H	2.852011000	-2.042413000	1.283889000
C	4.245478000	-0.526891000	-1.168681000
H	3.909247000	-0.198330000	-2.160842000
C	1.687767000	-0.605698000	2.371555000
H	1.663504000	0.466900000	2.593665000
H	0.753377000	-0.870074000	1.872030000
H	1.727485000	-1.141279000	3.325492000
C	4.215118000	-0.702395000	2.271519000
H	4.166747000	-1.165199000	3.263173000
H	5.076781000	-1.125873000	1.751730000
H	4.387824000	0.368940000	2.416634000
C	4.468658000	-2.038198000	-1.207253000
H	3.553583000	-2.576869000	-1.472984000
H	5.230902000	-2.276264000	-1.955750000
H	4.821357000	-2.411124000	-0.240609000
C	5.519895000	0.238980000	-0.813899000
H	5.925903000	-0.063220000	0.153491000
H	6.280173000	0.026538000	-1.573066000
H	5.367499000	1.321277000	-0.798083000
C	-3.173450000	1.815836000	-1.071291000
H	-3.966729000	1.216202000	-1.505250000
C	-0.849228000	2.095948000	-0.452507000
N	0.416275000	1.583480000	-0.374701000
Pd	0.735451000	-0.388500000	-0.988486000
H	1.050260000	-1.848646000	-1.408926000
S	-1.541345000	-0.354538000	-1.584988000
Ge	-2.155910000	-1.210229000	0.496570000
C	-1.217946000	-2.884660000	0.711567000
H	-0.147223000	-2.692198000	0.812917000
H	-1.592962000	-3.269123000	1.667841000
C	-1.826031000	0.109004000	1.872183000
H	-2.586837000	0.882822000	1.736913000
H	-0.842883000	0.568426000	1.769911000
C	-1.520675000	-3.867367000	-0.412206000
H	-1.264957000	-3.448262000	-1.391853000
H	-0.957022000	-4.800079000	-0.298547000
H	-2.584152000	-4.123629000	-0.430659000
C	-4.068948000	-1.484088000	0.365164000
H	-4.258476000	-2.286126000	1.089092000
H	-4.531952000	-0.572980000	0.757383000
C	-1.983045000	-0.582562000	3.226415000
H	-2.980967000	-1.022051000	3.337370000
H	-1.259840000	-1.396309000	3.341381000
H	-1.836815000	0.119107000	4.054705000
C	-4.621840000	-1.854174000	-1.005009000
H	-5.691048000	-2.089040000	-0.953739000
H	-4.498989000	-1.034768000	-1.719645000
H	-4.107830000	-2.723009000	-1.426585000

Sum of electronic and zero-point Energies= -3857.184802

Sum of electronic and thermal Free Energies= -3857.246408

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SnHEt$_3$

H	0.021008000	-1.124000000	-1.848376000
Sn	0.007466000	-0.323236000	-0.301185000
C	-0.022711000	1.836138000	-0.624276000
H	0.861317000	2.103294000	-1.214223000
H	-0.893930000	2.072746000	-1.245521000
C	-1.793041000	-0.916970000	0.780537000
H	-1.789652000	-2.009485000	0.867071000
H	-1.707216000	-0.523701000	1.800131000
C	-0.059935000	2.625929000	0.683340000
H	-0.947469000	2.382721000	1.278750000
H	0.813978000	2.413921000	1.309978000
H	-0.075929000	3.709509000	0.506496000
C	-3.081519000	-0.428982000	0.120379000
H	-3.110428000	0.664090000	0.047385000
H	-3.189945000	-0.822140000	-0.897004000
H	-3.971497000	-0.739074000	0.683978000
C	1.816681000	-0.876255000	0.787675000
H	1.830477000	-1.967941000	0.883514000
H	1.723205000	-0.475808000	1.803789000
C	3.098236000	-0.373655000	0.125098000
H	3.992154000	-0.665862000	0.692002000
H	3.213847000	-0.772859000	-0.889134000
H	3.110502000	0.719148000	0.043903000

Sum of electronic and zero-point Energies= -241.430896

Sum of electronic and thermal Free Energies= -241.472420

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(P,N,S)Pd$^+$…H-SnEt$_3$ (σ-complex, form 2)

C	-2.751928000	-1.424005000	-0.601467000
C	-4.250957000	0.249623000	0.427291000
C	-5.254780000	-0.738832000	0.550626000
C	-5.004036000	-2.019945000	0.112375000
C	-4.425118000	1.590458000	0.843795000
H	-6.209547000	-0.469732000	0.991152000
H	-5.768347000	-2.785563000	0.204276000
C	-3.414562000	2.506648000	0.679747000
C	-2.189506000	2.097737000	0.114295000
H	-5.371615000	1.887459000	1.286263000
H	-3.539034000	3.541924000	0.975967000
C	-1.084952000	3.075279000	-0.150940000
H	-1.262240000	3.533313000	-1.132746000
H	-1.075565000	3.884422000	0.584405000
P	0.555912000	2.227557000	-0.252021000
C	1.251506000	2.290035000	1.456885000
H	2.097613000	1.594378000	1.429810000
C	1.562431000	3.162877000	-1.480442000
H	1.080921000	2.875105000	-2.424901000
C	0.197808000	1.746731000	2.424026000
H	-0.631370000	2.452095000	2.538280000
H	-0.212734000	0.789412000	2.095217000

H	0.649035000	1.604068000	3.410554000
C	1.737712000	3.672074000	1.883676000
H	2.048178000	3.632402000	2.933348000
H	2.593215000	4.008391000	1.295070000
H	0.940203000	4.418048000	1.802126000
C	2.995054000	2.634266000	-1.486575000
H	3.026375000	1.554902000	-1.657449000
H	3.559248000	3.119433000	-2.289180000
H	3.504360000	2.850319000	-0.542318000
C	1.497334000	4.684747000	-1.354701000
H	2.019674000	5.045455000	-0.467129000
H	1.984970000	5.127519000	-2.229625000
H	0.470323000	5.058515000	-1.327211000
C	-3.763819000	-2.361436000	-0.463257000
H	-3.597306000	-3.377330000	-0.809084000
C	-2.995011000	-0.103421000	-0.138081000
N	-1.995929000	0.827450000	-0.245886000
Pd	-0.144933000	0.159025000	-0.872963000
H	1.251927000	-0.216716000	-1.497751000
S	-1.213058000	-1.841579000	-1.366604000
Sn	1.774969000	-1.528605000	0.128867000
C	3.717047000	-0.555273000	0.250717000
H	4.168622000	-0.615778000	-0.745235000
H	3.585016000	0.504687000	0.479556000
C	0.920790000	-1.809947000	2.114568000
H	1.486126000	-2.664252000	2.507846000
H	1.208109000	-0.938896000	2.709802000
C	1.921506000	-3.352570000	-1.043132000
H	2.992918000	-3.529544000	-1.193148000
H	1.490310000	-3.153857000	-2.029343000
C	4.599155000	-1.234750000	1.297497000
H	4.739069000	-2.301241000	1.087071000
H	5.597258000	-0.780112000	1.331942000
H	4.171329000	-1.153804000	2.302948000
C	-0.576118000	-2.071718000	2.188896000
H	-0.886923000	-2.264572000	3.223591000
H	-1.156762000	-1.219952000	1.823776000
H	-0.868706000	-2.935255000	1.585601000
C	1.251779000	-4.553326000	-0.381925000
H	1.674439000	-4.765067000	0.606259000
H	0.177683000	-4.387513000	-0.254148000
H	1.375425000	-5.459297000	-0.988704000

Sum of electronic and zero-point Energies= -1785.553423

Sum of electronic and thermal Free Energies= -1785.619393

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(P,N,S)Pd^{+}…H-SnEt$_3$ (σ-complex, form 1)

C	-2.595061000	-1.952817000	-0.538040000
C	-4.389278000	-0.509056000	0.357398000
C	-5.223471000	-1.642715000	0.491883000
C	-4.749859000	-2.881938000	0.122997000
C	-4.797758000	0.796728000	0.715601000
H	-6.225683000	-1.516065000	0.888809000
H	-5.382275000	-3.758565000	0.224563000
C	-3.943787000	1.859241000	0.552497000
C	-2.648586000	1.642226000	0.040587000
H	-5.796470000	0.947145000	1.115172000
H	-4.243887000	2.869036000	0.808026000
C	-1.718100000	2.786334000	-0.217356000
H	-1.945499000	3.195840000	-1.210368000
H	-1.865478000	3.595042000	0.503624000
P	0.039678000	2.220789000	-0.265757000
C	0.735190000	2.489490000	1.422393000
H	1.662695000	1.904388000	1.420588000
C	0.864454000	3.218786000	-1.577476000
H	0.382232000	2.824698000	-2.482595000
C	-0.233268000	1.875830000	2.435786000
H	-1.147564000	2.472608000	2.514919000
H	-0.516124000	0.853070000	2.174342000
H	0.237152000	1.857310000	3.423495000
C	1.052818000	3.943207000	1.759467000
H	1.375569000	4.004010000	2.804411000
H	1.857605000	4.340890000	1.138522000
H	0.172610000	4.584250000	1.646254000
C	2.352296000	2.884894000	-1.636232000
H	2.518405000	1.813084000	-1.774358000
H	2.811808000	3.409405000	-2.479872000
H	2.868393000	3.202398000	-0.725093000
C	0.601960000	4.723797000	-1.510683000
H	1.149134000	5.197705000	-0.694070000
H	0.942714000	5.178730000	-2.446681000
H	-0.459523000	4.959890000	-1.396918000
C	-3.447624000	-3.037126000	-0.390600000
H	-3.102306000	-4.025306000	-0.679733000
C	-3.070147000	-0.671567000	-0.149844000
N	-2.233668000	0.410715000	-0.269662000
Pd	-0.284072000	0.030159000	-0.750771000
H	1.287833000	-0.193409000	-1.167792000
S	-0.978245000	-2.140286000	-1.220764000
Sn	2.094938000	-1.146580000	0.137751000
C	3.851706000	0.136641000	0.240169000
H	4.343760000	0.119603000	-0.737632000
H	3.513780000	1.162469000	0.410147000
C	1.314739000	-1.412761000	2.153468000
H	2.058042000	-2.065748000	2.627510000
H	1.386759000	-0.442375000	2.652319000
C	2.480876000	-2.990473000	-0.942418000
H	2.274867000	-2.799707000	-2.000793000
H	1.747285000	-3.726403000	-0.600816000
C	4.806939000	-0.307375000	1.347741000
H	5.166644000	-1.330319000	1.195155000
H	5.689639000	0.342974000	1.392910000
H	4.329255000	-0.273609000	2.333082000
C	-0.081810000	-2.005140000	2.283380000
H	-0.344033000	-2.158814000	3.337888000
H	-0.841680000	-1.353265000	1.841703000
H	-0.163180000	-2.970231000	1.774762000
C	3.907825000	-3.498031000	-0.743412000
H	4.651300000	-2.772206000	-1.089912000
H	4.121678000	-3.710457000	0.309836000
H	4.077049000	-4.427706000	-1.301148000

Sum of electronic and zero-point Energies= -1785.546363

Sum of electronic and thermal Free Energies= -1785.612675

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TS_HSnEt$_3$

C	-2.096494000	1.779363000	-0.834931000
C	-1.322508000	3.710347000	0.484252000
C	-2.642505000	4.218787000	0.486507000
C	-3.643208000	3.528114000	-0.159048000
C	-0.237748000	4.353383000	1.127274000
H	-2.846548000	5.152322000	1.001646000
H	-4.657686000	3.913920000	-0.161934000
C	1.021172000	3.806019000	1.078451000
C	1.223947000	2.585903000	0.398134000
H	-0.413678000	5.287240000	1.653440000
H	1.865424000	4.295051000	1.551073000
C	2.596049000	2.002729000	0.237437000
H	3.077996000	2.521700000	-0.600936000
H	3.214197000	2.195182000	1.118339000

P	2.561771000	0.197055000	-0.199582000
C	2.929949000	-0.713949000	1.363187000
H	2.858957000	-1.768493000	1.073822000
C	3.887341000	-0.092620000	-1.454618000
H	3.424949000	0.296031000	-2.371266000
C	1.829971000	-0.404840000	2.376389000
H	1.860861000	0.642997000	2.692589000
H	0.838241000	-0.605500000	1.966035000
H	1.962621000	-1.026689000	3.267137000
C	4.323411000	-0.463912000	1.934491000
H	4.413619000	-0.991386000	2.890284000
H	5.107047000	-0.839677000	1.274002000
H	4.508190000	0.597571000	2.126670000
C	4.094601000	-1.598614000	-1.617614000
H	3.150501000	-2.121323000	-1.801482000
H	4.755665000	-1.786428000	-2.469344000
H	4.562986000	-2.033033000	-0.728635000
C	5.200043000	0.654986000	-1.225255000
H	5.732120000	0.294602000	-0.342787000
H	5.849910000	0.494992000	-2.092178000
H	5.053143000	1.733310000	-1.121733000
C	-3.373077000	2.311898000	-0.820037000
H	-4.179454000	1.782526000	-1.318138000
C	-1.053554000	2.483670000	-0.179316000
N	0.203649000	1.949811000	-0.174974000
Pd	0.443350000	0.047882000	-0.988404000
H	0.713284000	-1.340011000	-1.620131000
S	-1.763580000	0.250768000	-1.682209000
Sn	-1.311779000	-1.882447000	0.190368000
C	0.290264000	-3.353033000	0.388153000
H	0.442541000	-3.780709000	-0.608171000
H	1.206990000	-2.831467000	0.665674000
C	-1.905424000	-1.057568000	2.123976000
H	-2.904311000	-1.475225000	2.294203000
H	-1.232360000	-1.535912000	2.843951000
C	-2.957085000	-2.828925000	-0.870861000
H	-2.942713000	-3.882247000	-0.565819000
H	-2.717305000	-2.804178000	-1.939278000
C	-0.079668000	-4.421546000	1.412786000
H	-1.006336000	-4.942586000	1.147249000
H	0.707027000	-5.183100000	1.490935000
H	-0.217247000	-3.995615000	2.412901000
C	-1.915455000	0.452625000	2.311538000
H	-2.184076000	0.712774000	3.343050000
H	-0.935900000	0.893078000	2.109027000
H	-2.639012000	0.936479000	1.651491000
C	-4.312752000	-2.191399000	-0.592143000
H	-4.580202000	-2.252853000	0.468398000
H	-4.321436000	-1.132624000	-0.871861000
H	-5.111621000	-2.686234000	-1.158665000

Sum of electronic and zero-point Energies= -1785.548864

Sum of electronic and thermal Free Energies= -1785.612344

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FP_(PNSSnEt$_3$)PdH$^+$

C	-1.573862000	1.789287000	-0.918703000
C	-0.603209000	3.673901000	0.322691000
C	-1.855911000	4.328674000	0.271443000
C	-2.919625000	3.731344000	-0.364509000
C	0.525474000	4.214400000	0.985013000
H	-1.958926000	5.302463000	0.740253000
H	-3.881634000	4.231411000	-0.409552000
C	1.707831000	3.518489000	1.015525000
C	1.792617000	2.261699000	0.376248000
H	0.439820000	5.182894000	1.468941000
H	2.583411000	3.917684000	1.515103000
C	3.093039000	1.514029000	0.318662000
H	3.705631000	1.975785000	-0.466445000
H	3.650416000	1.622234000	1.253905000
P	2.874883000	-0.268428000	-0.155358000
C	2.856013000	-1.253133000	1.409800000
H	2.666705000	-2.276106000	1.060877000
C	4.329090000	-0.722386000	-1.200062000
H	4.074038000	-0.261339000	-2.163174000
C	1.664205000	-0.803288000	2.256467000
H	1.796966000	0.220115000	2.623311000
H	0.731824000	-0.842364000	1.685496000
H	1.562909000	-1.458970000	3.127178000
C	4.161325000	-1.227061000	2.199831000
H	4.020904000	-1.763651000	3.144541000
H	4.974768000	-1.715532000	1.659874000
H	4.469997000	-0.205422000	2.443951000
C	4.366204000	-2.239296000	-1.383396000
H	3.401873000	-2.630991000	-1.722279000
H	5.119136000	-2.498375000	-2.134351000
H	4.636400000	-2.744971000	-0.451109000
C	5.673517000	-0.160647000	-0.737725000
H	5.994671000	-0.589984000	0.213253000
H	6.433581000	-0.408258000	-1.486477000
H	5.659038000	0.927504000	-0.634993000
C	-2.778697000	2.461405000	-0.962020000
H	-3.631120000	2.001621000	-1.450132000
C	-0.458032000	2.397817000	-0.286014000
N	0.734581000	1.732621000	-0.234853000
Pd	0.841179000	-0.179660000	-1.063560000
H	1.012134000	-1.598644000	-1.665401000
S	-1.409722000	0.161178000	-1.657128000
Sn	-2.190794000	-1.399775000	0.253261000
C	-0.893558000	-3.137662000	0.134934000
H	-0.760431000	-3.376182000	-0.924623000
H	0.083644000	-2.841442000	0.526753000
C	-2.172013000	-0.440524000	2.211915000
H	-3.211152000	-0.518545000	2.551296000
H	-1.585114000	-1.130572000	2.828737000
C	-4.207875000	-1.839385000	-0.420306000
H	-4.672714000	-2.395879000	0.402520000
H	-4.126266000	-2.529755000	-1.266501000
C	-1.475253000	-4.320627000	0.907070000
H	-2.450587000	-4.625131000	0.512171000
H	-0.813228000	-5.193374000	0.846482000
H	-1.608975000	-4.090280000	1.970134000
C	-1.662123000	0.984435000	2.374095000
H	-1.698040000	1.284103000	3.428941000
H	-0.625909000	1.084166000	2.043629000
H	-2.263935000	1.700945000	1.809732000
C	-5.038098000	-0.614648000	-0.788409000
H	-5.101211000	0.102522000	0.037365000
H	-4.614822000	-0.089798000	-1.651027000
H	-6.064466000	-0.896461000	-1.054588000

Sum of electronic and zero-point Energies= -1785.553679

Sum of electronic and thermal Free Energies= -1785.618437

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HBPin

C	-0.781472000	-0.190348000	0.051541000
C	0.781301000	-0.190971000	-0.051540000
O	-1.072247000	1.194816000	0.405601000
O	1.073271000	1.193724000	-0.406057000
B	0.000809000	1.932042000	-0.000467000
H	0.001330000	3.123708000	-0.000737000
C	1.348541000	-1.098069000	-1.127405000
H	0.980357000	-0.827677000	-2.118971000
H	2.439872000	-1.022508000	-1.135103000
H	1.082913000	-2.140595000	-0.927065000
C	-1.349255000	-1.096666000	1.127812000
H	-2.440552000	-1.020576000	1.135434000
H	-1.084112000	-2.139329000	0.927547000
H	-0.980954000	-0.826457000	2.119366000
C	-1.472135000	-0.449399000	-1.282666000
H	-1.069213000	0.193033000	-2.071157000
H	-1.362094000	-1.492406000	-1.592107000
H	-2.539132000	-0.233024000	-1.178708000
C	1.471524000	-0.449596000	1.282993000
H	2.538699000	-0.234144000	1.178851000
H	1.068993000	0.193942000	2.070768000
H	1.360643000	-1.492208000	1.593452000

Sum of electronic and zero-point Energies= -411.585296

Sum of electronic and thermal Free Energies= -411.618334

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(P,N,S)Pd^{+}…H-BPin (σ-complex)

C	-1.821577000	2.521856000	-0.191934000
C	-4.039810000	1.640484000	0.433199000
C	-4.503516000	2.962647000	0.620150000
C	-3.648283000	4.020049000	0.404700000
C	-4.861386000	0.504341000	0.610659000
H	-5.532270000	3.120606000	0.927437000
H	-3.996214000	5.038997000	0.543763000
C	-4.359368000	-0.752410000	0.382057000
C	-3.013985000	-0.910596000	-0.004472000
H	-5.894472000	0.639525000	0.917317000
H	-4.978313000	-1.635662000	0.489217000
C	-2.465136000	-2.261499000	-0.334457000
H	-2.947403000	-3.043726000	0.258081000
H	-2.679062000	-2.476516000	-1.387906000
P	-0.637451000	-2.272676000	-0.098871000
C	0.080581000	-3.473457000	-1.292521000
H	-0.467128000	-4.412381000	-1.140077000
C	-0.427632000	-2.816743000	1.654526000
H	-1.223744000	-2.249256000	2.156028000
C	1.566069000	-3.692778000	-1.010044000
H	1.740359000	-4.159492000	-0.038565000
H	1.984234000	-4.350277000	-1.778738000
H	2.119403000	-2.747743000	-1.043979000
C	-0.138462000	-2.969894000	-2.719380000
H	0.255912000	-3.708023000	-3.425046000
H	-1.193058000	-2.811477000	-2.960455000
H	0.393908000	-2.027005000	-2.884457000
C	0.910087000	-2.394954000	2.256337000
H	1.082098000	-1.321862000	2.154047000
H	0.915759000	-2.646124000	3.322186000
H	1.749705000	-2.915565000	1.788507000
C	-0.703174000	-4.311050000	1.820318000
H	0.083960000	-4.913669000	1.358437000
H	-0.724804000	-4.552856000	2.887936000
H	-1.663842000	-4.612945000	1.392630000
C	-2.318861000	3.803404000	-0.005042000
H	-1.669071000	4.654921000	-0.183611000
C	-2.688707000	1.425796000	0.042320000
N	-2.207268000	0.149896000	-0.132849000
Pd	-0.213122000	-0.068697000	-0.482478000
S	-0.171625000	2.251890000	-0.753774000
H	1.287958000	-0.575751000	-0.908532000
C	3.792887000	1.716559000	-0.326473000
C	3.812874000	0.796635000	0.943908000
B	1.997487000	0.358542000	-0.310533000
O	2.764033000	1.076346000	-1.162081000
O	2.448702000	0.246005000	0.959937000
C	3.307254000	3.128957000	-0.041307000
H	3.133159000	3.643582000	-0.989983000
H	2.370737000	3.126969000	0.521271000
H	4.059097000	3.688812000	0.521142000
C	5.088691000	1.740750000	-1.111546000
H	5.898366000	2.131698000	-0.488464000
H	5.367649000	0.746935000	-1.466470000
H	4.979545000	2.398759000	-1.978050000
C	4.741523000	-0.402160000	0.810720000
H	4.552893000	-1.091932000	1.637737000
H	4.572814000	-0.936414000	-0.128710000
H	5.789228000	-0.093563000	0.852824000
C	4.049294000	1.523248000	2.251345000
H	3.289351000	2.285242000	2.432417000
H	4.027390000	0.807762000	3.078189000
H	5.032593000	2.002492000	2.242715000

Sum of electronic and zero-point Energies= -1955.675099

Sum of electronic and thermal Free Energies= -1955.735782

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TS_HBPin

C	-0.605600000	2.748268000	-0.409306000
C	-2.888627000	2.882033000	0.513495000
C	-2.691010000	4.262731000	0.753295000
C	-1.488808000	4.849500000	0.431460000
C	-4.081985000	2.193489000	0.838824000
H	-3.494521000	4.838801000	1.201253000
H	-1.329375000	5.905916000	0.622196000
C	-4.192819000	0.841842000	0.612815000
C	-3.102812000	0.139463000	0.059630000
H	-4.905908000	2.746607000	1.279961000
H	-5.098619000	0.301736000	0.863021000
C	-3.129614000	-1.337037000	-0.199548000
H	-3.834225000	-1.849409000	0.461359000
H	-3.456812000	-1.514227000	-1.230457000
P	-1.412516000	-2.025456000	-0.019053000
C	-1.321597000	-3.564585000	-1.019409000
H	-2.140969000	-4.206572000	-0.671696000
C	-1.270450000	-2.356675000	1.793443000
H	-1.768572000	-1.476673000	2.223653000
C	0.017620000	-4.265245000	-0.792479000
H	0.137818000	-4.608927000	0.237328000
H	0.081731000	-5.139046000	-1.448582000
H	0.853757000	-3.600364000	-1.036217000
C	-1.521553000	-3.222727000	-2.495973000
H	-1.464752000	-4.141387000	-3.088601000
H	-2.491240000	-2.758994000	-2.696094000
H	-0.736479000	-2.544045000	-2.847237000
C	0.179772000	-2.357960000	2.268805000
H	0.688006000	-1.430416000	1.995601000
H	0.201335000	-2.454452000	3.359428000
H	0.744169000	-3.195091000	1.849907000
C	-2.037807000	-3.611968000	2.205365000
H	-1.562887000	-4.515567000	1.812457000

H	-2.045203000	-3.686363000	3.297612000
H	-3.078056000	-3.593558000	1.866509000
C	-0.447005000	4.096812000	-0.152369000
H	0.486505000	4.586291000	-0.412972000
C	-1.832638000	2.124754000	-0.059697000
N	-1.977672000	0.780404000	-0.257270000
Pd	-0.252220000	-0.218876000	-0.744893000
S	0.650736000	1.855526000	-1.318276000
H	1.043409000	-1.072830000	-0.984986000
C	4.063214000	0.449493000	-0.295934000
C	3.511666000	0.077723000	1.120013000
B	1.818826000	0.260839000	-0.367516000
O	2.933001000	0.110353000	-1.158420000
O	2.080520000	0.358498000	0.974921000
C	4.327704000	1.940411000	-0.462585000
H	4.495083000	2.154280000	-1.521841000
H	3.479562000	2.540052000	-0.121977000
H	5.217823000	2.245453000	0.094151000
C	5.262435000	-0.362548000	-0.742211000
H	6.099373000	-0.210410000	-0.053914000
H	5.033212000	-1.428994000	-0.785198000
H	5.578485000	-0.037576000	-1.737621000
C	3.649871000	-1.404093000	1.442895000
H	3.091009000	-1.626730000	2.355171000
H	3.255673000	-2.027325000	0.635171000
H	4.696253000	-1.672408000	1.611666000
C	4.048242000	0.928363000	2.253244000
H	3.820704000	1.985581000	2.105126000
H	3.600968000	0.608244000	3.198727000
H	5.133056000	0.810039000	2.334211000

Sum of electronic and zero-point Energies= -1955.669124

Sum of electronic and thermal Free Energies= -1955.727814

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FP_(PNSBPin)PdH$^+$

C	1.999273000	1.772204000	-0.970469000
C	1.582050000	3.270720000	0.919655000
C	2.791375000	3.943038000	0.622236000
C	3.566984000	3.538130000	-0.438079000
C	0.738805000	3.634816000	1.997431000
H	3.090193000	4.780839000	1.244740000
H	4.494024000	4.052687000	-0.668292000
C	-0.418023000	2.936435000	2.234510000
C	-0.767740000	1.859166000	1.389698000
H	1.022826000	4.469161000	2.631848000
H	-1.070912000	3.194266000	3.060690000
C	-1.994075000	1.037124000	1.660710000
H	-1.783511000	0.379204000	2.513485000
H	-2.831193000	1.675553000	1.959296000
P	-2.470126000	-0.055383000	0.232731000
C	-3.921259000	0.778390000	-0.540024000
H	-4.659726000	0.898292000	0.262933000
C	-2.970954000	-1.646146000	1.026688000
H	-2.187421000	-1.785506000	1.782554000
C	-4.514122000	-0.068076000	-1.662829000
H	-4.916768000	-1.015481000	-1.296594000
H	-5.332306000	0.482131000	-2.139191000
H	-3.761583000	-0.285059000	-2.428336000
C	-3.488939000	2.155493000	-1.043677000
H	-4.350238000	2.670551000	-1.481546000
H	-3.092292000	2.788985000	-0.244787000
H	-2.719054000	2.060133000	-1.817664000
C	-2.906066000	-2.825628000	0.059301000
H	-1.914023000	-2.916488000	-0.390776000
H	-3.124461000	-3.750828000	0.602864000
H	-3.635465000	-2.733064000	-0.749822000
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H	-4.349435000	-0.684965000	2.431725000
C	3.172184000	2.443215000	-1.236714000
H	3.801607000	2.124147000	-2.061542000
C	1.171416000	2.179857000	0.106890000
N	0.002779000	1.519832000	0.358744000
Pd	-0.615554000	0.035691000	-0.986112000
S	1.526863000	0.371707000	-1.999841000
H	-1.185932000	-1.035937000	-1.945348000
C	2.217163000	-3.095579000	-0.028267000
C	2.203774000	-2.054478000	1.142704000
B	1.897211000	-1.013849000	-0.808046000
O	1.687152000	-2.308460000	-1.150279000
O	2.398207000	-0.785601000	0.431400000
C	3.618114000	-3.529036000	-0.432203000
H	3.561138000	-4.084770000	-1.372013000
H	4.274357000	-2.666585000	-0.581041000
H	4.061722000	-4.180397000	0.325334000
C	1.309766000	-4.289930000	0.180911000
H	1.622765000	-4.851225000	1.066323000
H	0.269208000	-3.985372000	0.307360000
H	1.371540000	-4.956468000	-0.683780000
C	0.849123000	-1.941606000	1.830628000
H	0.864484000	-1.077272000	2.499970000
H	0.053087000	-1.789491000	1.094160000
H	0.625000000	-2.833358000	2.421393000
C	3.319110000	-2.219212000	2.152715000
H	4.302393000	-2.141244000	1.685611000
H	3.238397000	-1.443585000	2.919612000
H	3.239305000	-3.192998000	2.644741000

Sum of electronic and zero-point Energies= -1955.693325

Sum of electronic and thermal Free Energies= -1955.753175

VII. References

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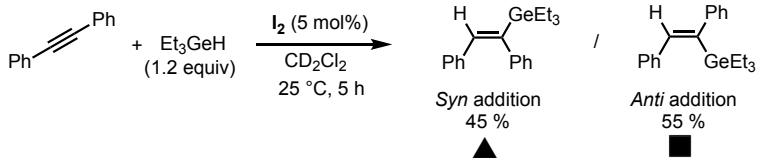
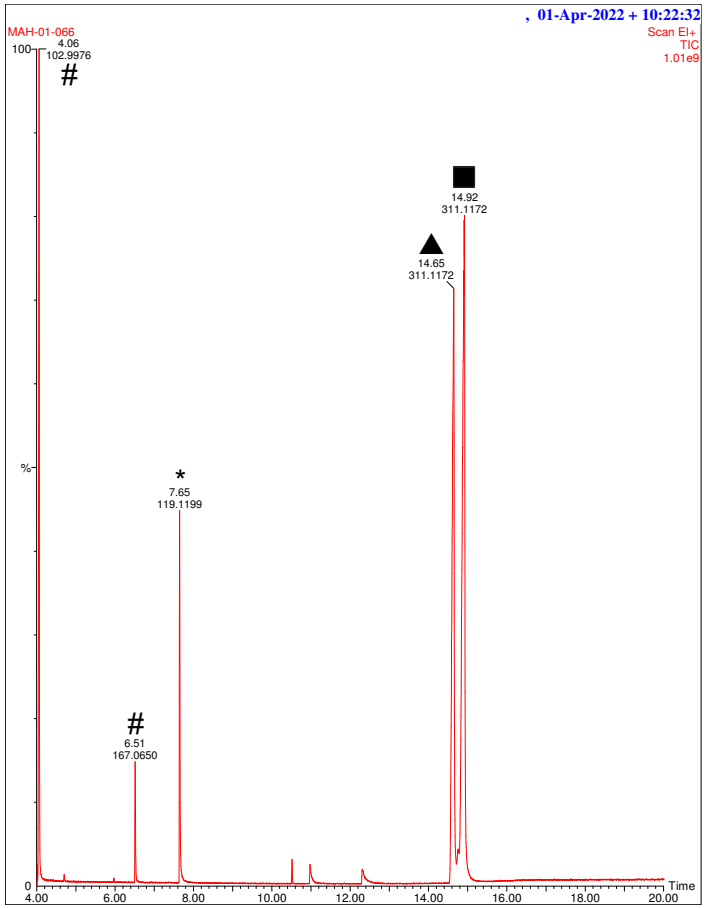
Chromatogram obtained for hydrogermylation of diphenylacetylene by GC/MS in DCM:

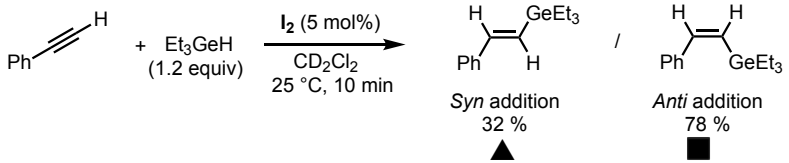


* 1,2,4,5-tetramethylbenzene = internal standard of the reaction

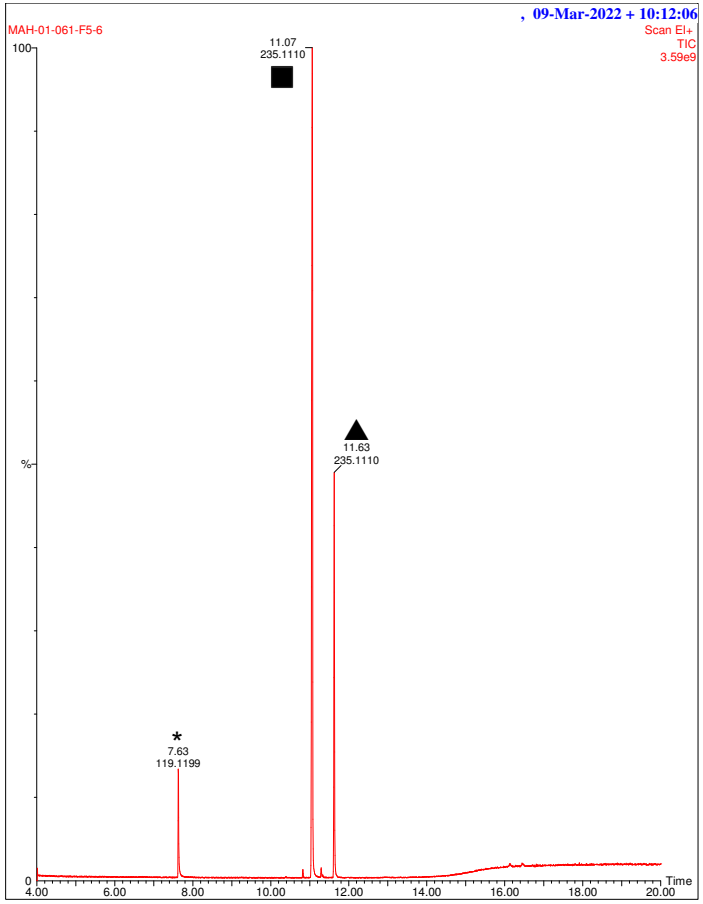
Products from decomposition of Et_3GeH



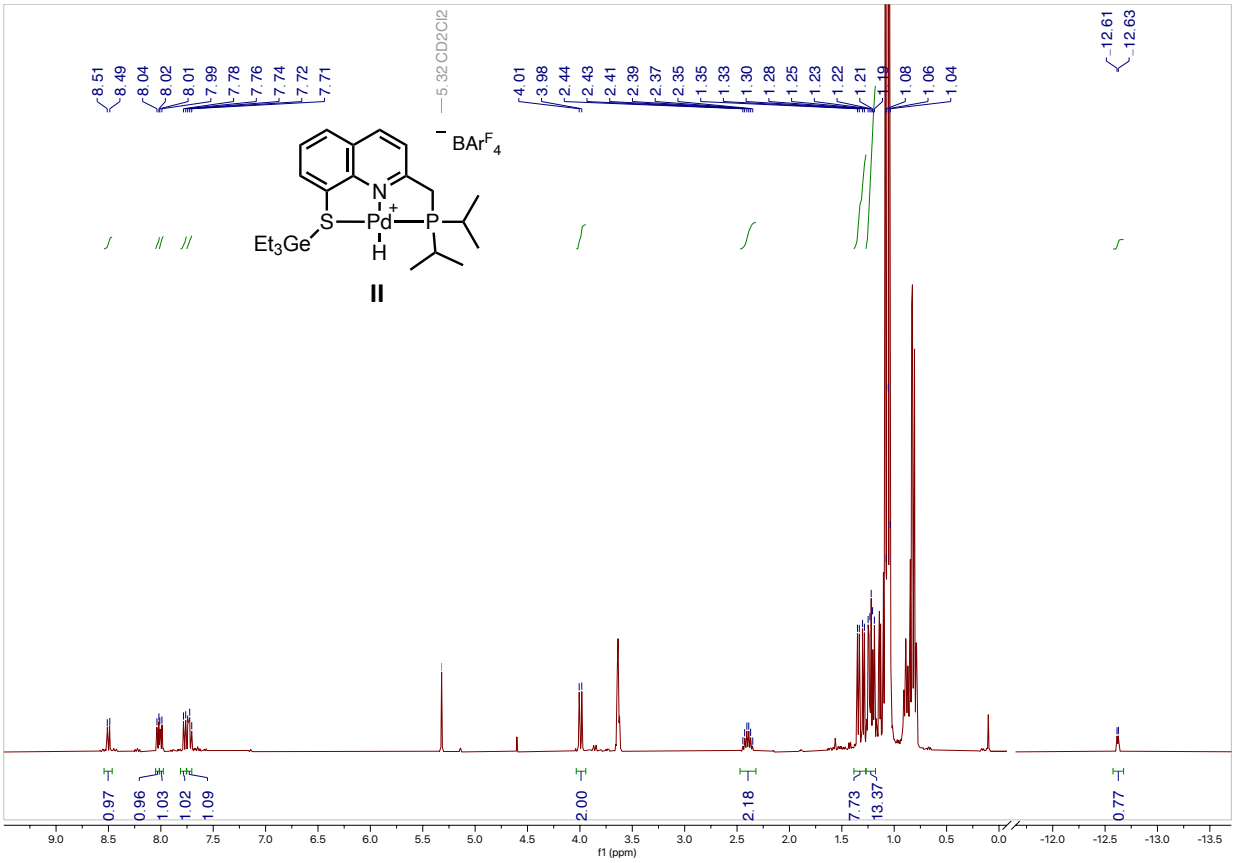
Chromatogram obtained after purification for hydrogermylation of phenylacetylene by GC/MS in DCM:



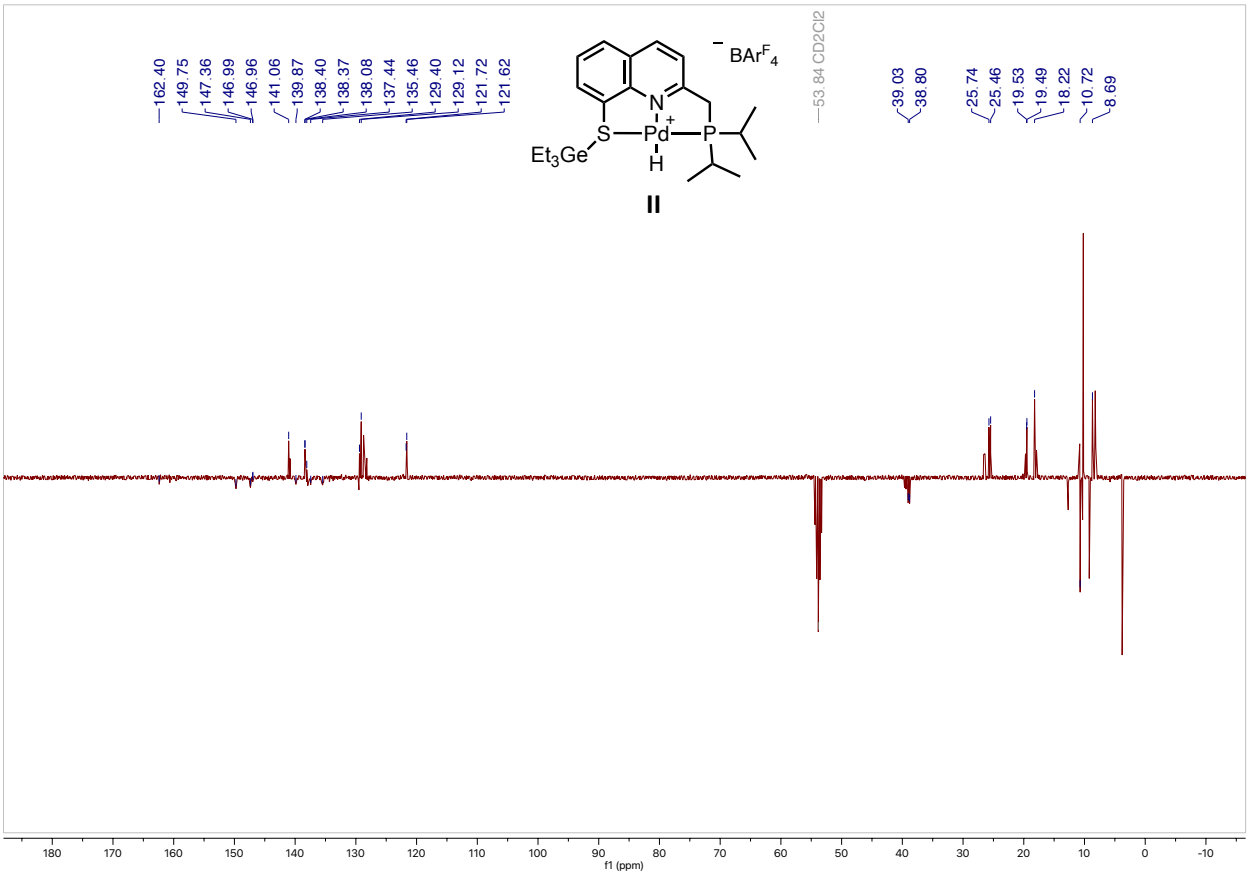
* 1,2,4,5-tetramethylbenzene = internal standard of the reaction



^{1}H NMR (500 MHz, CD_2Cl_2):



^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2):



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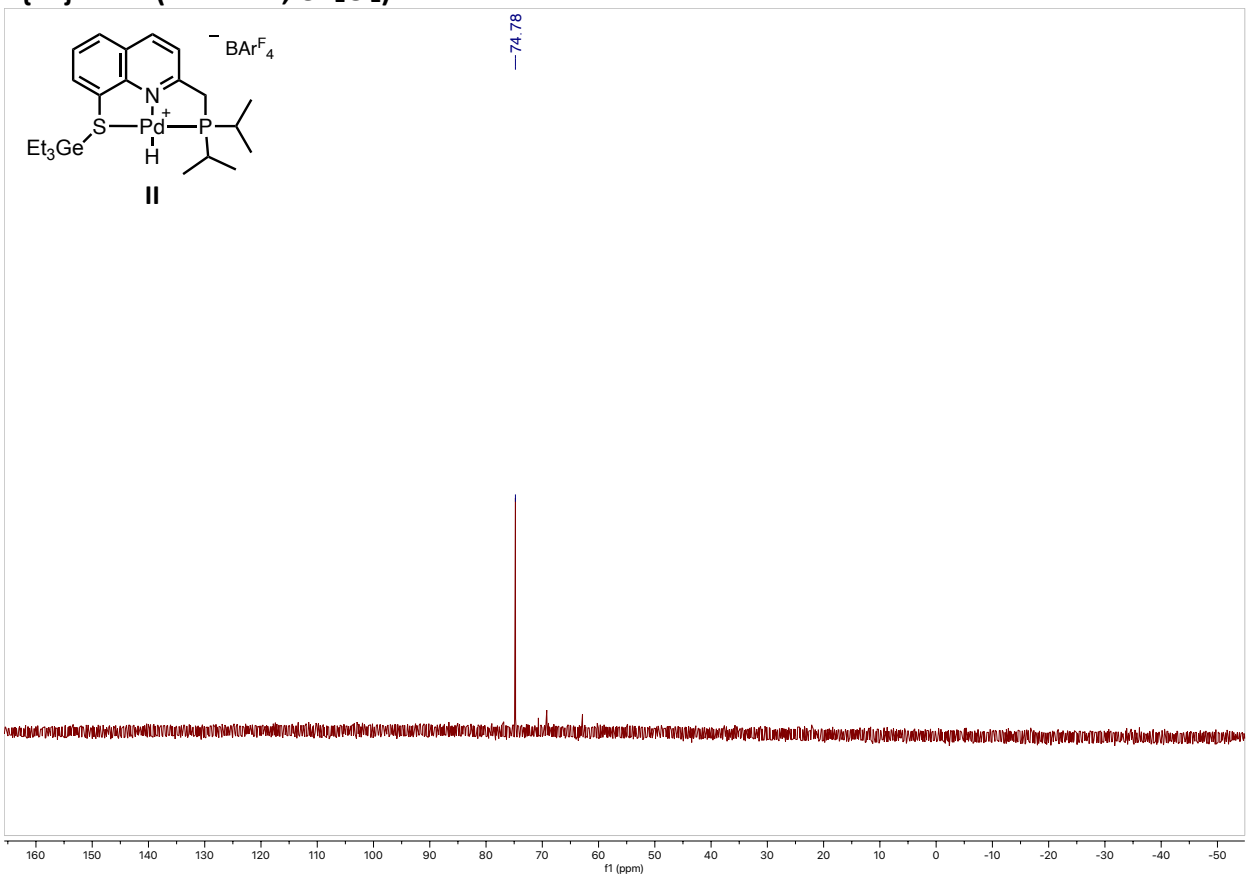
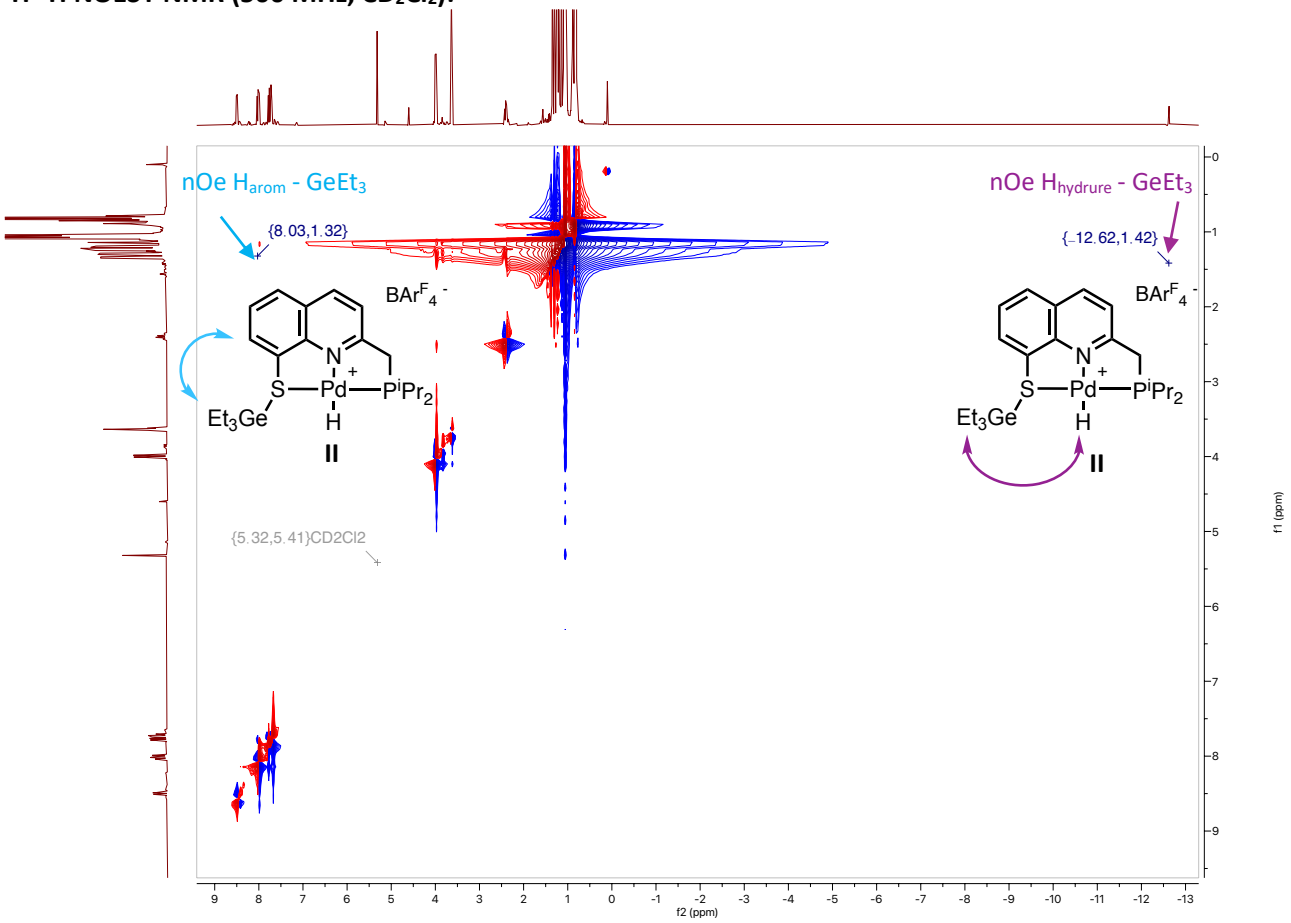
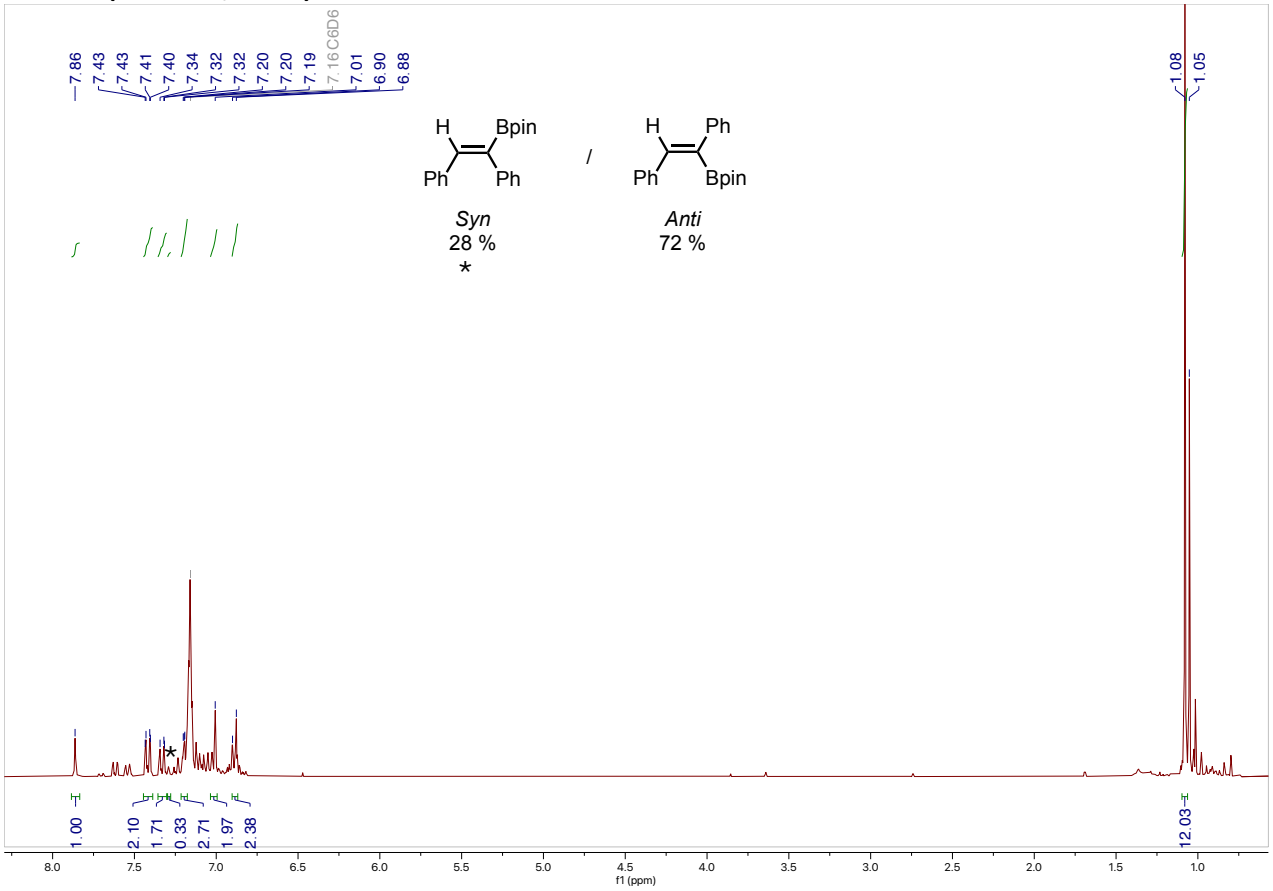


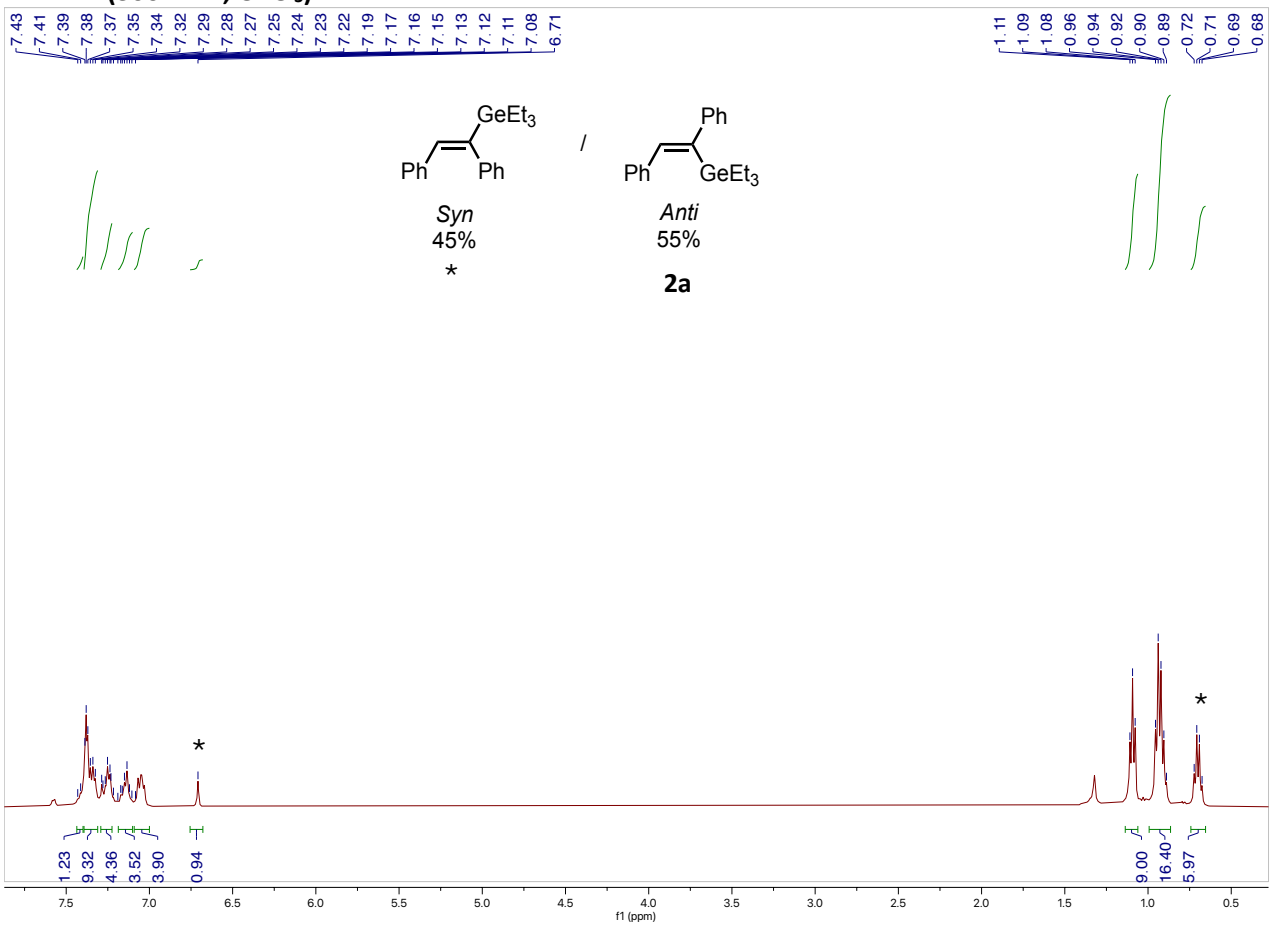
^{1}H-^{1}H NOESY NMR (500 MHz, CD_2Cl_2):



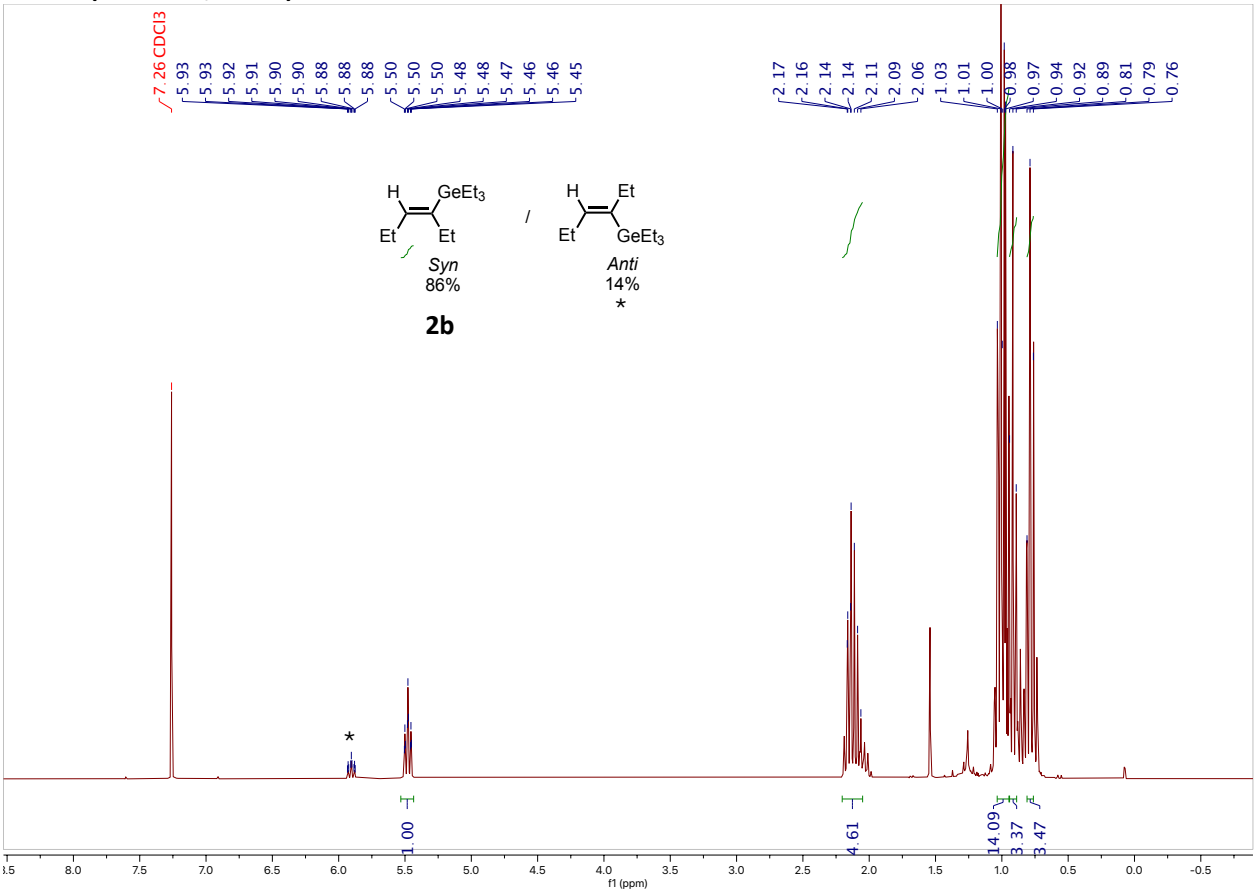
^{1}H NMR (300 MHz, $CDCl_3$):



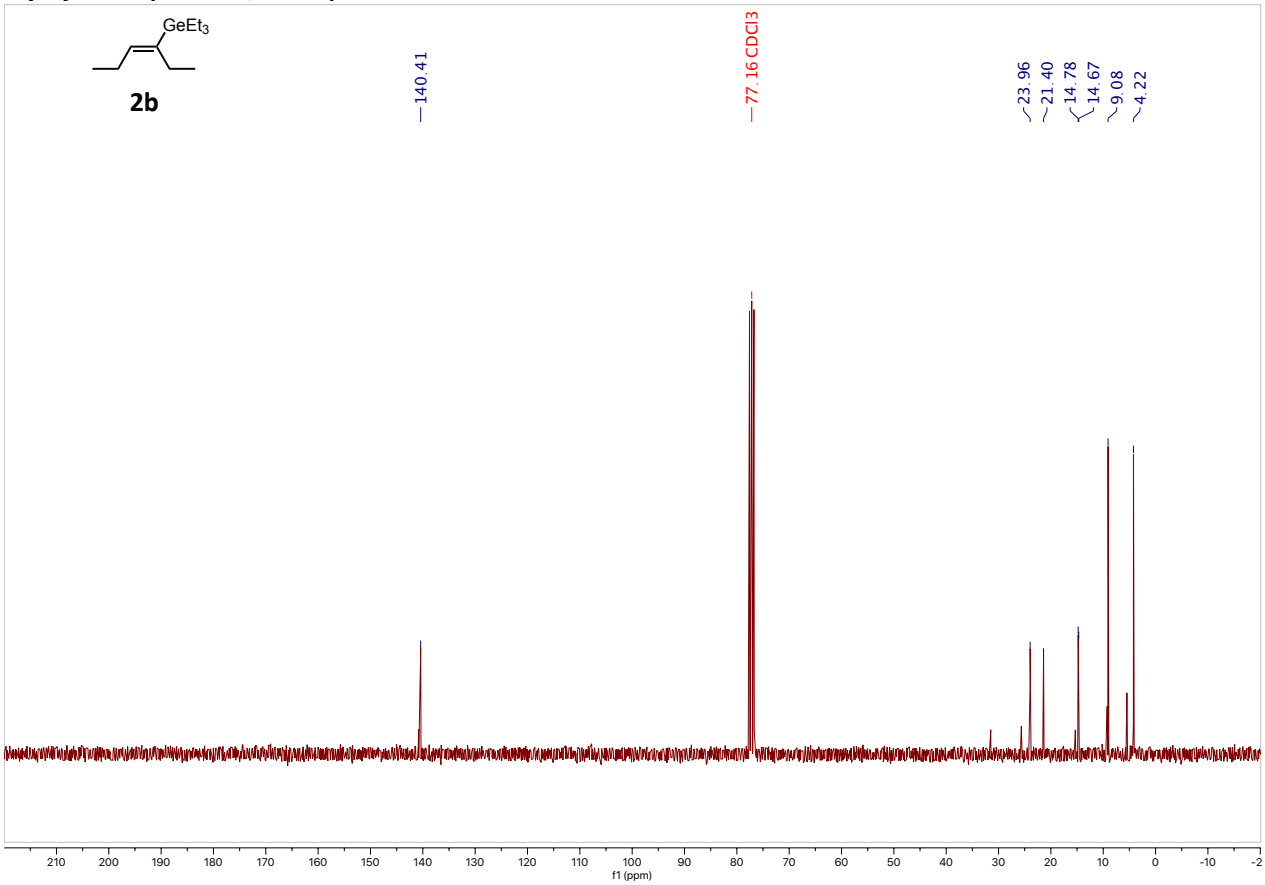
^{1}H NMR (300 MHz, $CDCl_3$):



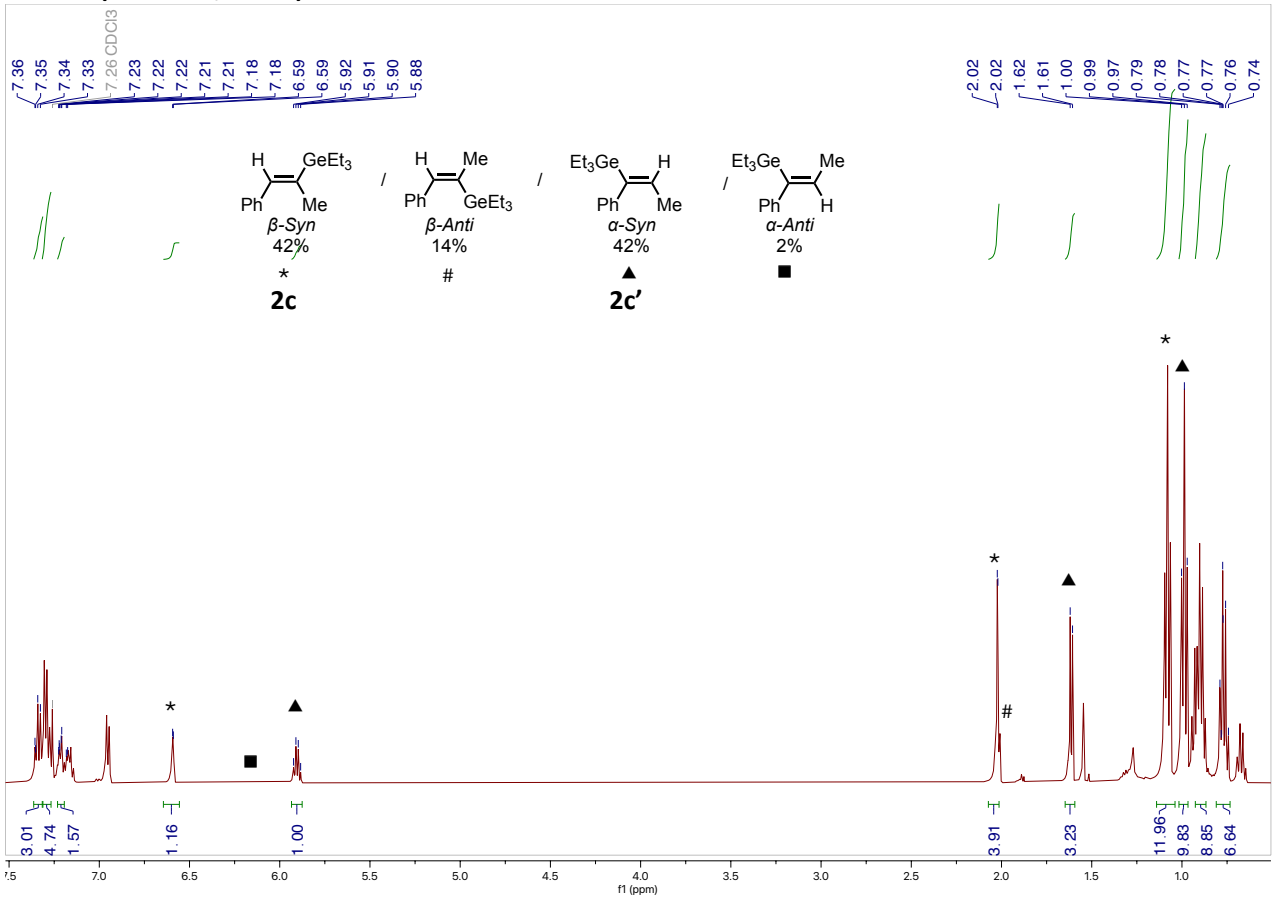
^{1}H NMR (300 MHz, $CDCl_3$):



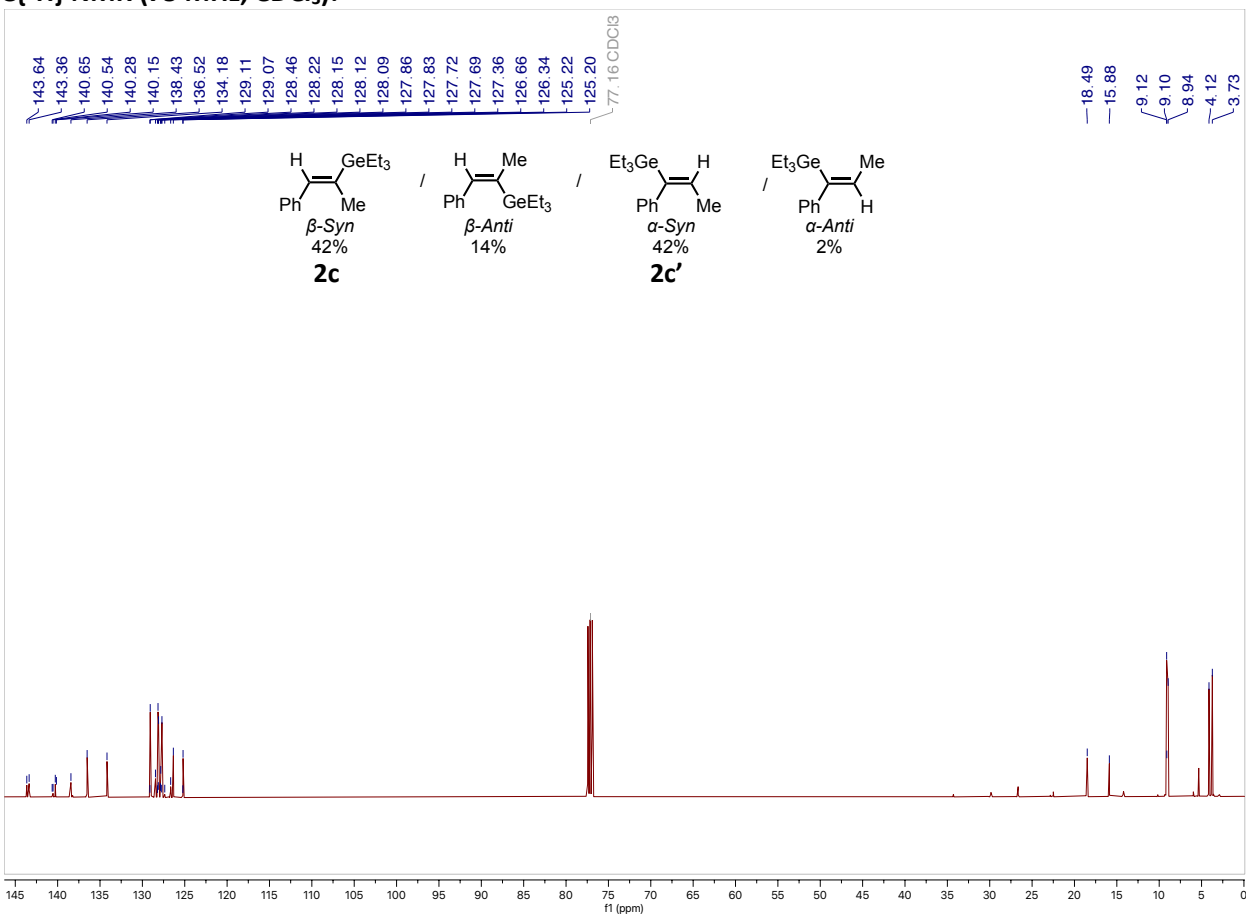
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):



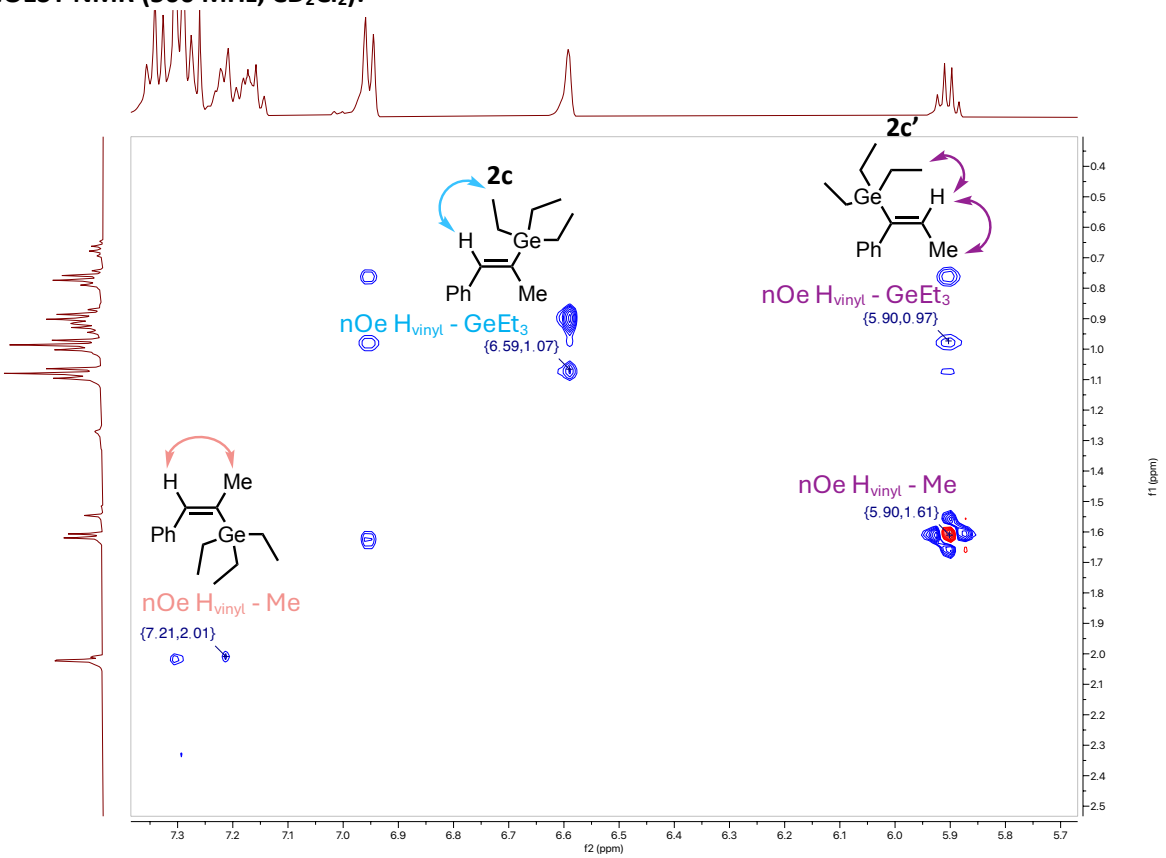
^{1}H NMR (300 MHz, $CDCl_3$):



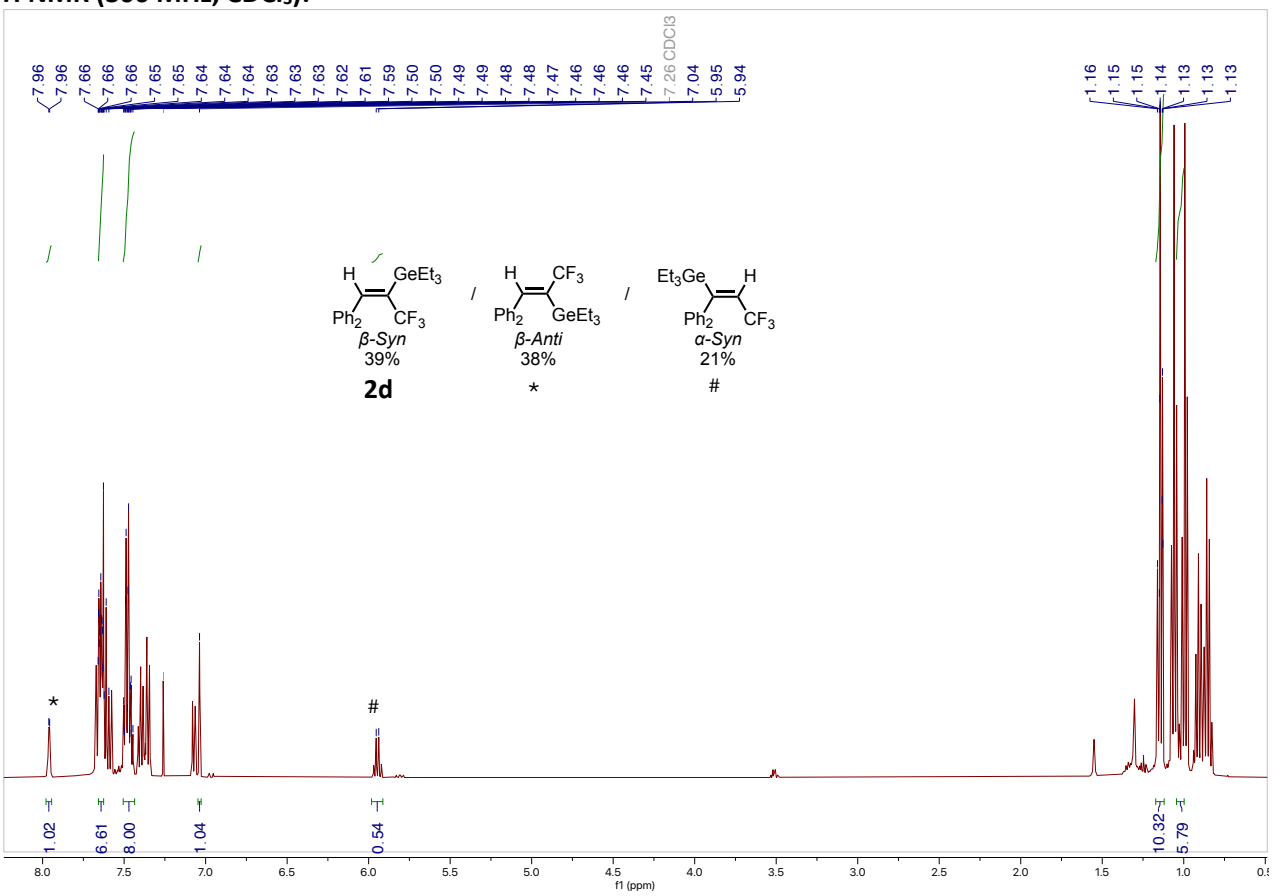
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):



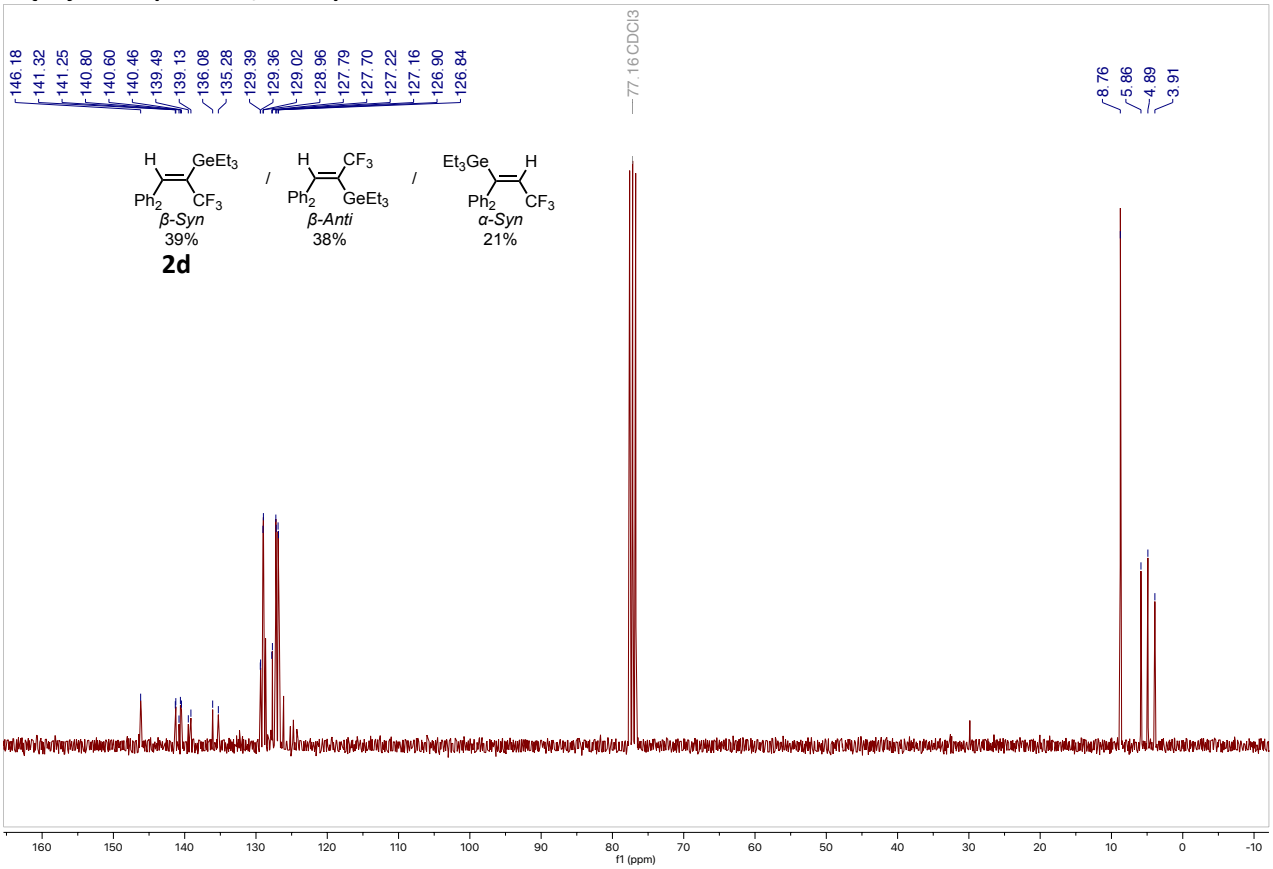
^{1}H-^{1}H NOESY NMR (500 MHz, CD_2Cl_2):



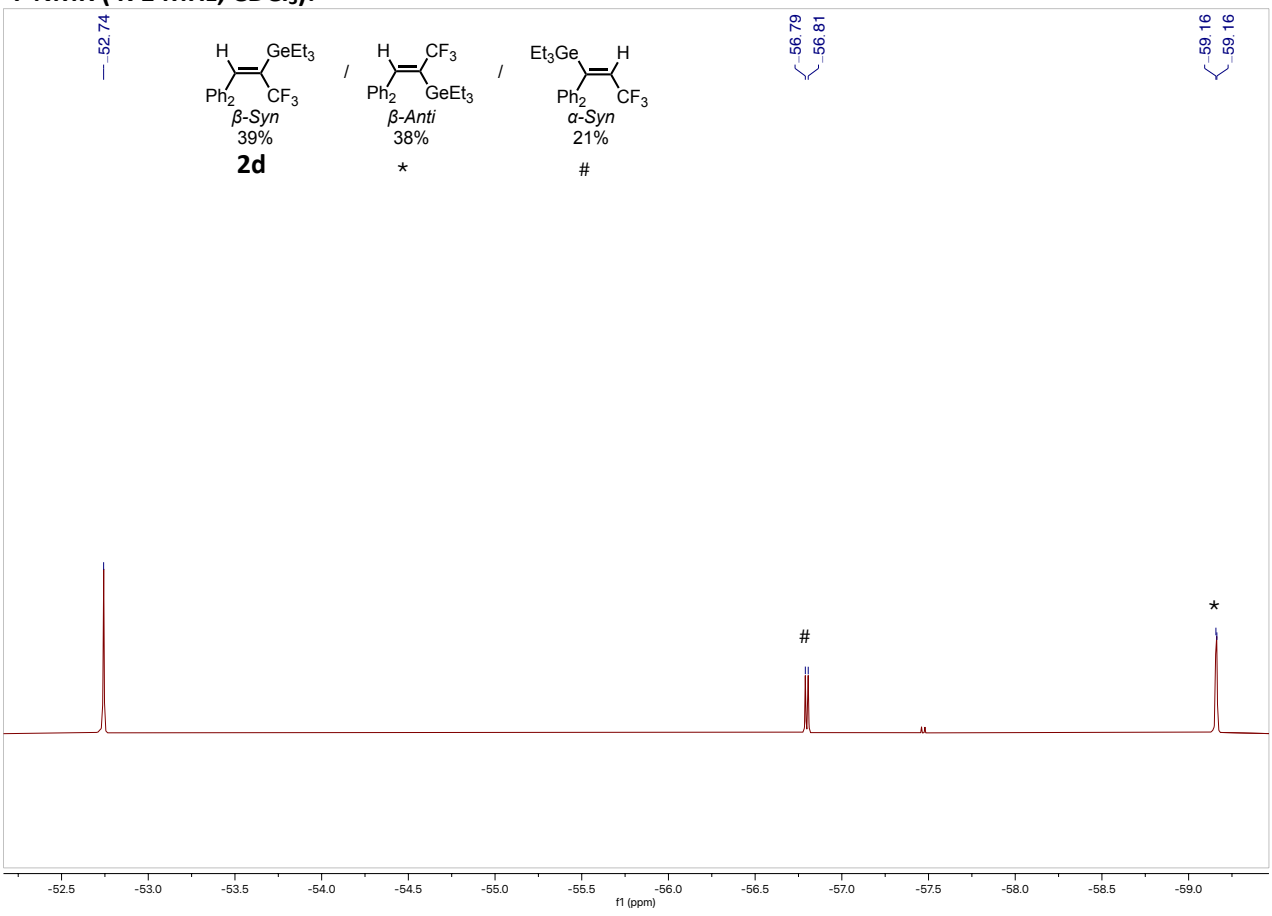
^{1}H NMR (300 MHz, $CDCl_3$):



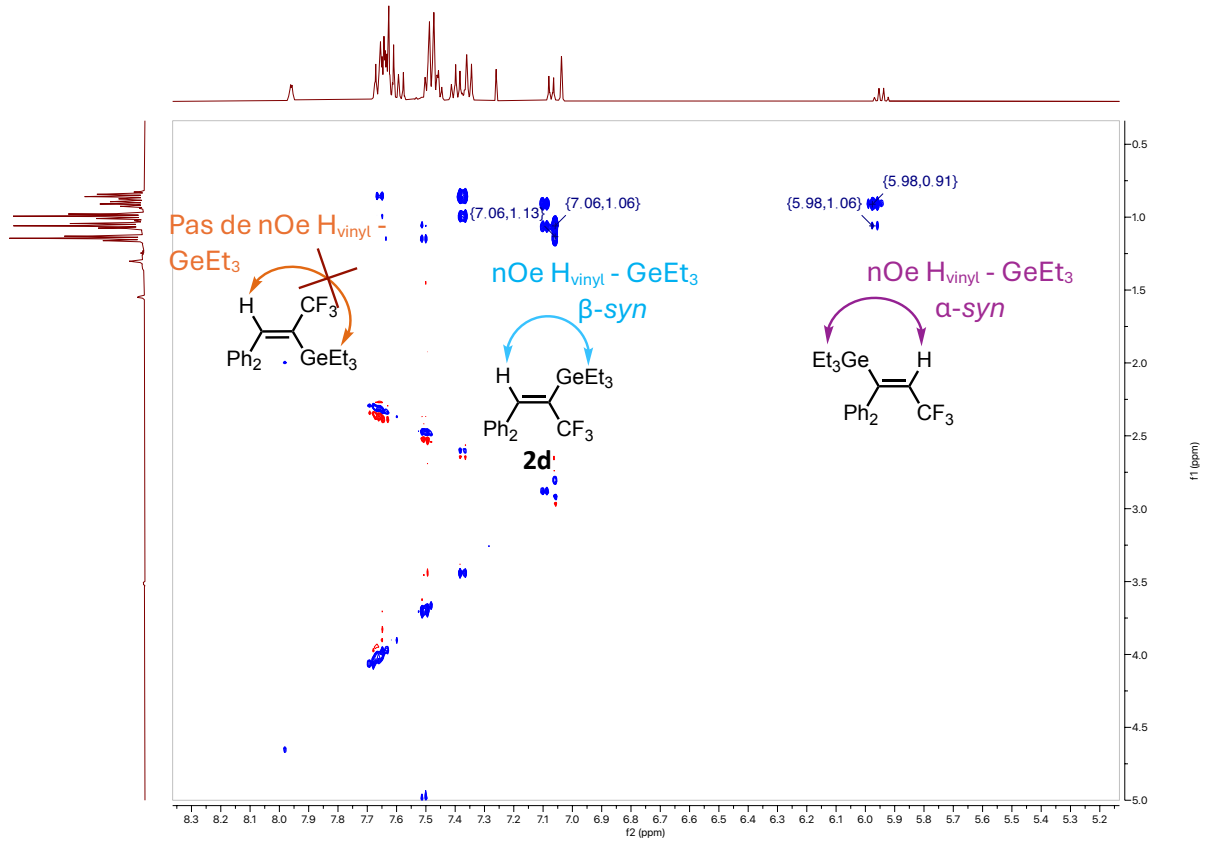
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):



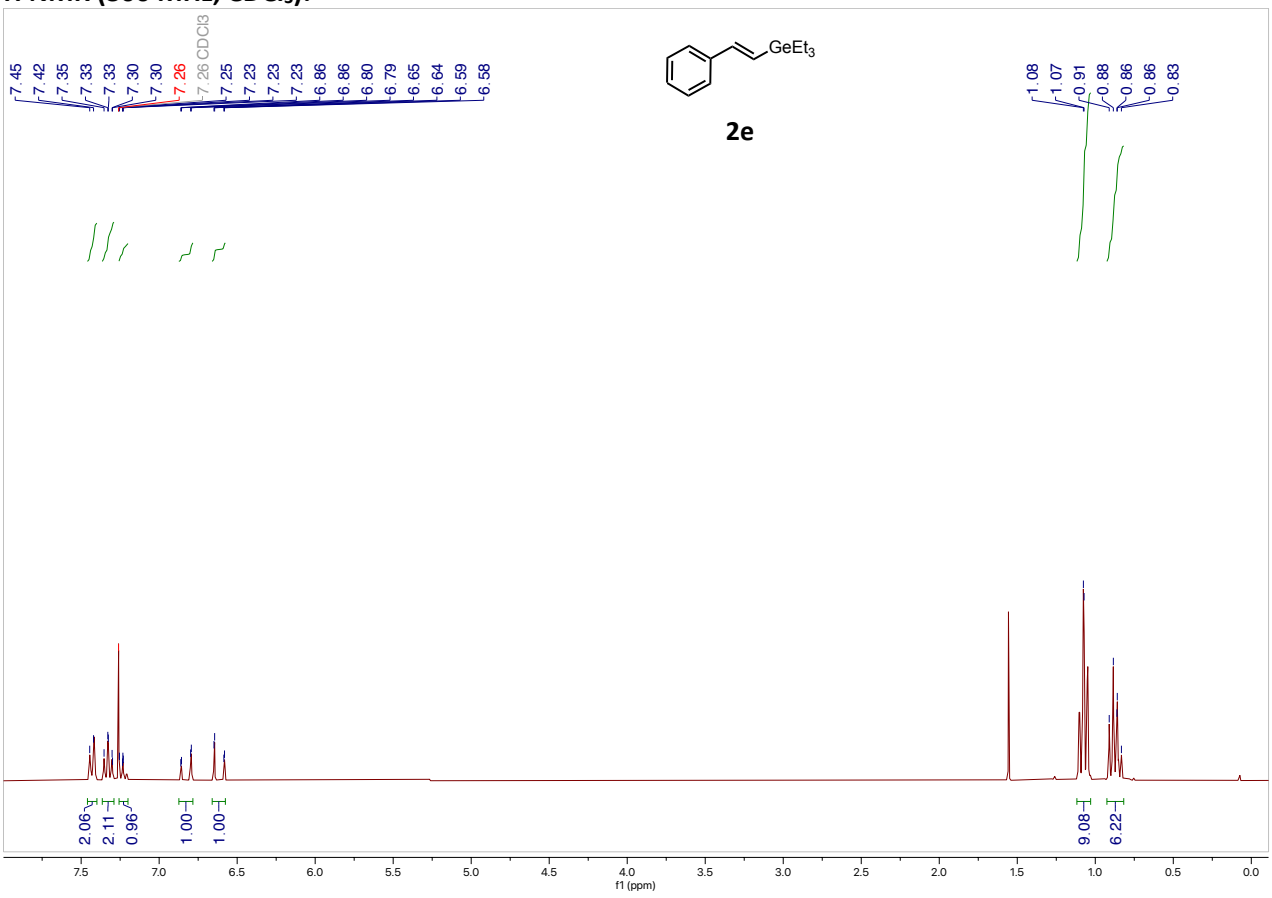
^{19}F NMR (471 MHz, $CDCl_3$):



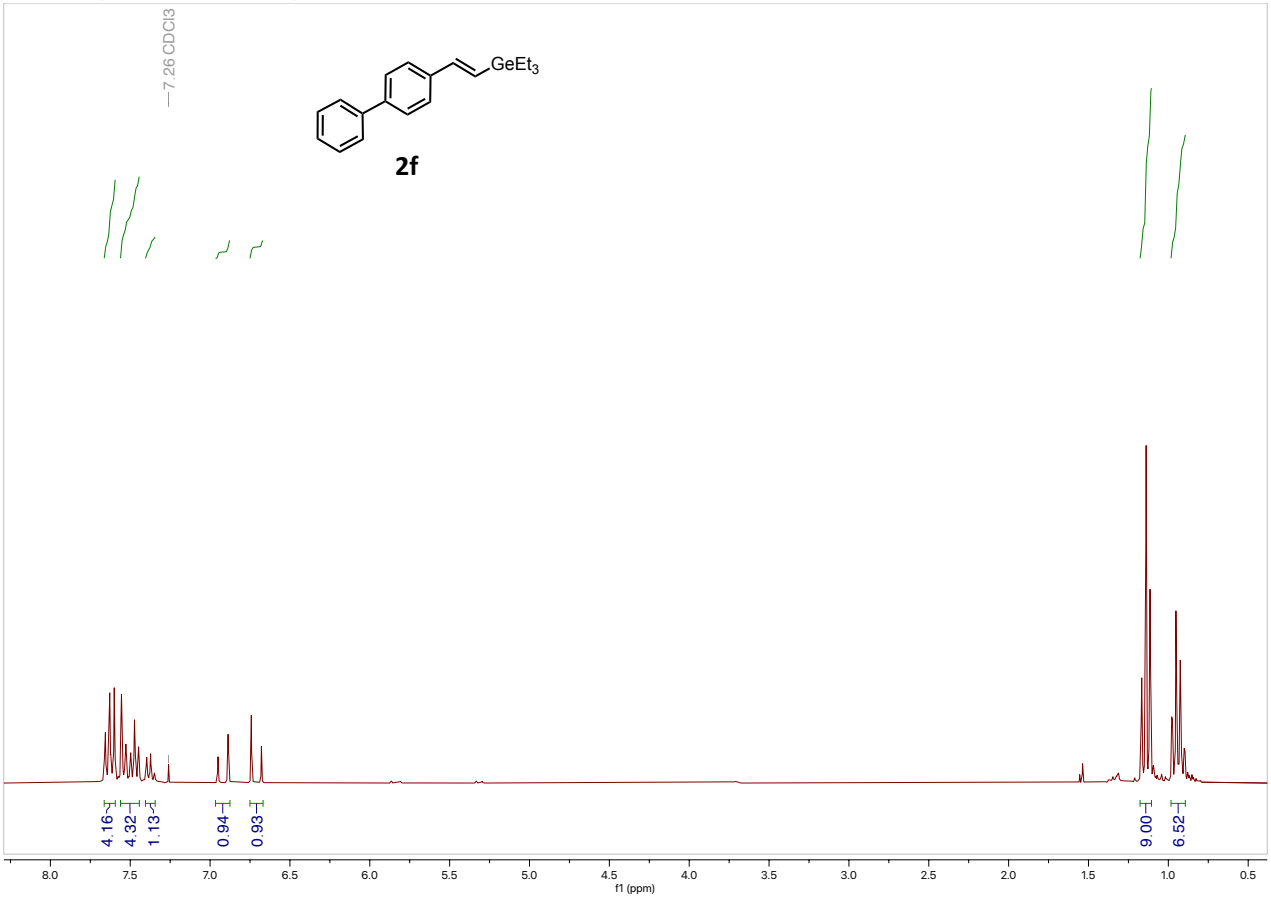
^{1}H-^{1}H NOESY NMR (500 MHz, CD_2Cl_2):



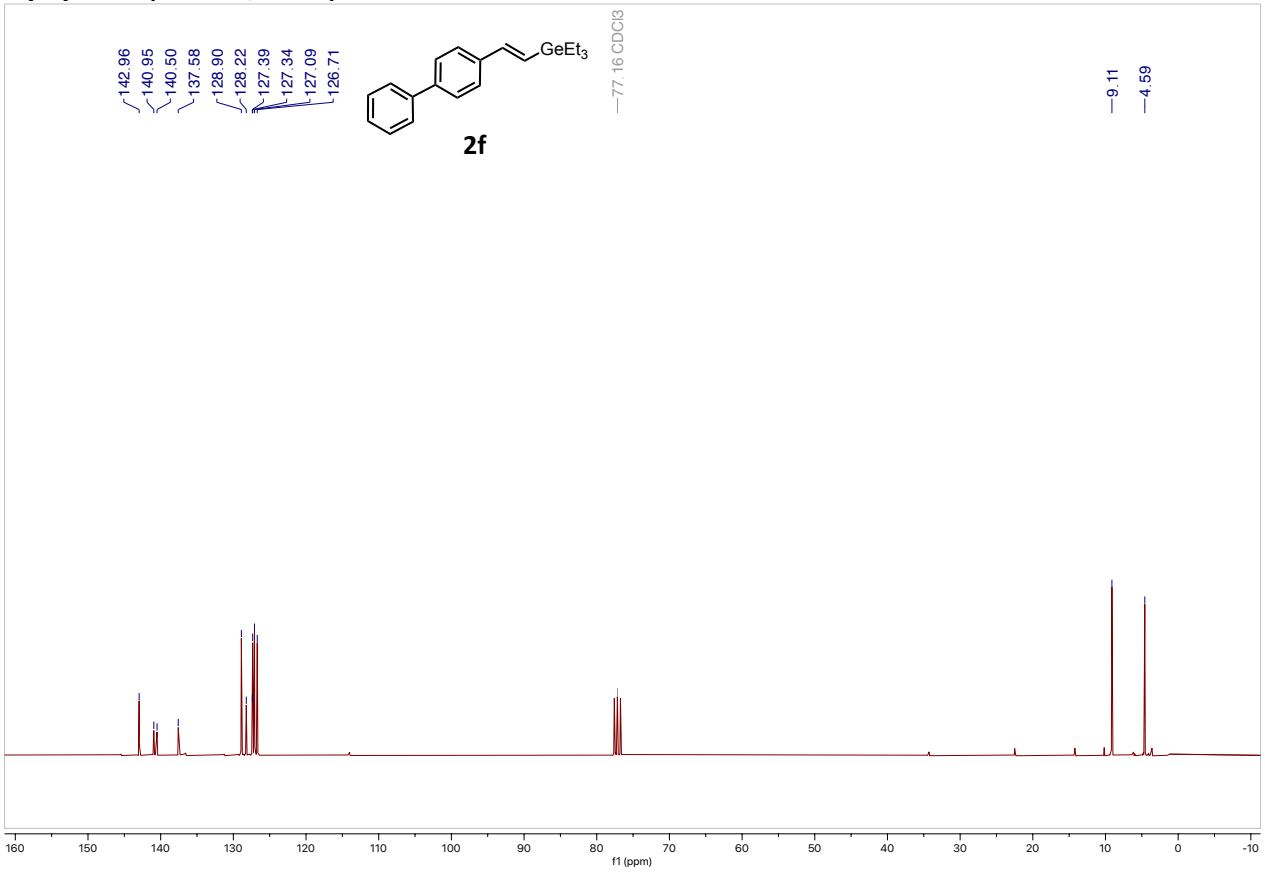
^{1}H NMR (300 MHz, $CDCl_3$):



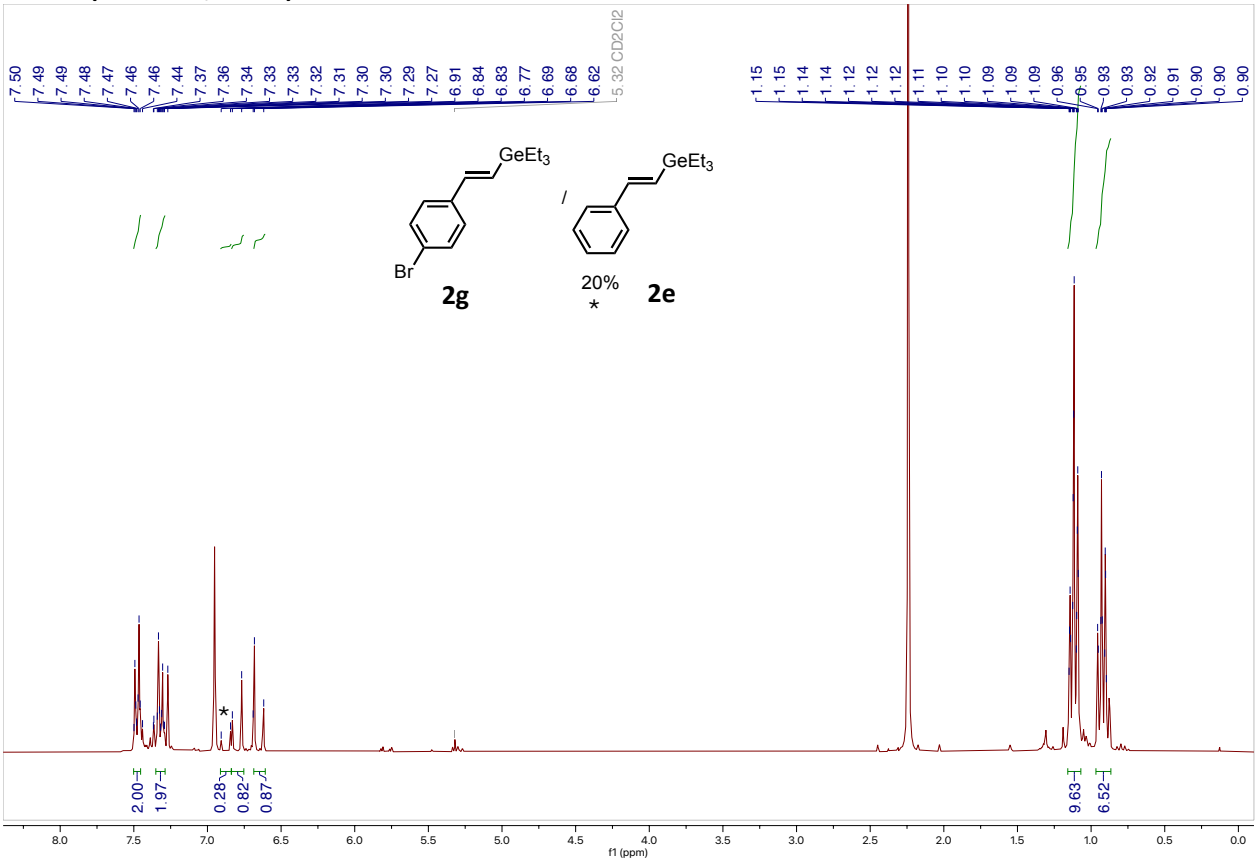
^{1}H NMR (300 MHz, $CDCl_3$):



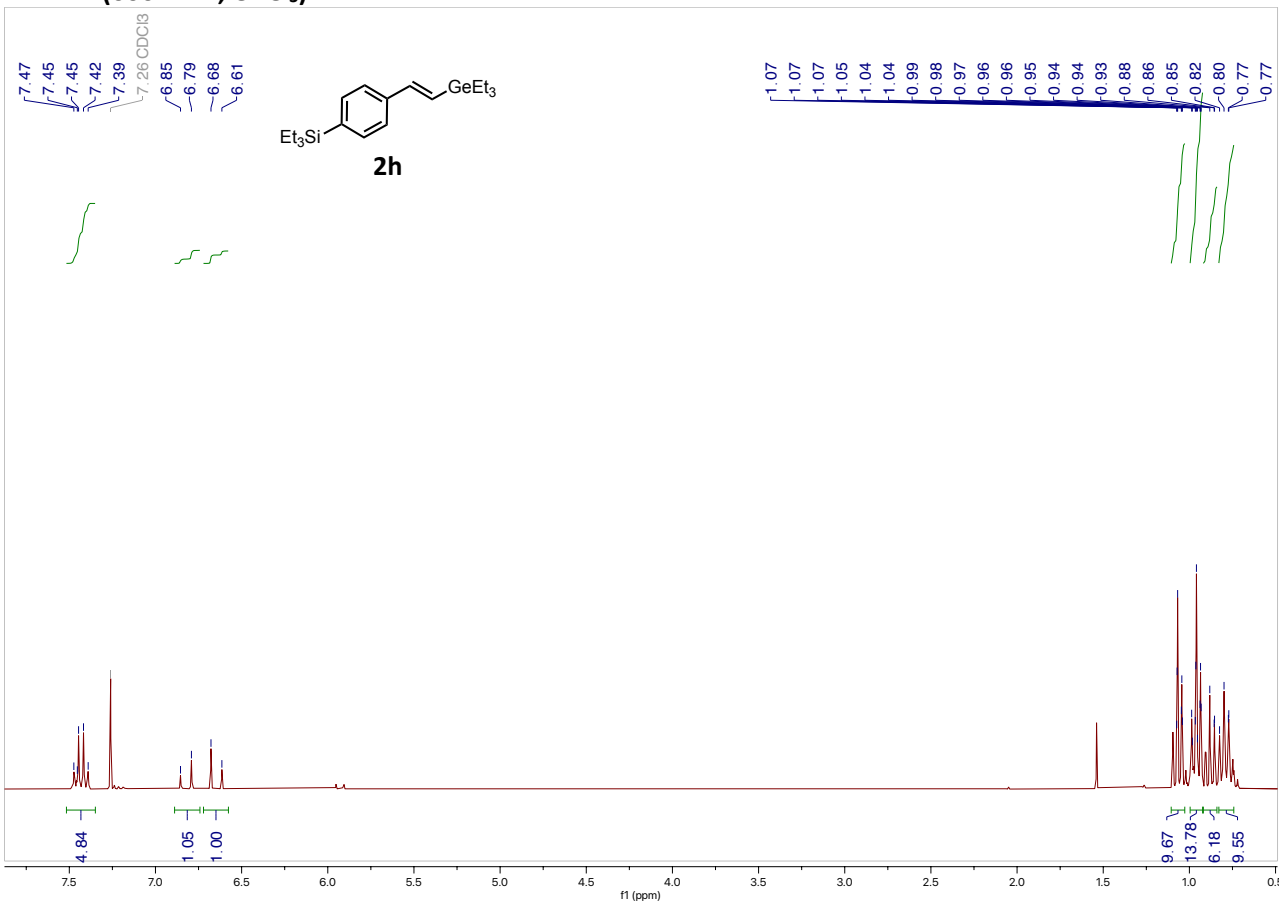
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):



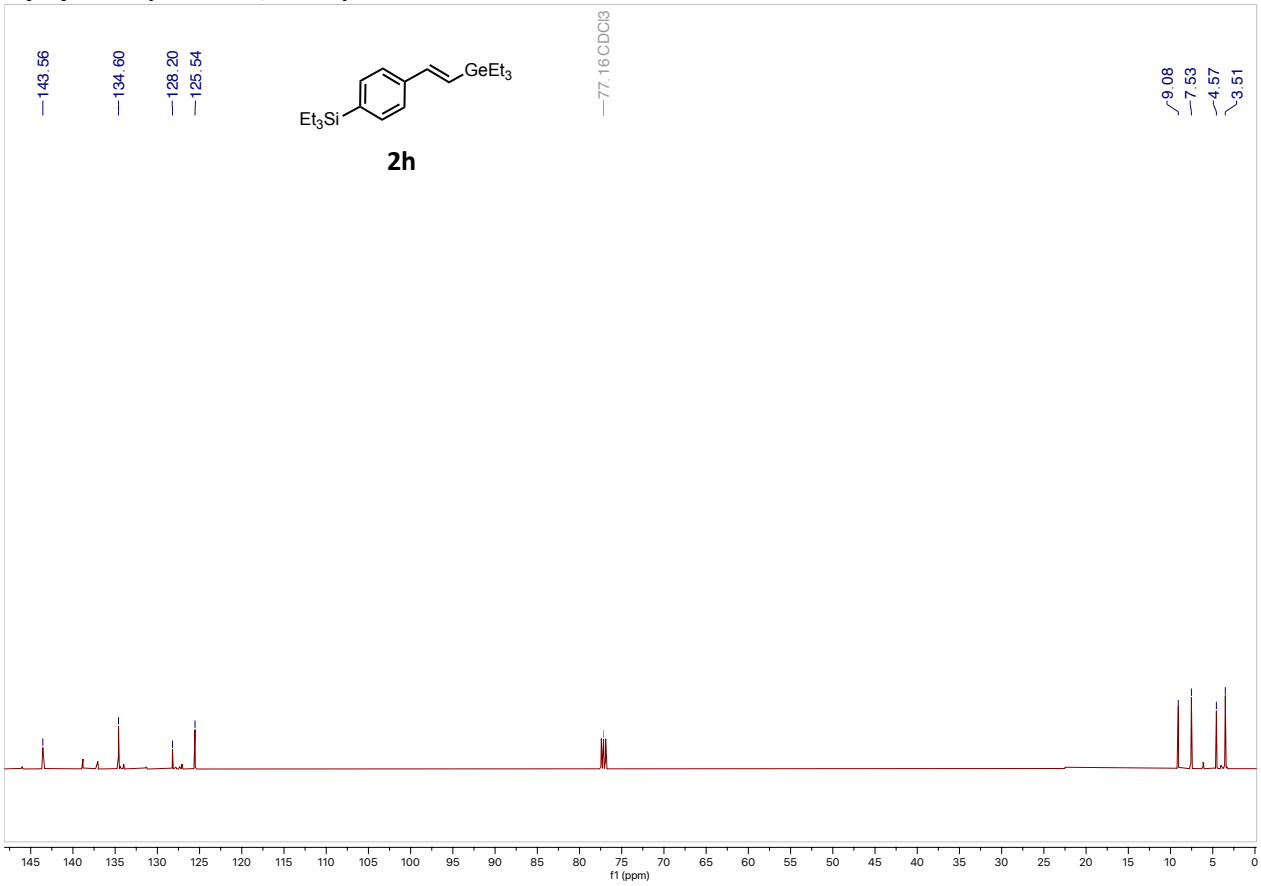
^{1}H NMR (300 MHz, $CDCl_3$):



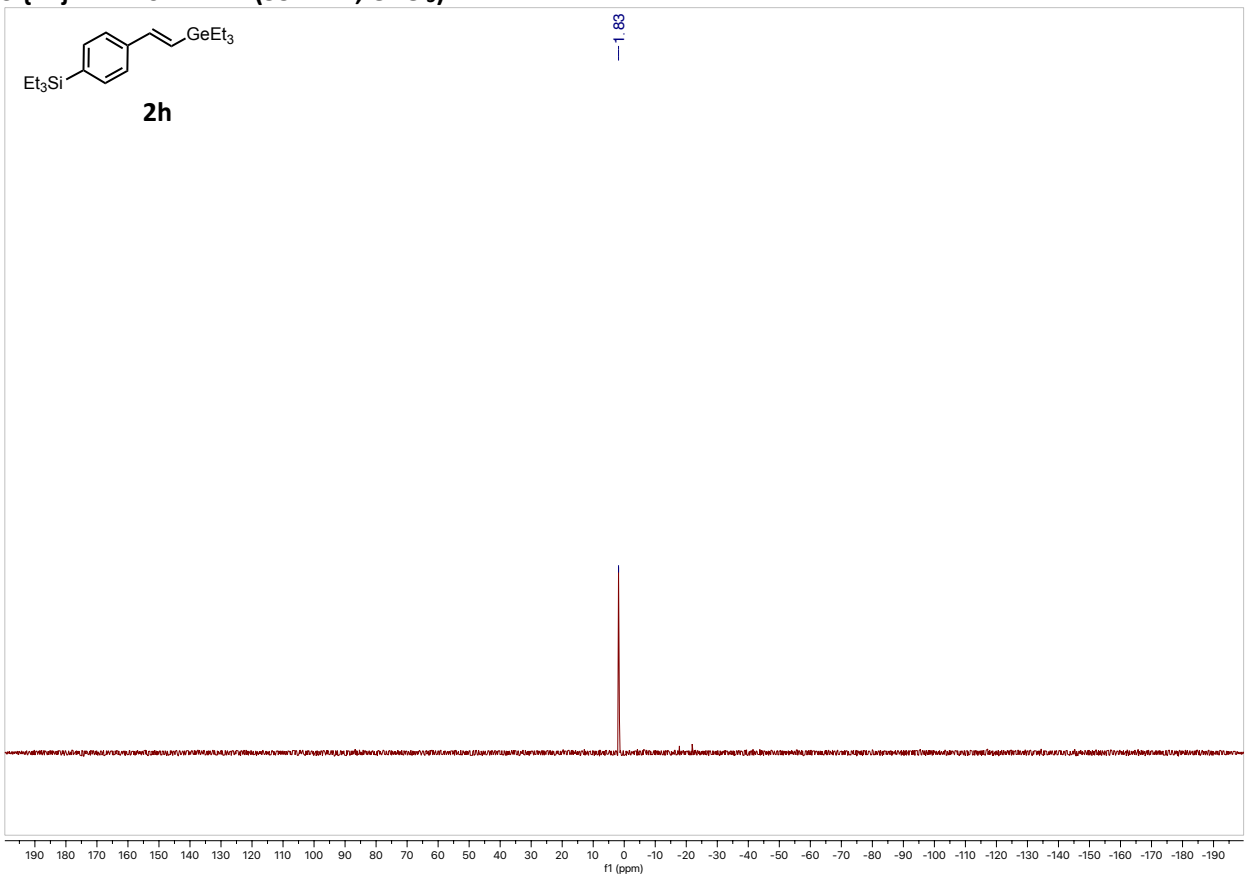
^{1}H NMR (600 MHz, $CDCl_3$):



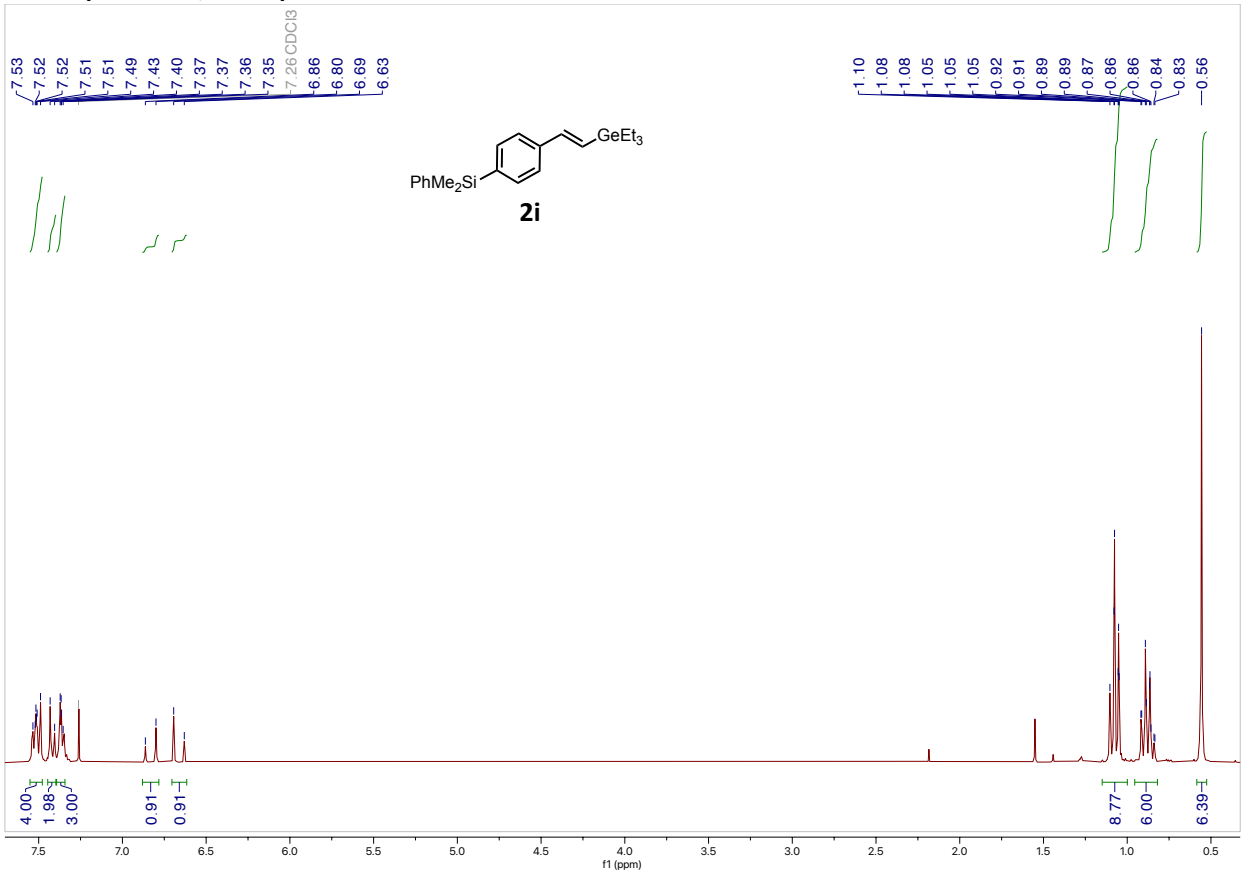
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):



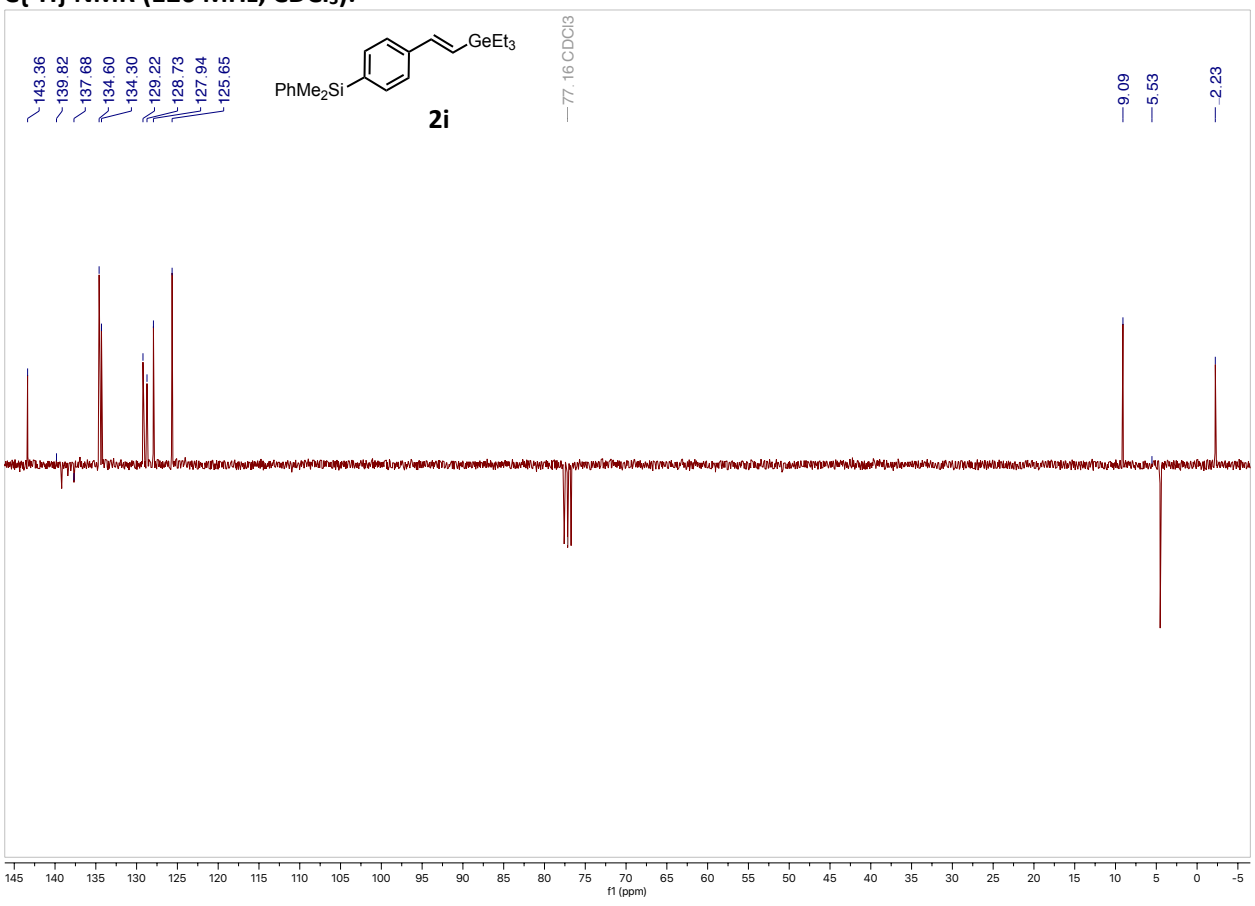
$^{29}Si\{^1H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$):



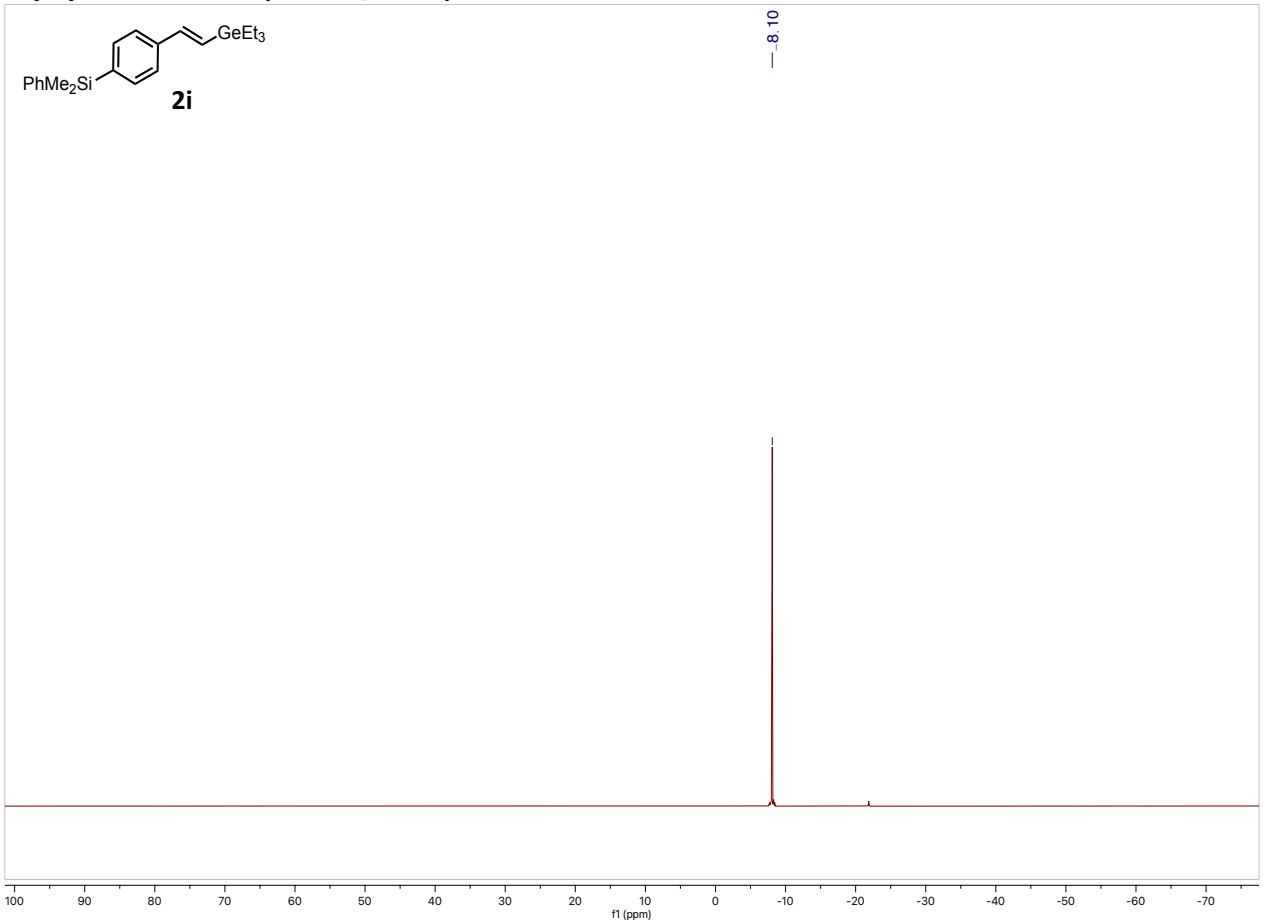
^{1}H NMR (300 MHz, $CDCl_3$):



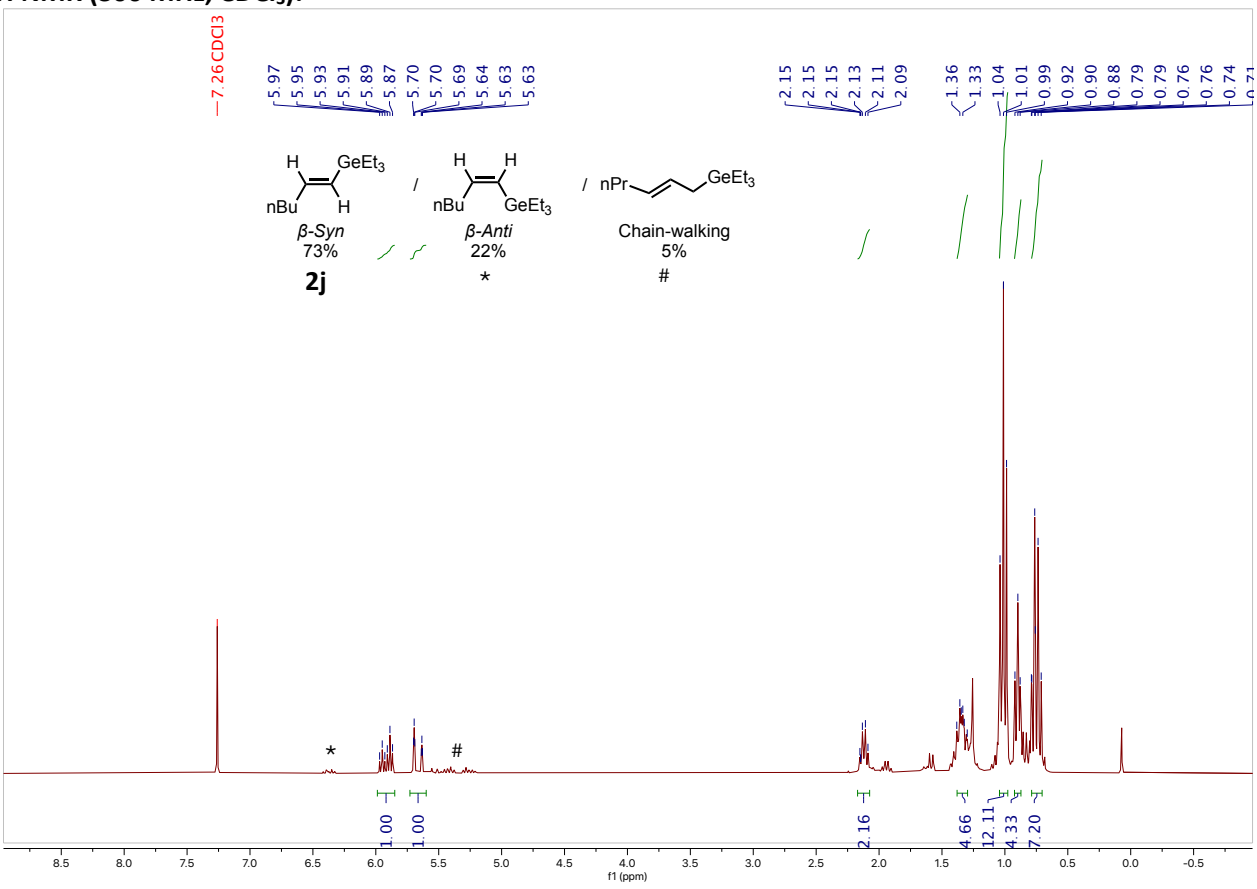
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):



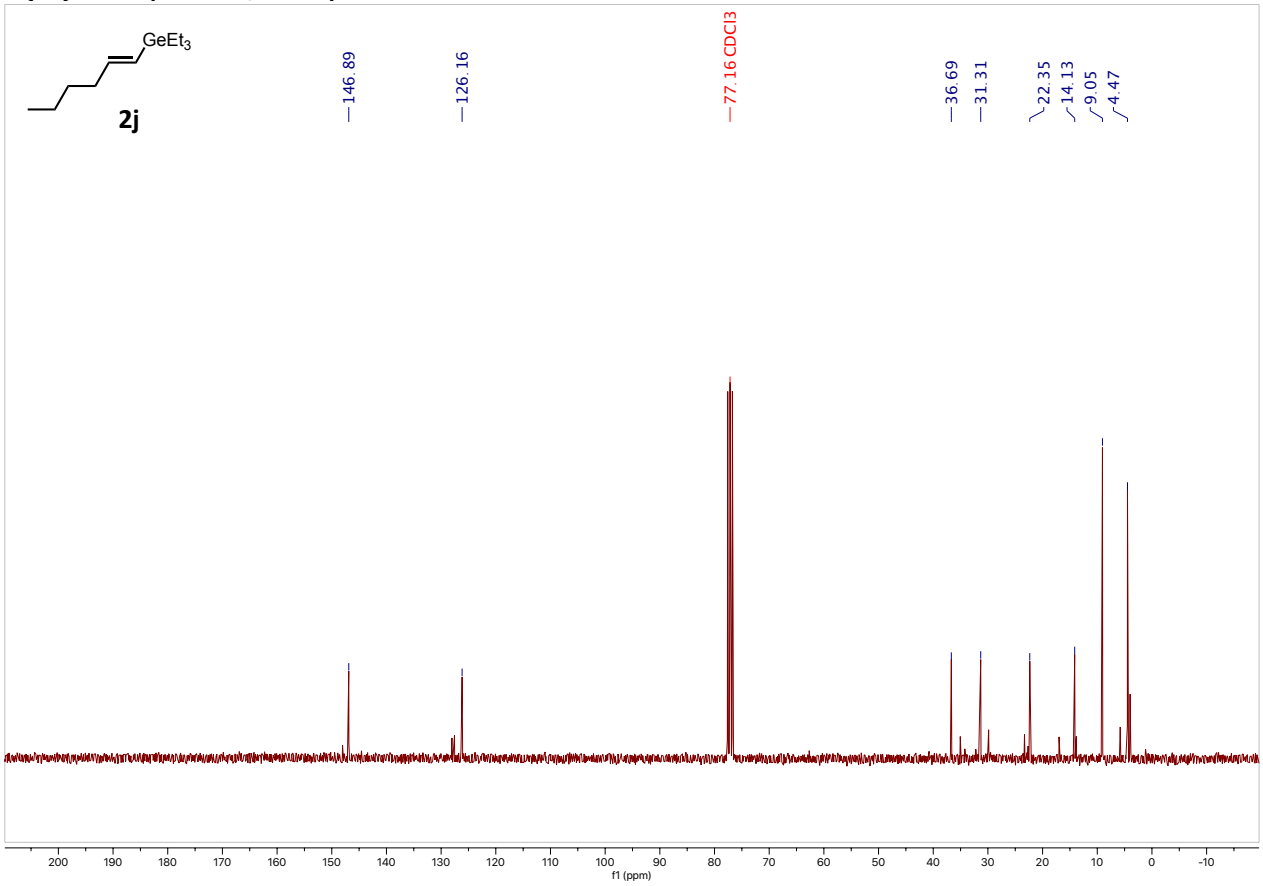
$^{29}Si\{^{1}H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$):



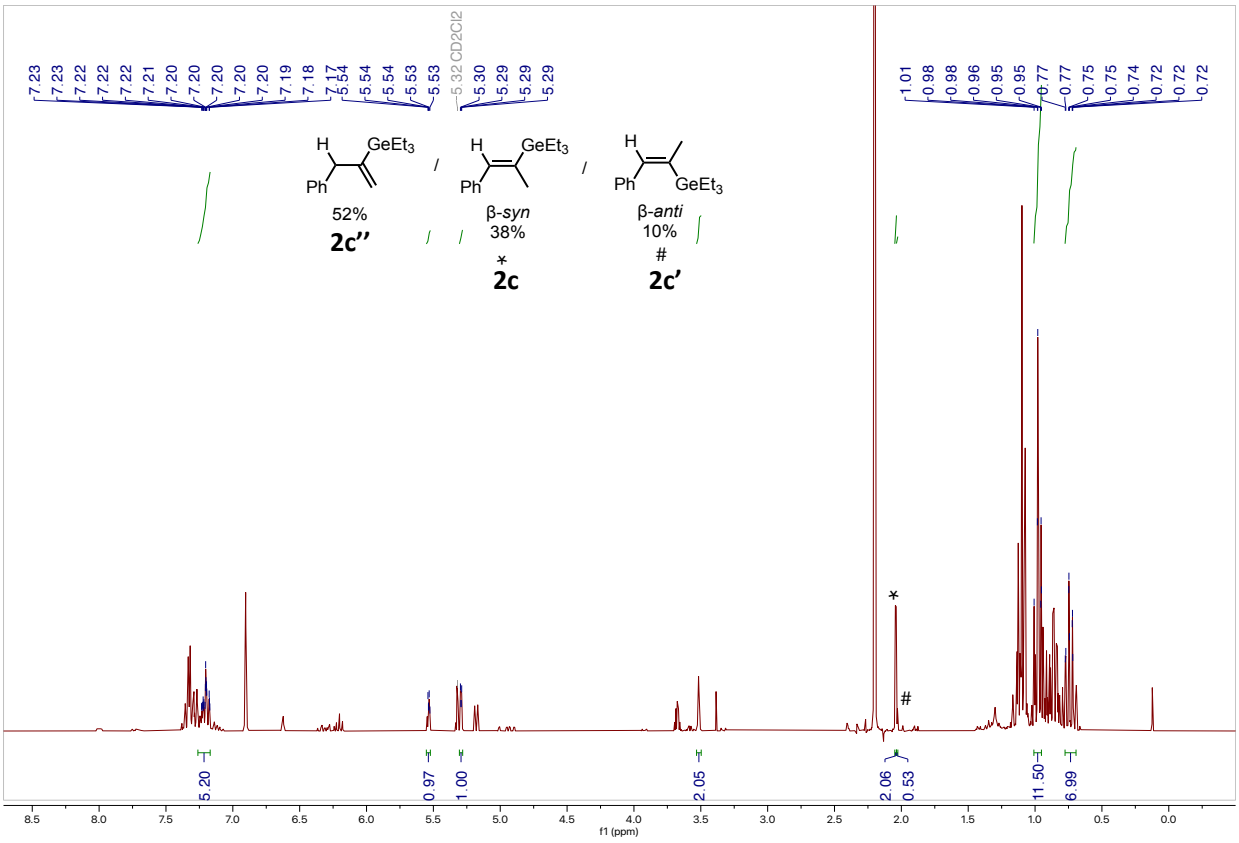
^{1}H NMR (300 MHz, $CDCl_3$):



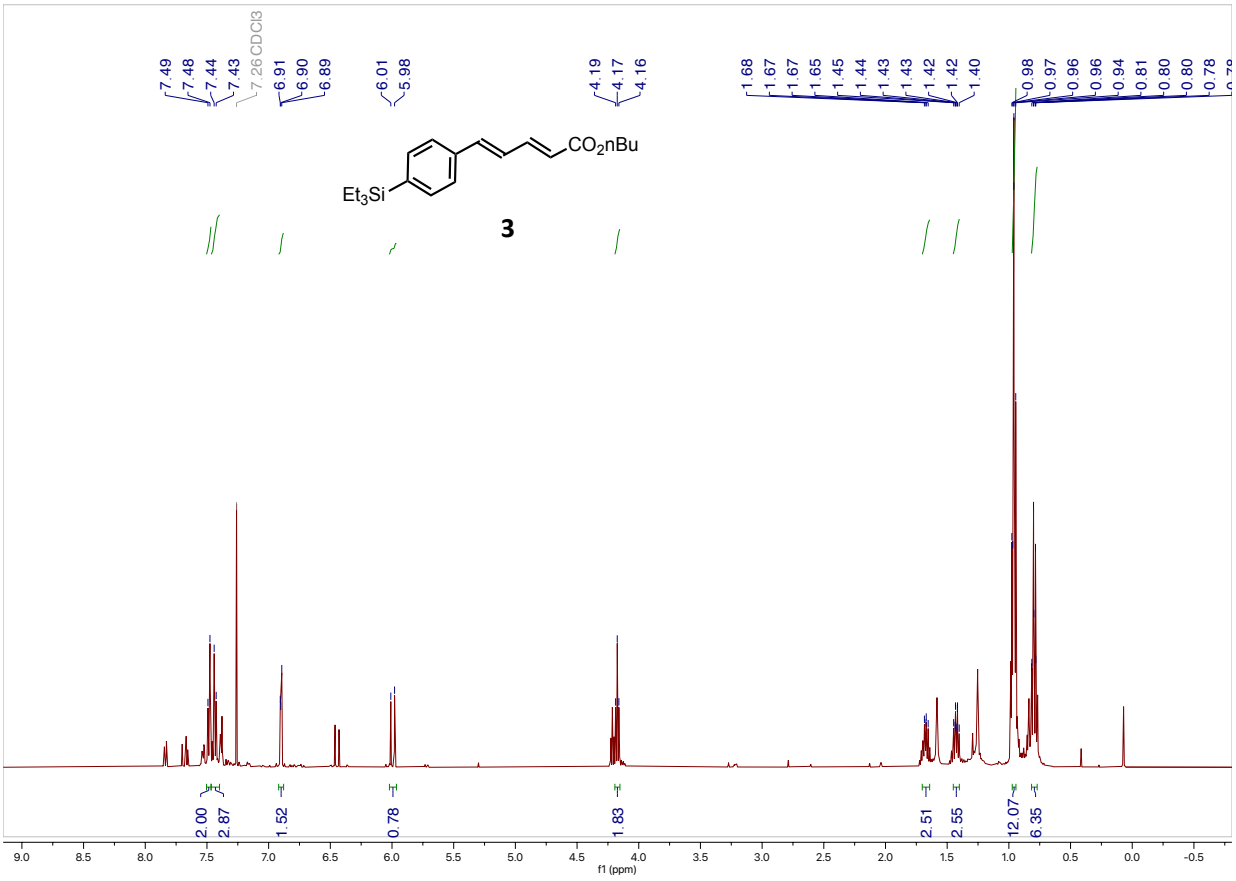
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):



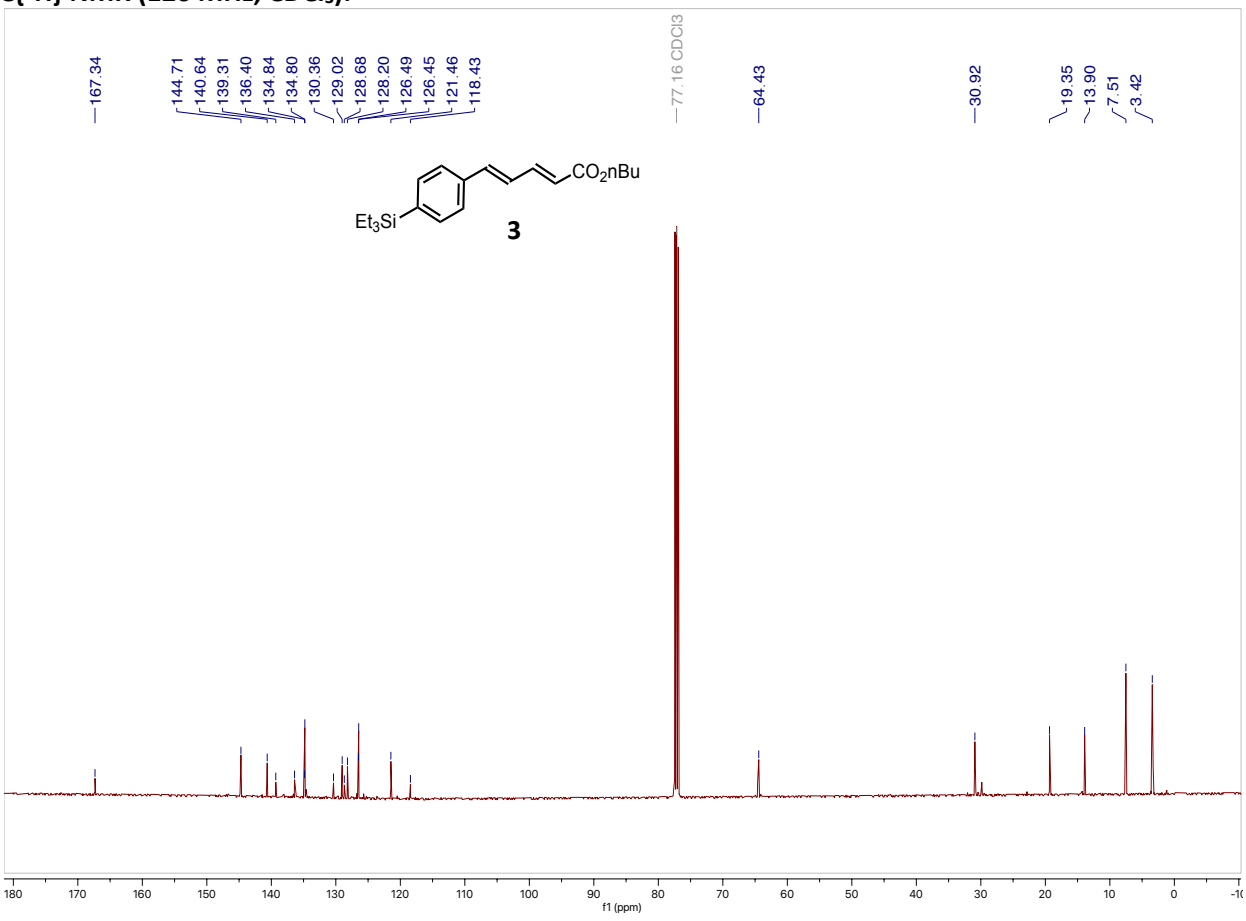
^{1}H NMR (300 MHz, CD_2Cl_2):



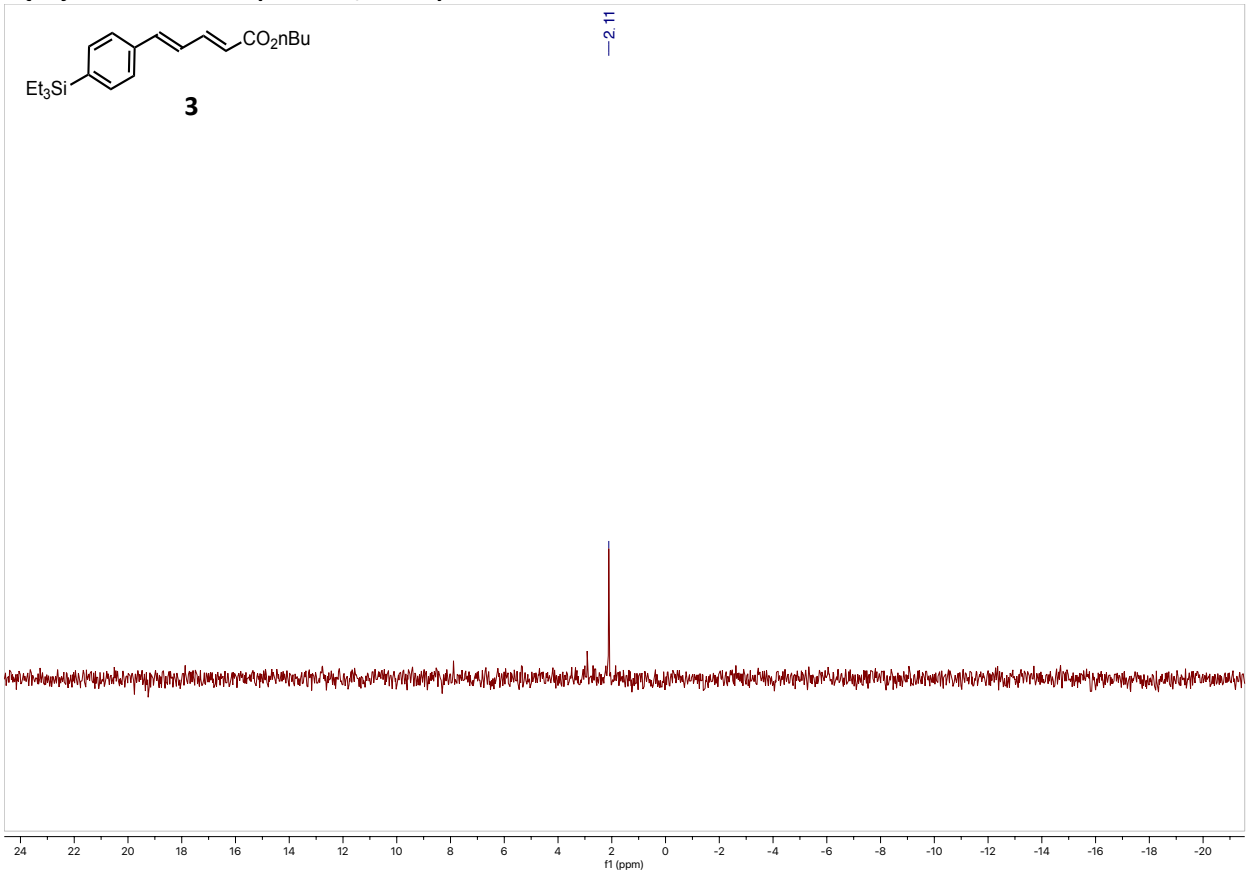
^{1}H NMR (500 MHz, $CDCl_3$):



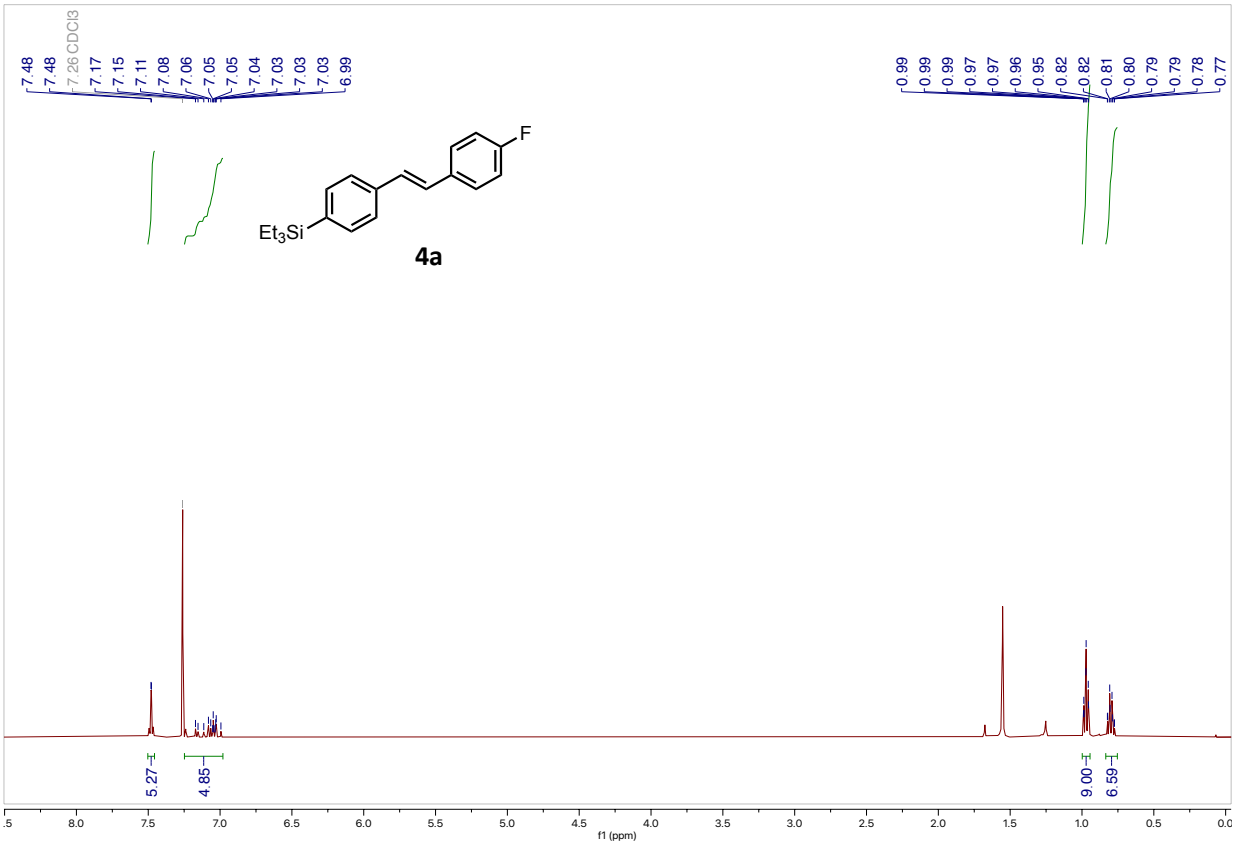
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):



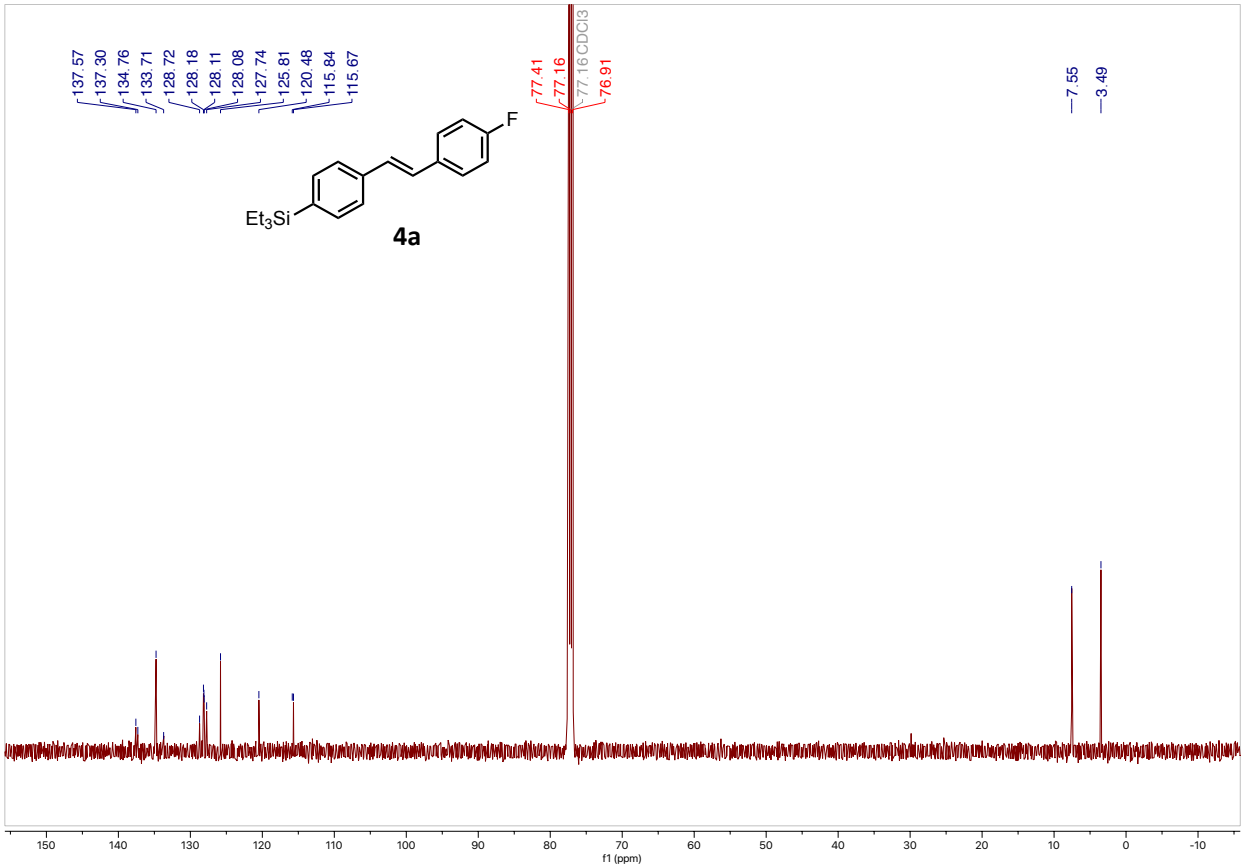
$^{29}Si\{^{1}H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$):



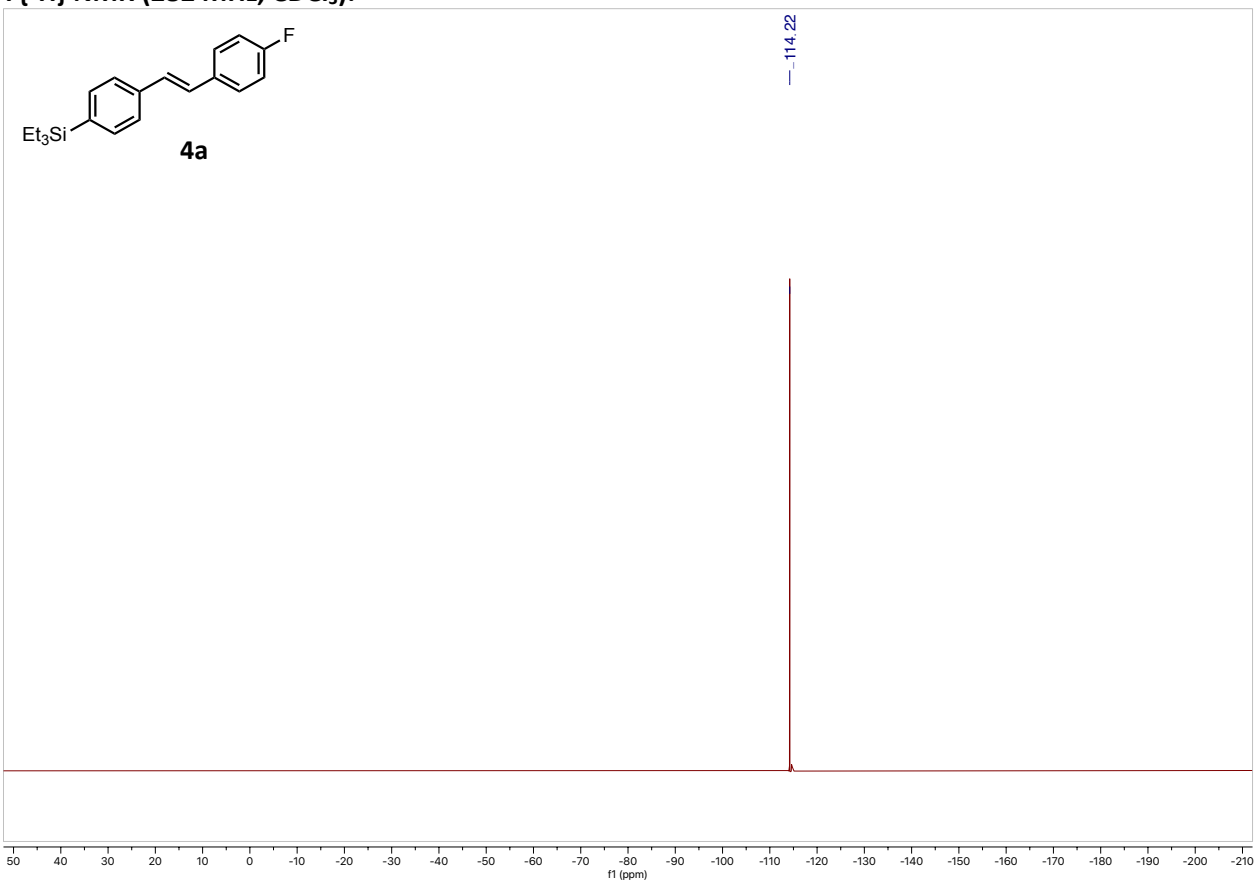
^{1}H NMR (500 MHz, $CDCl_3$):



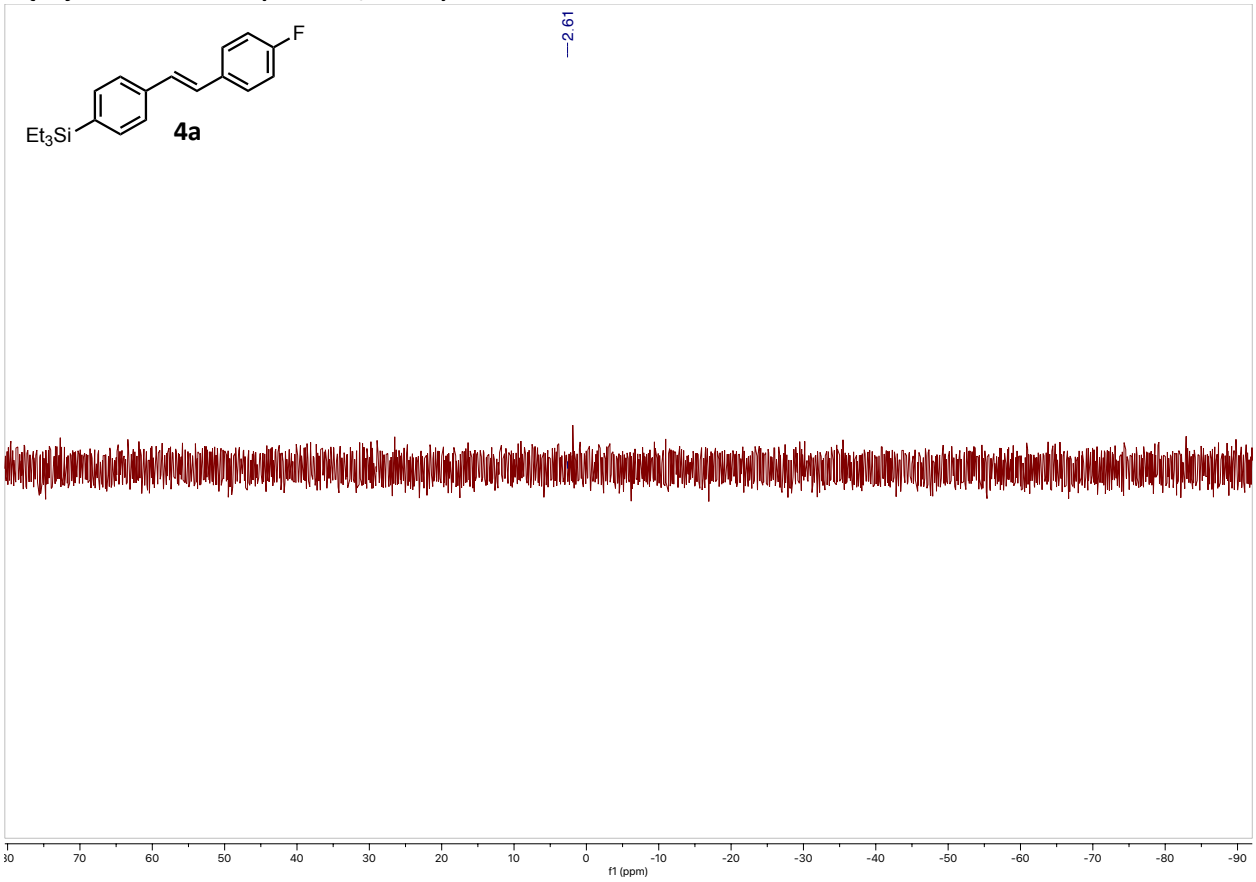
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



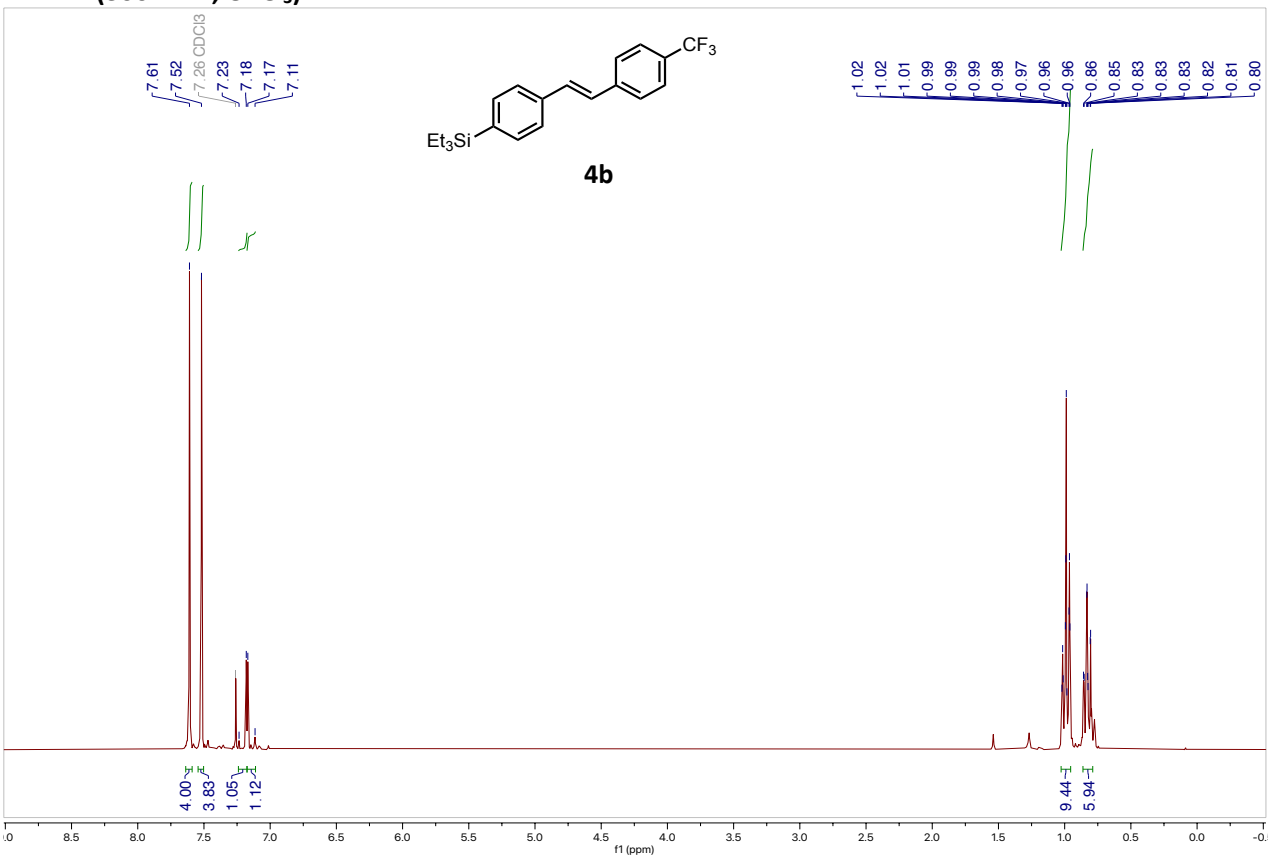
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$):



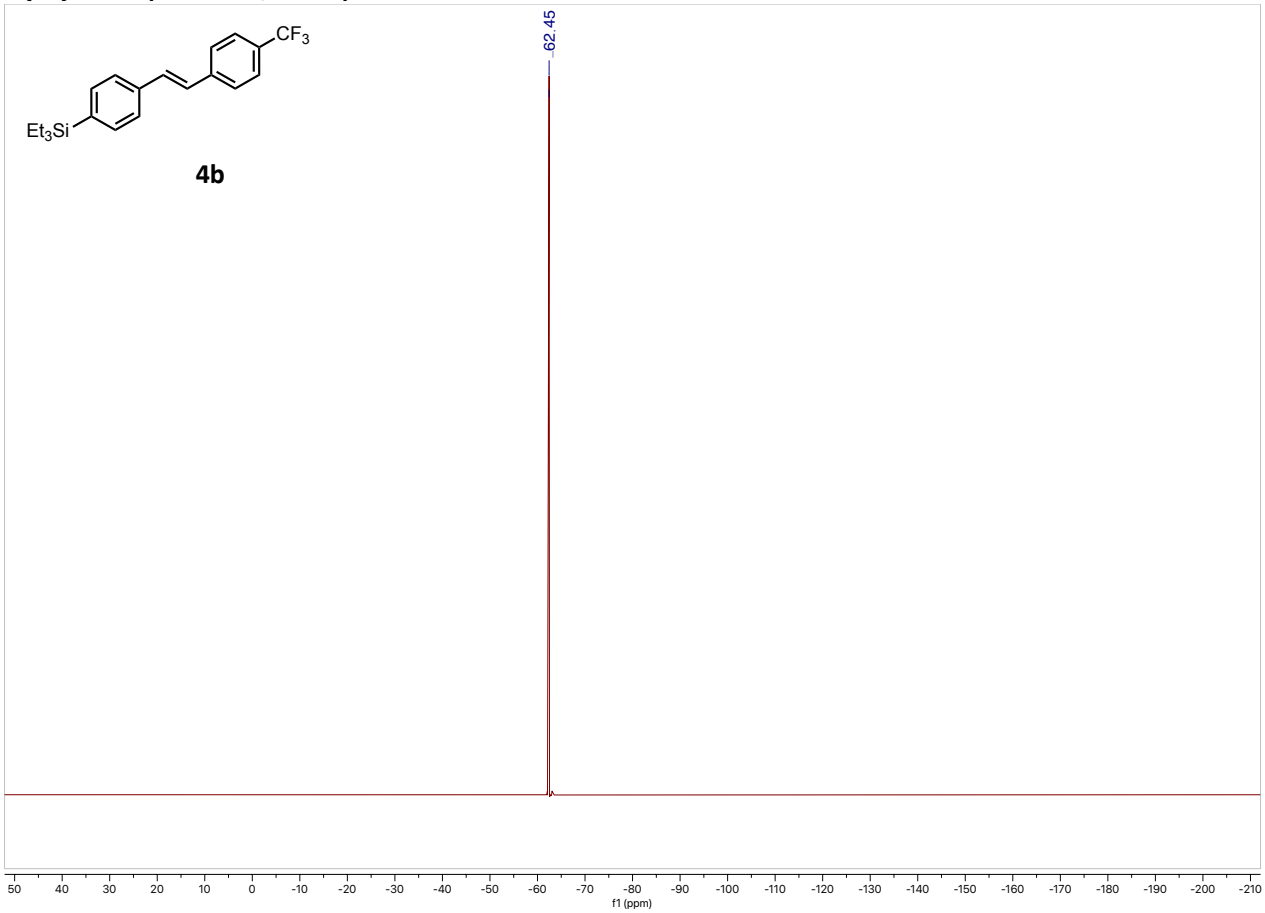
$^{29}Si\{^{1}H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$):



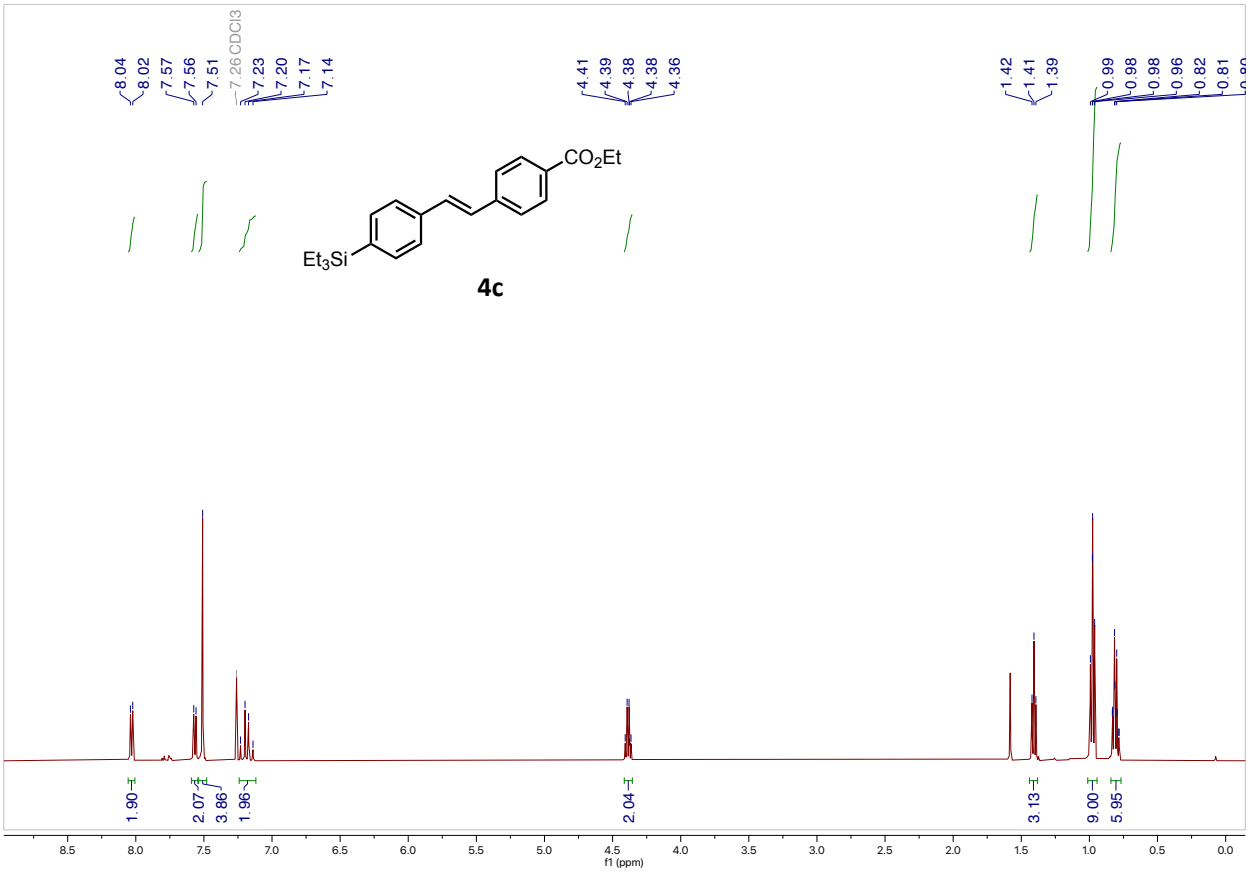
^{1}H NMR (300 MHz, $CDCl_3$):



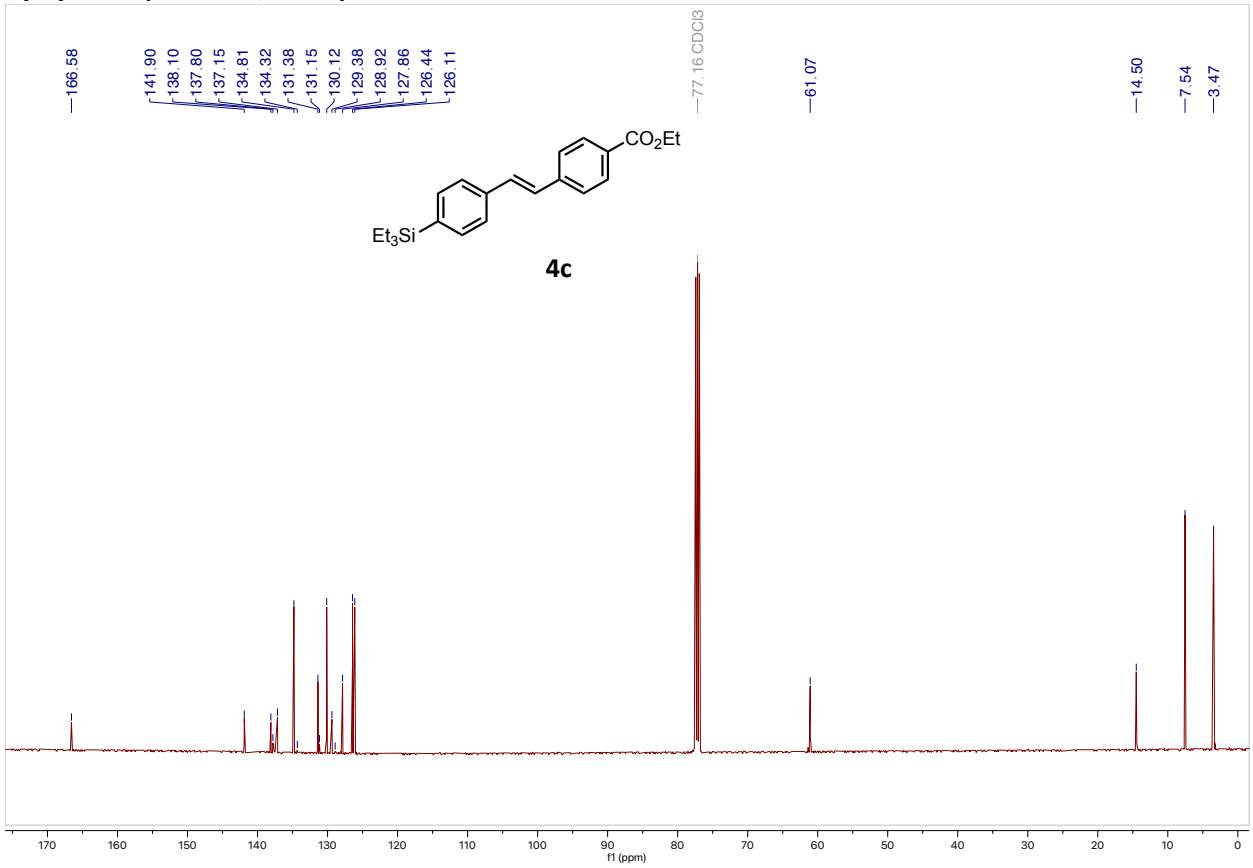
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$):



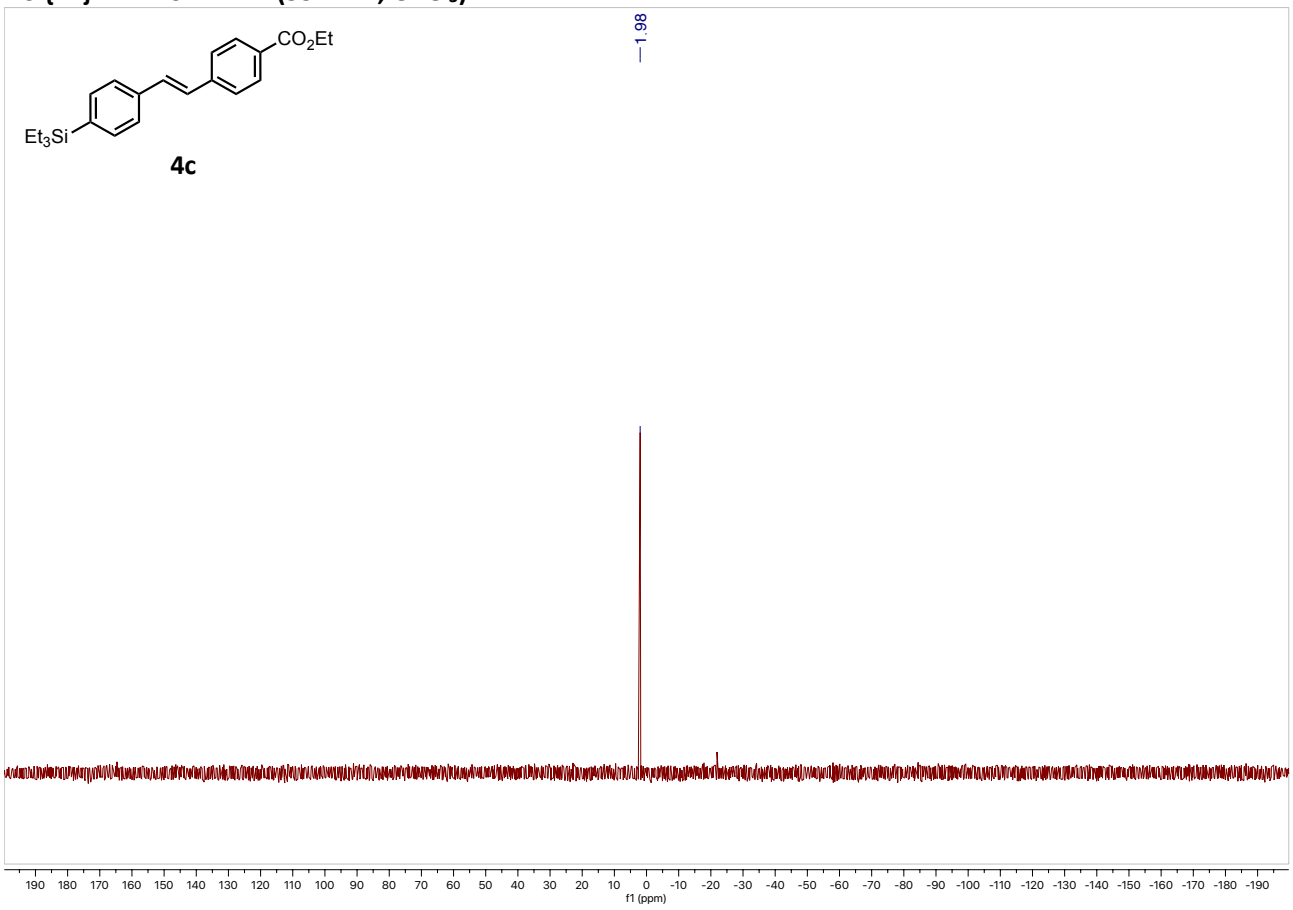
^{1}H NMR (500 MHz, $CDCl_3$):



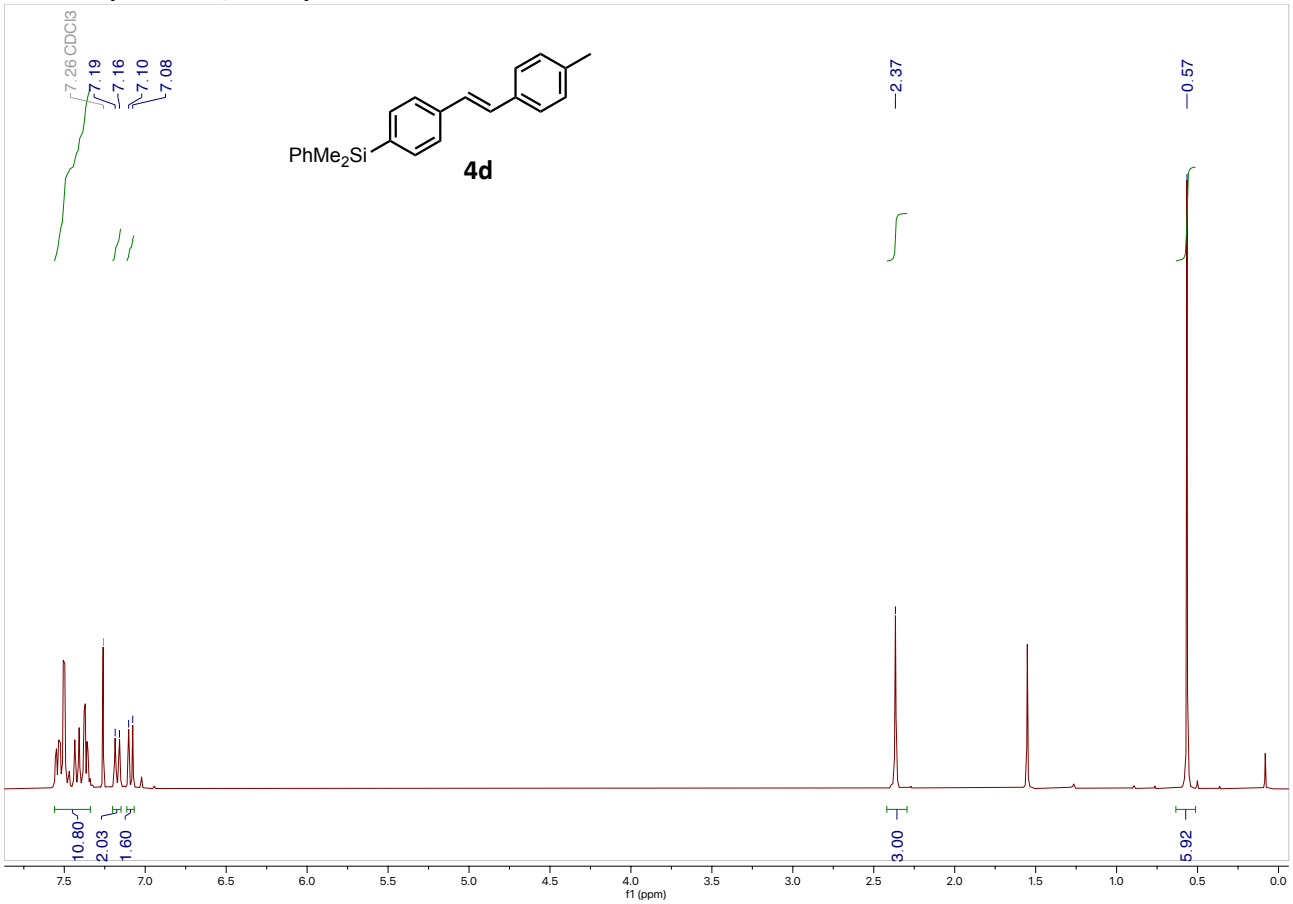
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



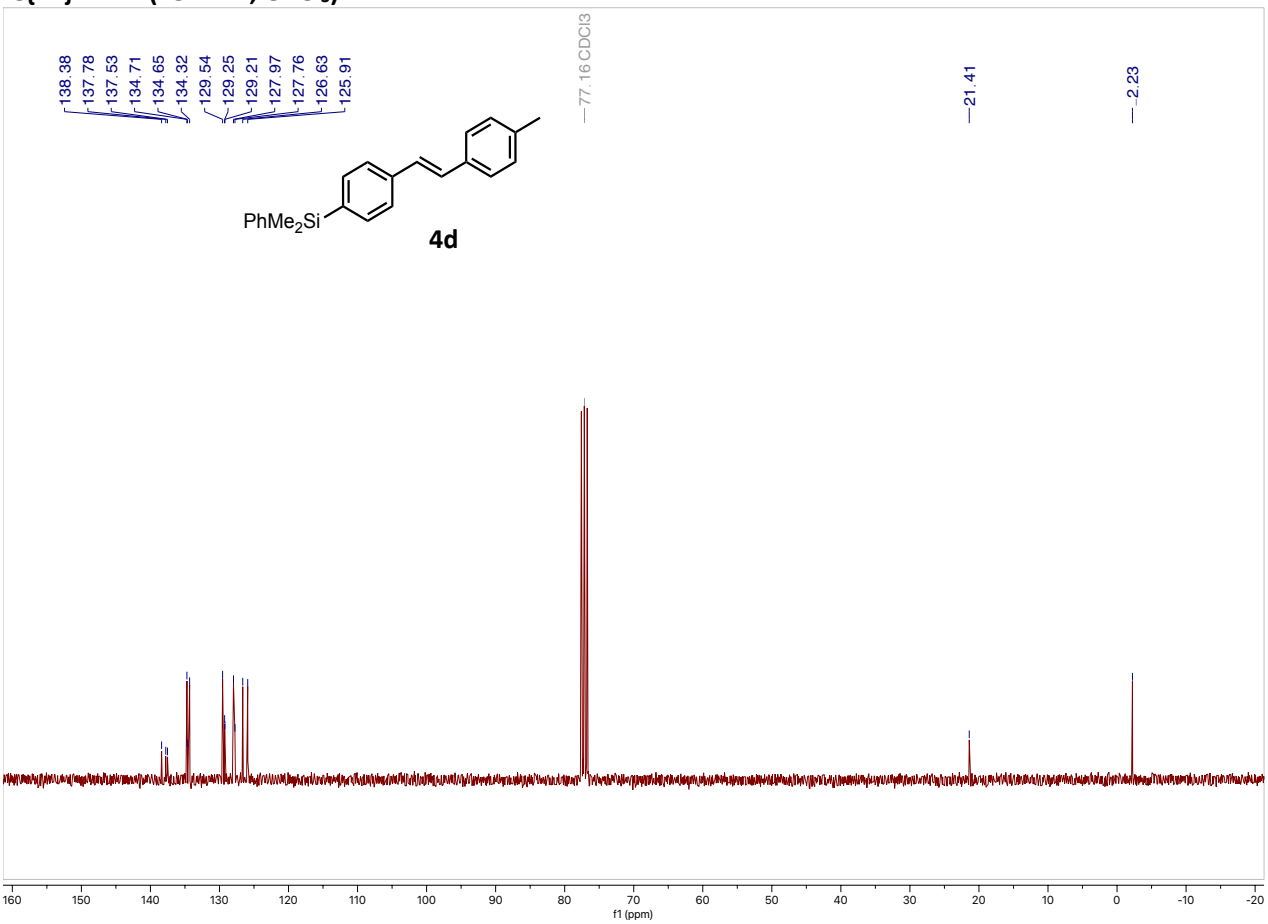
$^{29}Si\{^{1}H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):



$^{29}Si\{^{1}H\}$ DEPT 6H NMR (99 MHz, $CDCl_3$):