Supporting Information for

A Glimpse at the Chemistry of GeH_2 in Solution. Direct Detection of an Intramolecular Germylene-Alkene π-Complex.

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Synthesis and Characterization of Compounds and Photochemical Studies

^{1}H and ^{13}C NMR spectra were recorded on Bruker AV200 or AV500 spectrometers in $CDCl_3$, C_6D_6, or C_6D_{12} and were referenced to the residual solvent proton and ^{13}C signals, respectively. GC/MS analyses were carried out on a Varian Saturn 2200 GC/MS/MS system equipped with a VF-5ms capillary column (30m×0.25mm; 0.25 μm; Varian, Inc.). High-resolution electron mass spectra and exact masses were determined on a Micromass TofSpec 2E mass spectrometer using electron impact ionization (70 eV). Infrared spectra were recorded as thin films on potassium bromide plates using a Bio-Rad FTS-40 FTIR spectrometer. Column chromatography was carried out using acid-washed 230-400 mesh silica gel (Silicycle).

Hexanes (EMD OmniSolv), diethyl ether (Caledon Reagent) and tetrahydrofuran (Caledon Reagent) were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc.). Triethylamine and n-butyl amine were refluxed over solid KOH for 12 hours and distilled. Triethylsilane (Et_3SiH), triethylgermane (Et_3GeH) and tri-n-butylstannane (Bu_3SnH) were stirred at room temperature for 18 hours over lithium aluminum hydride and distilled at atmospheric pressure (Et_3SiH) or under mild vacuum (Bu_3SnH, Et_3GeH). 4,4-Dimethyl-1-pentene (DMP), and isoprene were purified by passage of the neat liquids through a silica gel microcolumn. 3,3-Dimethyl-1-butyne (TBE) was distilled. Glacial acetic acid and acetic acid-O*d* were used as received from Sigma-Aldrich. 2-Methyl-3-phenyl-1,3-butadiene and 1,1-dichloro-3-methyl-4-phenylgermacyclopent-3-ene (**5**) were synthesized as described previously.[1]

3-Methyl-4-phenylgermacyclopent-3-ene (**4**). A flame-dried 250 mL 2-neck roundbottom flask fitted with reflux condenser, magnetic stirrer and nitrogen inlet was charged with anhydrous ether (75 mL), and then lithium aluminum hydride (1.1 g, 0.03 mol) was added under nitrogen. The mixture was cooled to -78 ^{o}C with a dry ice / isopropanol bath, and 1,1-dichloro-3-methyl-4-phenylgermacyclopent-3-ene (**5**, 5.5 g, 0.019 mol) was added via syringe over 10 min. The

cooling bath was then removed and the mixture was allowed to stir for three hours. The ether solution was decanted from the residual solids, which were then washed with fresh ether (2 x 25 mL) and decanted similarly. The combined ether fractions were poured into saturated aqueous ammonium chloride (25 mL), the layers were separated, and the aqueous phase was extracted once with ether (25 mL). The combined ether fractions were washed with water (2 x 20 mL), dried over anhydrous magnesium sulfate, and filtered. Evaporation of the solvent on the rotary evaporator afforded a colorless oil, which was distilled under vacuum. The product (bp 61-62 ^{o}C, 0.1 mm Hg; 3.40 g, 0.0155 mol, 82%) was identified as **4** on the basis of its ^{1}H and ^{13}C NMR, IR, and mass spectra (Ge isotopomeric clusters are indicated with an asterisk): IR (neat; cm^{-1}), 2905 (m), 2057 (s), 1492 (m), 1440 (m), 1135 (m), 872 (s), 756 (s); ^{1}H NMR (C_6D_6), δ = 1.66 (s, 3H), 1.76 (m, 2H), 2.08 (m, 2H), 5.11 (p, 2H; J = 3.5 Hz), 7.07 (t, 1 H), 7.12 (d, 2H), 7.19 (t, 2H); ^{13}C NMR (C_6D_6), δ = 20.6, 21.3, 21.4, 126.4, 128.3, 128.5, 135.0, 137.1, 143.4**;** EI-MS, m/z (I) = 220* (80), 194 (75), 178* (25), 151 (30), 145 (60), 138 (70), 129 (100), 128 (97), 115 (38), 91 (22). HRMS: Exact mass: calc. for $C_{11}H_{14}{}^{74}Ge$, 220.0307; found 220.0305.

3-Methyl-4-phenylgermacyclopent-3-ene-1,1-d_2 (**4**-d_2) was prepared from **5** and lithium aluminum deuteride in analogous fashion to **4**, and exhibited the following spectroscopic data: IR (neat; cm^{-1}): 2907 (m), 1488 (s), 1441 (m), 1405 (w), 754 (s), 701 (s), 674 (m), 626 (s); ^{1}H NMR (C_6D_6), δ = 1.66 (s, 3H), 1.74 (s, 2 H), 2.07 (s, 2 H), 7.07 (t, 1 H), 7.12 (d, 2H), 7.19 (t, 2H); ^{13}C NMR (C_6D_6), δ = 20.5, 21.1, 21.2, 126.4, 128.3, 128.5, 135.0, 137.1, 143.4**;** EI-MS, m/z (I) = 222* (100), 207* (9), 206* (11), 179* (18), 151* (14), 147 (41), 146* (21), 143 (18), 129* (28), 128 (24), 118* (9), 115 (16), 77 (14), 74* (21); HRMS: Exact mass: calc. for $C_{11}H_{12}D_2{}^{74}Ge$, 222.0433; found 222.0433.

Steady state photolysis experiments were carried out using a Rayonet® photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round and 2 ×

RPR2537 (254 nm) lamps. Aliquots (*ca*. 0.7 mL) of 0.025 M solutions of **4** or **4**-d_2 in C_6D_{12} or THF-d_8 were placed in quartz NMR tubes, sealed with a septum and deoxygenated with a fine stream of dry argon for ca. 10 minutes prior to adding the desired amount of substrate (AcOH, AcOD, MeOH, or DMB) via microlitre syringe. The photolyses were monitored at periodic intervals by ^{1}H NMR spectroscopy. Product yields were determined from the relative slopes of concentration vs. time plots covering the range of ca. 0-6% conversion of the starting material, which were constructed using the individual peak integrals for the reactant and identifiable products, standardized against the total integrated intensity of the aromatic protons in the spectra. No special precautions were taken to prevent losses of H_2 from the AcOH photolysates during the experiments, but a control experiment showed these to be minimal over the time periods typical of most experiments. COSY-45 and ^{1}H-^{13}C HSQC and HMBC NMR spectroscopies were employed in order to secure the spectral assignments reported in Figure 1 and the associated text of the paper for the partial structures of the two minor products (**9** and **10**) formed in the photolysis of **4** in the presence of AcOH. The ^{13}C resonances associated with these fragments are as follows. **9** (C_6D_{12}), δ = 23, 35.5, 110.5, 143.0; **10** (C_6D_{12}), δ = 22.1, 49.7, 111.0, 149.2.

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser, filled with F_2/Kr/Ne (248 nm; ~20 ns; 100 ± 5 mJ) mixtures, and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.[27] Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was between *ca.* 0.7 and 0.9, and were flowed continuously through a thermostatted 7 x 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of nitrogen or argon gas through the solution for at least 30 minutes prior to and then throughout the duration of each experiment. The glassware, sample cells, and transfer lines used for these experiments were stored in a 65 ^{o}C vacuum oven when not in use, and the oven was vented with dry nitrogen just prior to assembling the sample-handling system at the beginning of

an experiment. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted directly into the flow cell. Transient decay and growth rate constants were calculated by non-linear least squares analysis of the absorbance-time profiles using the Prism 3.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate-concentration data (5-7 points) that spanned as large a range in transient decay rate as possible. Errors are quoted as twice the standard deviation obtained from the least-squares analyses.

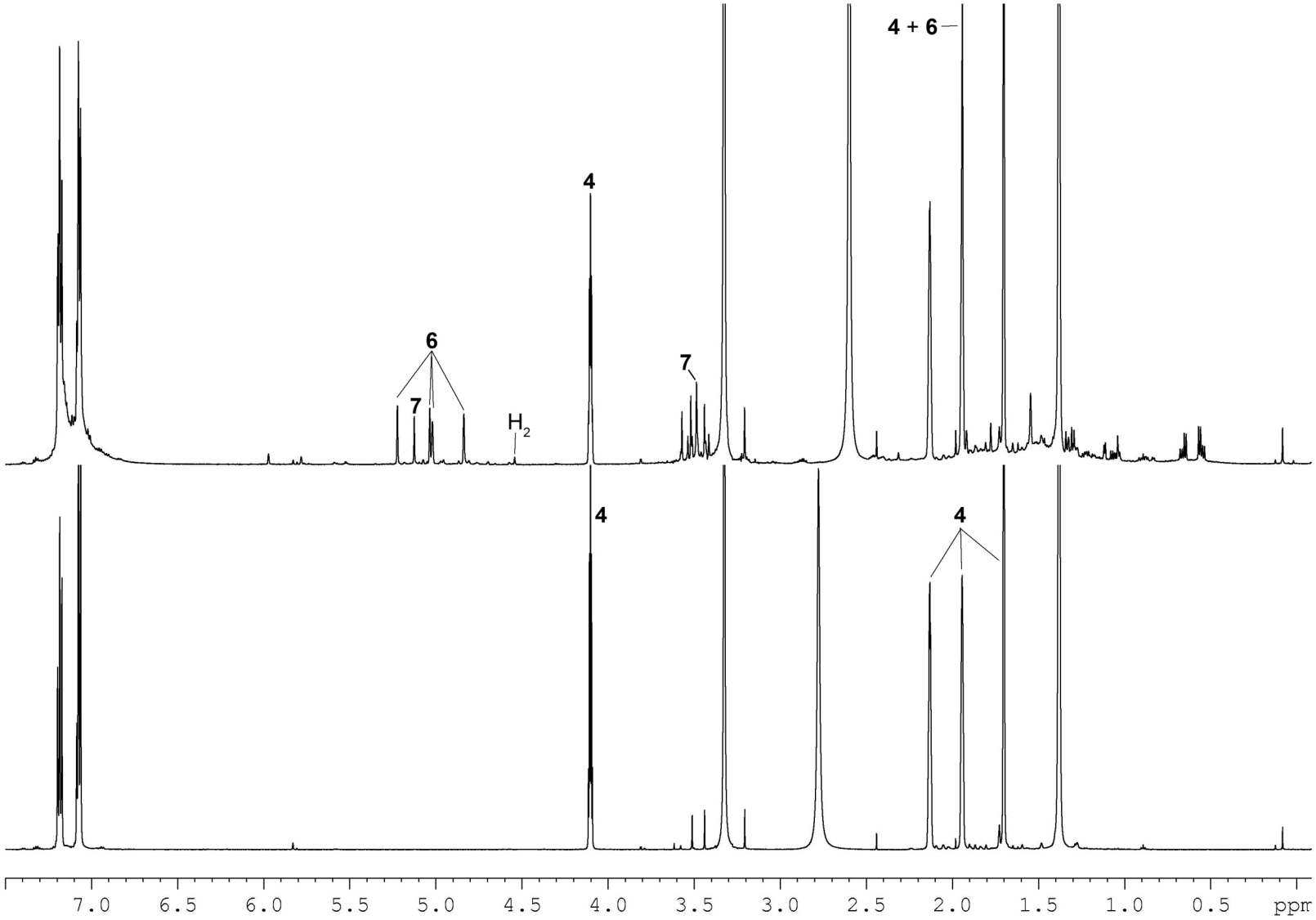

Figure S1. ^{1}H NMR spectra of a deoxygenated solution of **4** (0.025M) in C_6D_{12} containing MeOH (0.25M) before irradiation (bottom) and after 16 min irradiation (top).

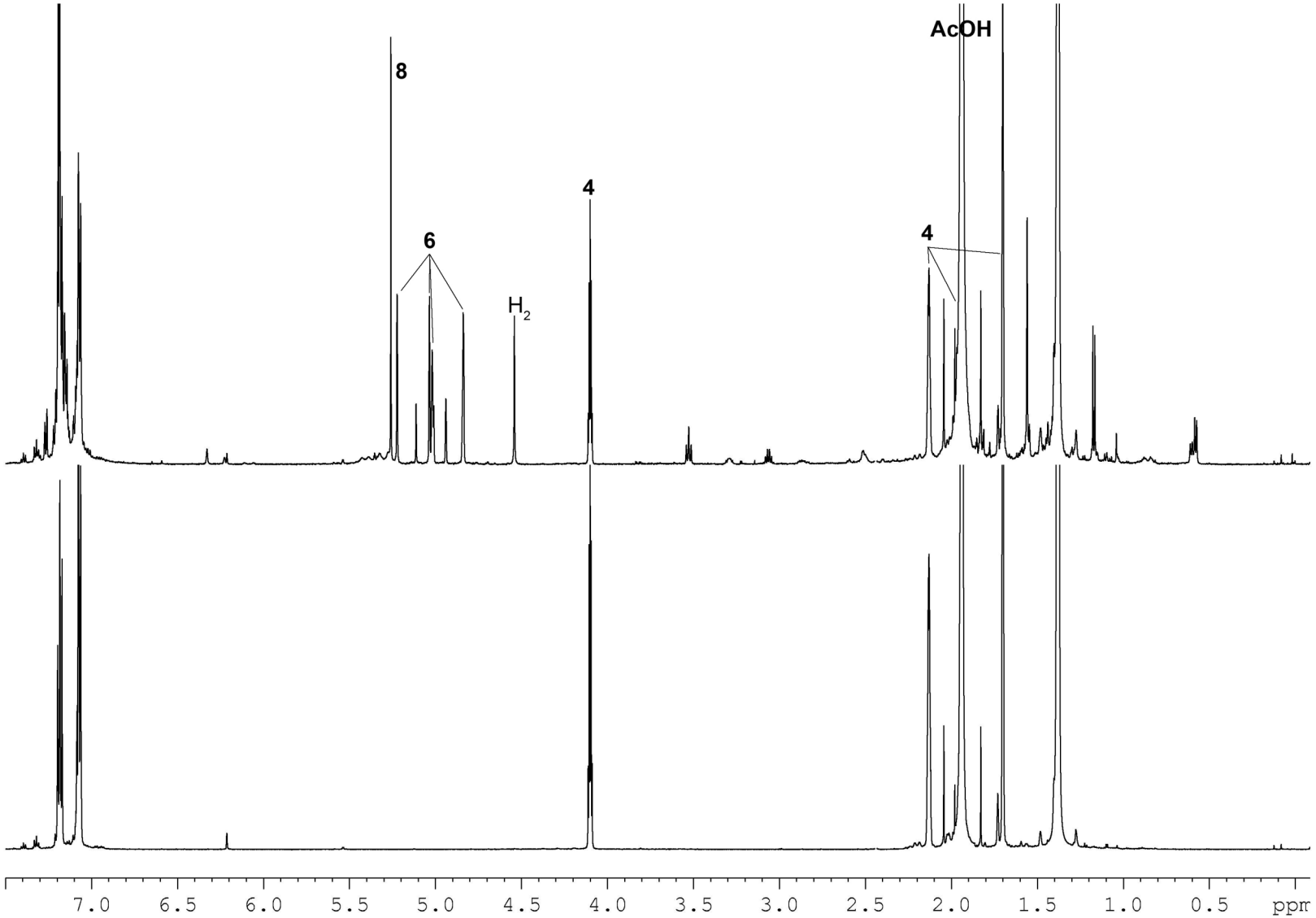

Figure S2. ^{1}H NMR spectra of a deoxygenated solution of **4** (0.025M) in C_6D_{12} containing AcOH (0.25M) before irradiation (bottom) and after 16 min irradiation (top).

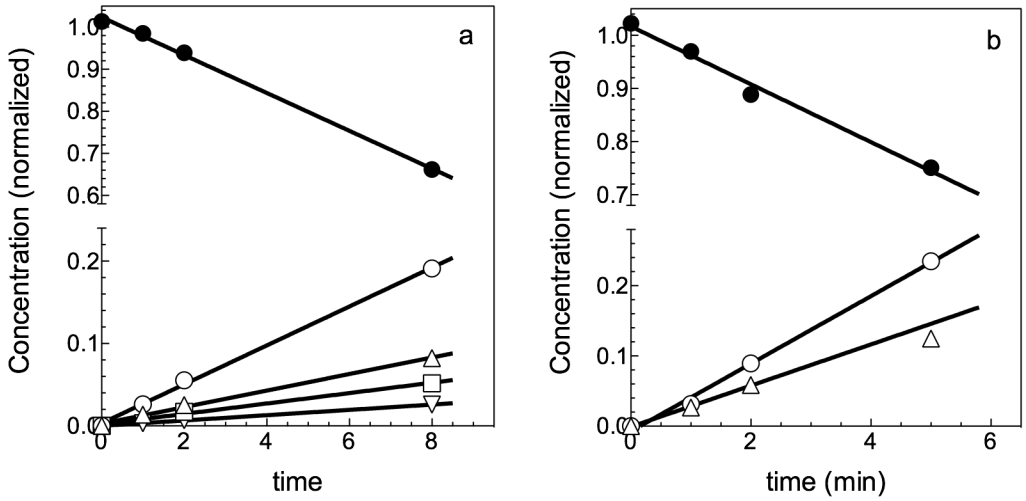

Figure S3. Concentration vs. time plots from steady-state photolysis (a) of **4** (0.025 M) in C_6D_{12} containing AcOH (0.25 M) and (b) of **4** (0.05 M) in THF-d_8 containing AcOH (0.25 M), showing the variations in the concentrations of **4** (●), **6** (○), **8** (△), H_2 (□), and the unidentified alkenes (▽) with photolysis time up to *ca.* 30% conversion of **4**.

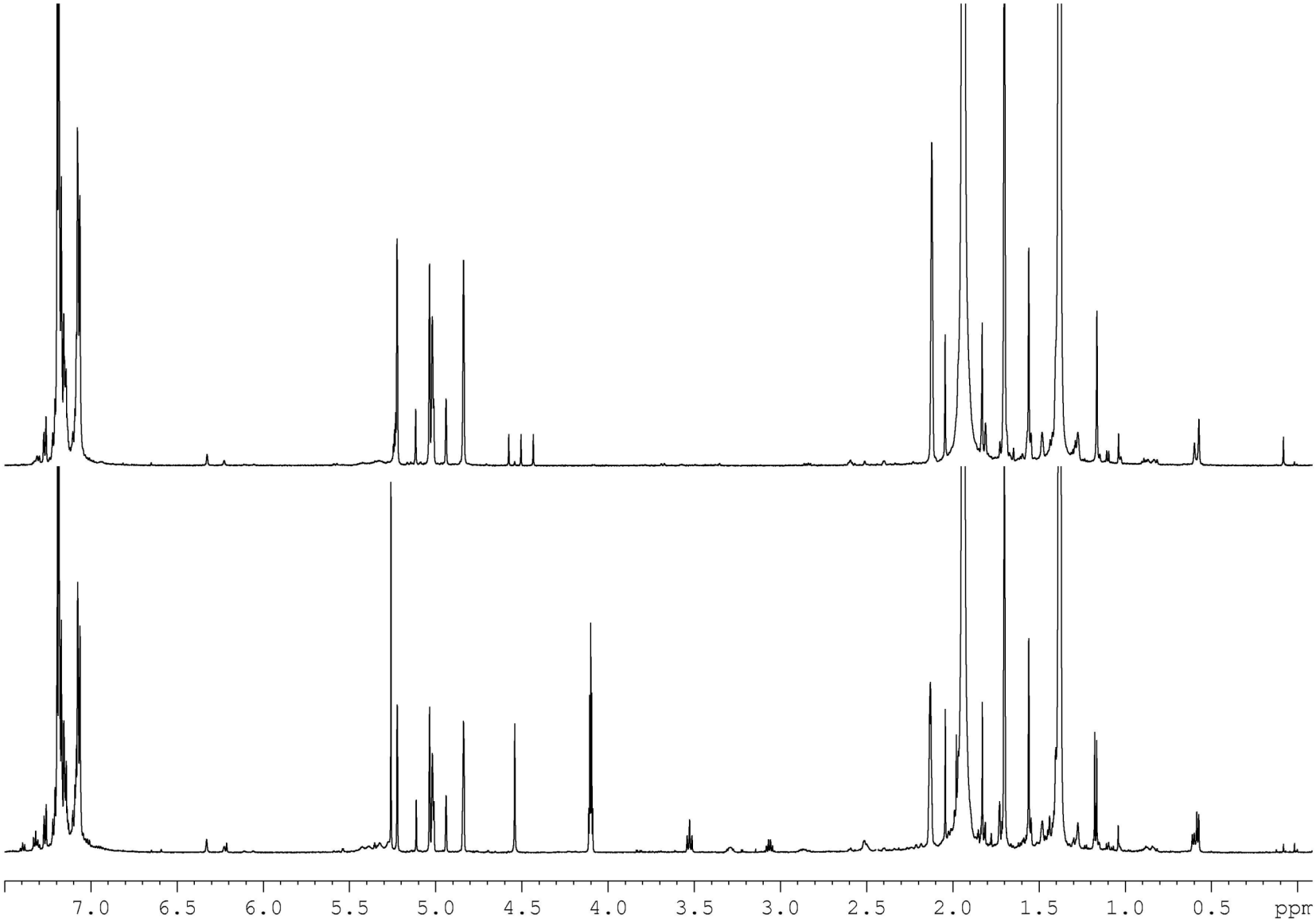

Figure S4. ^{1}H NMR spectra of a deoxygenated solution of **4**-d_2 (0.025M) in C_6D_{12} containing AcOH (0.25M) after 16 min irradiation (top); the bottom half of the figure shows Fig. S2 (top), to facilitate comparisons.

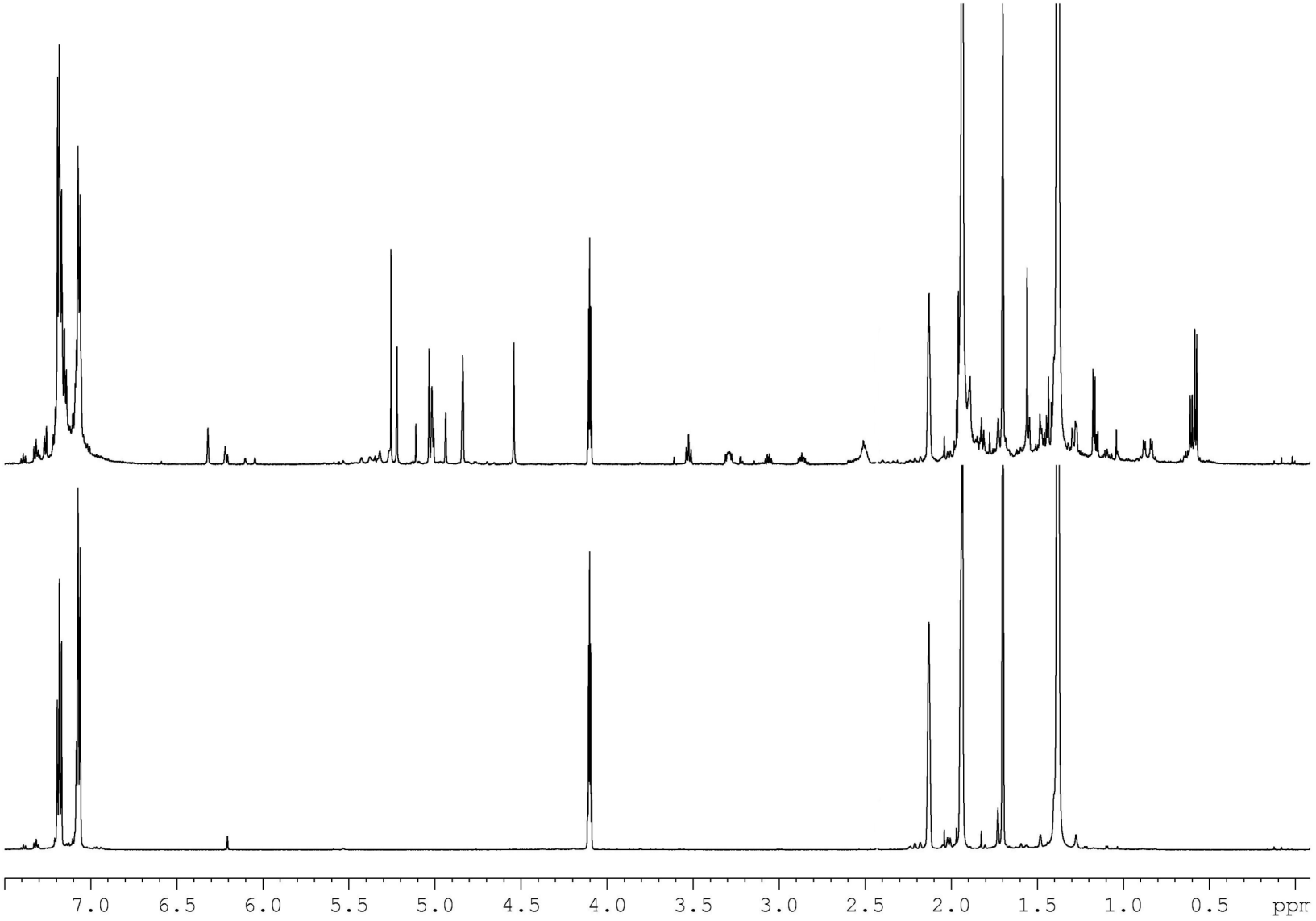

Figure S5. ^{1}H NMR spectra of a deoxygenated solution of **4** (0.025M) in C_6D_{12} containing AcOH (0.05M) before irradiation (bottom) and after 16 min irradiation (top).

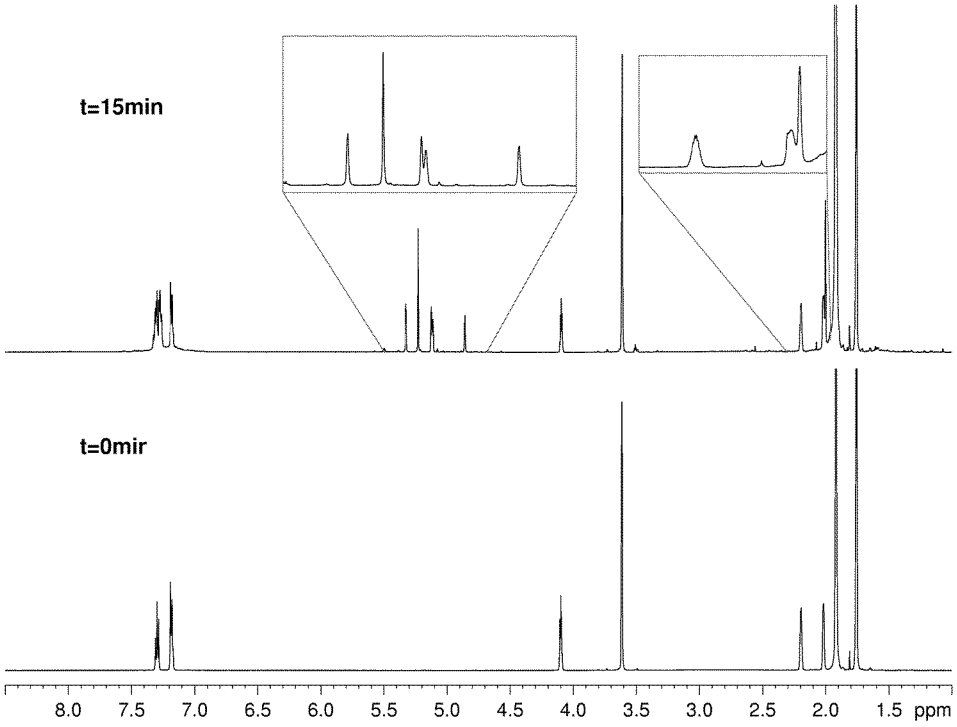

Figure S6. ^{1}H NMR spectra of a deoxygenated solution of **4** (0.05M) in THF-d_8 containing AcOH (0.25 M), before irradiation (bottom) and after 15min of irradiation (top).

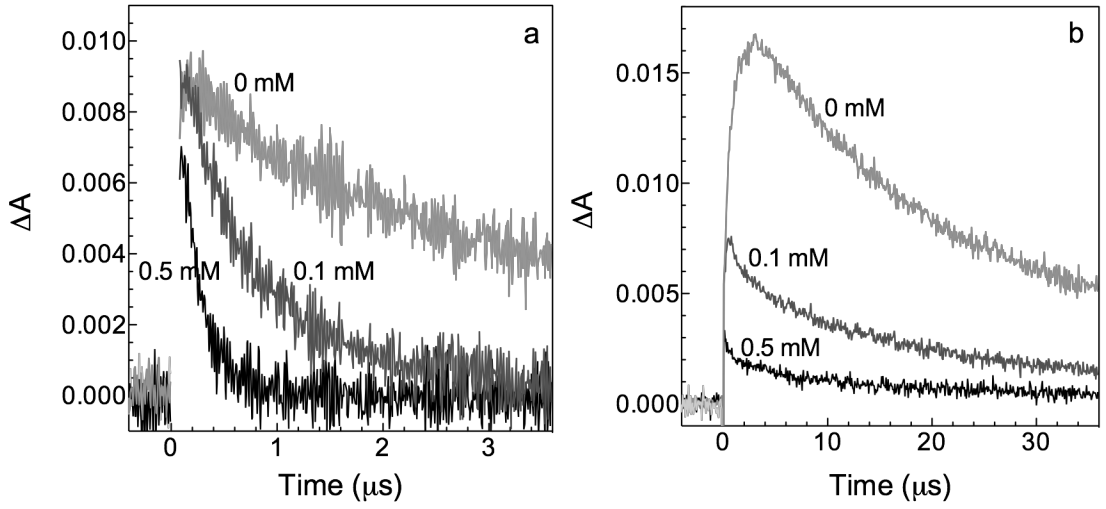

Figure S7. Absorbance vs. time profiles recorded at (a) 470 nm and (b) 380 nm by laser photolysis of **4** in deoxygenated hexanes containing 0, 0.1, and 0.5 mM AcOH.

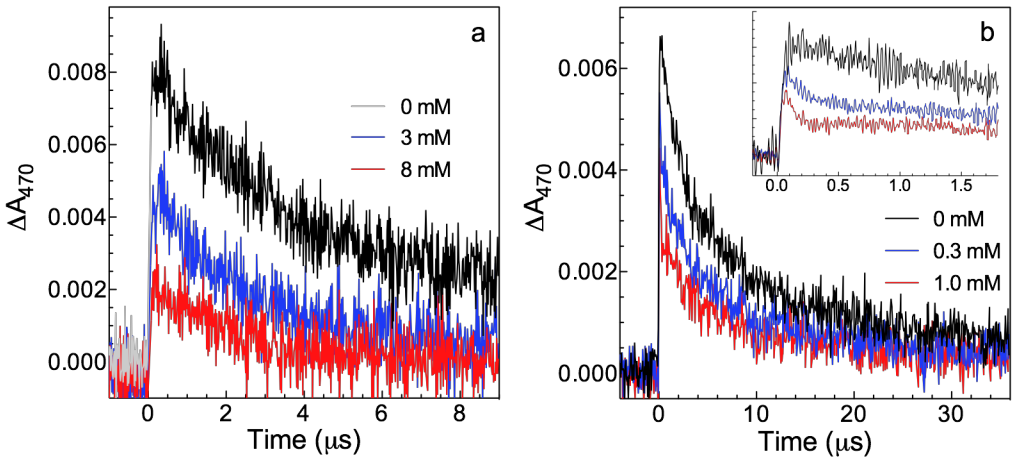

Figure S8. Absorbance vs. time profiles for the 460 nm transient (monitored at 470 nm) in hexanes in the presence of varying concentrations of (a) MeOH and (b) THF at 25 °C.

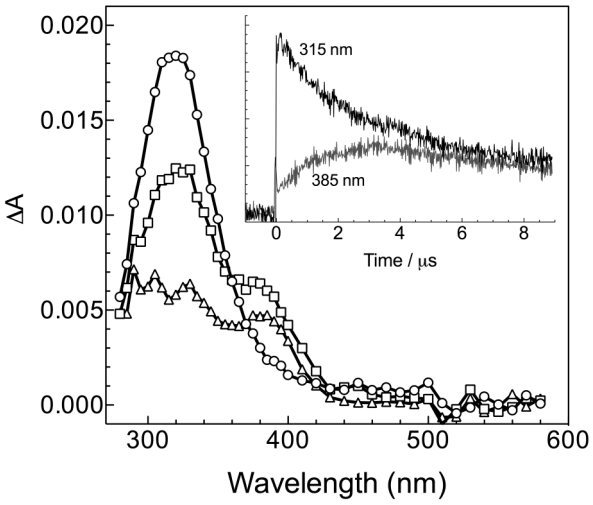

Figure S9. Transient absorption spectra from laser flash photolysis of **4** in deoxygenated hexanes containing 4 mM THF, recorded 110-180 ns (-○-), 1.7-1.8 μs (-□-) and 8.6-8.7 μs (-Δ-) after the laser pulse. The inset shows typical transient growth/decay profiles, recorded at 315 and 380 nm.

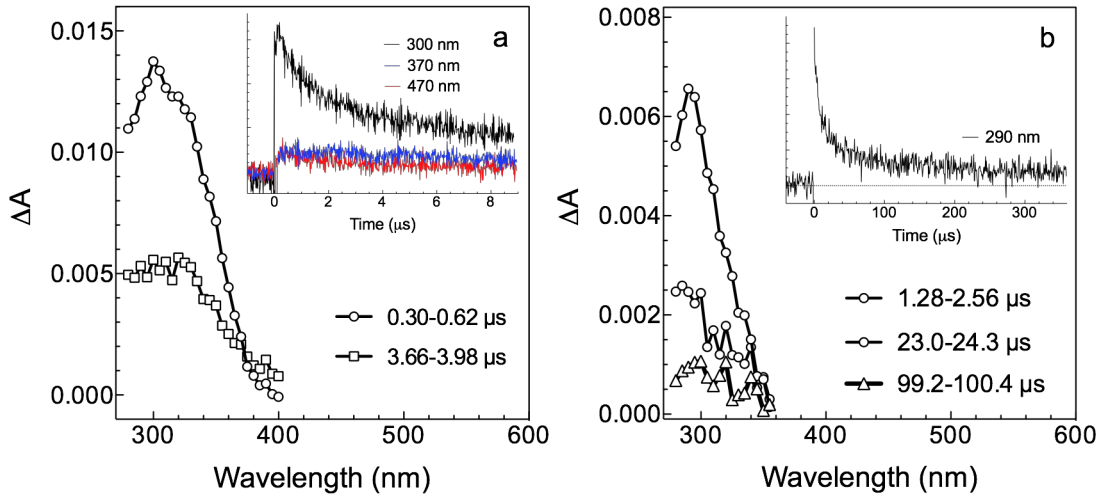

Figure S10. (a) Transient absorption spectra from laser photolysis of **4** in deoxygenated hexanes solution containing 9 mM MeOH at 25 °C, recorded 0.30-0.62 μs (-○-) and 3.66-3.98 μs (···□···) after the laser pulse; the inset shows transient growth/decay profiles recorded at 300, 370, and 470 nm. (b) Transient absorption spectra from laser photolysis of **4** in deoxygenated MeOH at 25 °C, recorded 1.28-2.56 μs (-○-), 23.0-24.3 μs (···□···), and 34.3-34.4 μs (···Δ···) after the laser pulse; the inset shows a transient decay profile recorded at 290 nm.

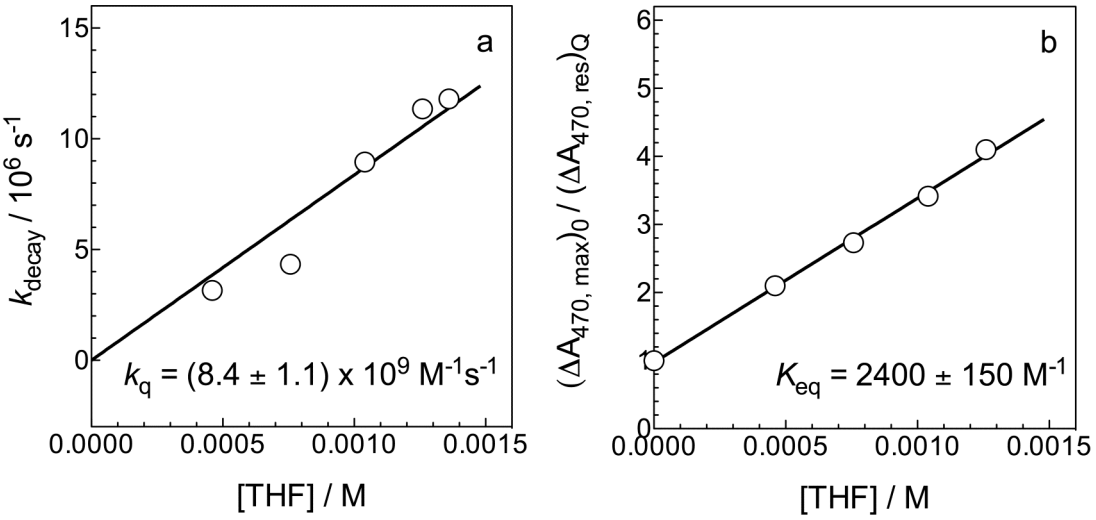

Figure S11. Plots of (a) k_{decay} vs. [THF] and (b) $(\Delta A_{470,max})_0/(\Delta A_{470,res})_Q$ vs. [THF] for quenching of the 460 nm transient from laser photolysis of **4** (monitored at 470 nm) in hexanes at 25 ˚C. The solid lines are the linear least squares fits of the data to equations 7 and 8, respectively.

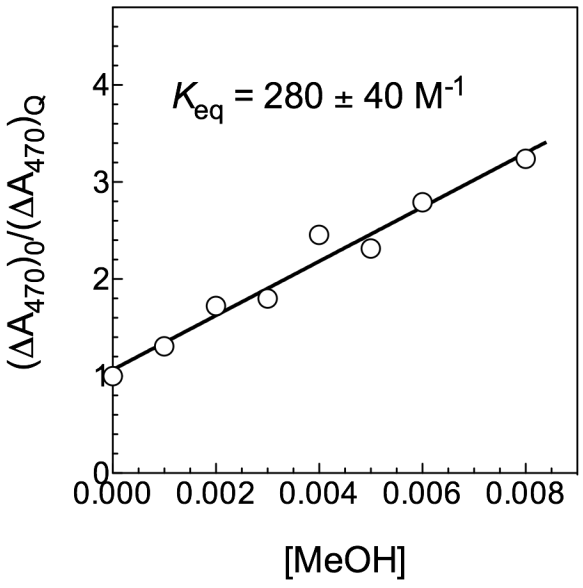

Figure S12. Plot of ΔA_0 / ΔA_Q vs. [Q] for the 460 nm transient (monitored at 470 nm) in hexanes containing 0 – 8 mM MeOH.

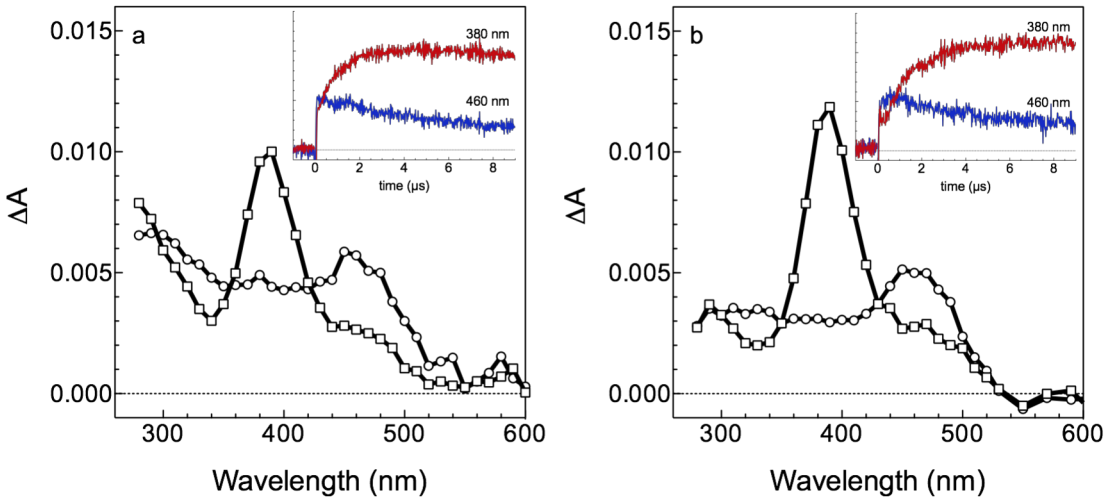

Figure S13. Transient absorption spectra from laser photolysis of (a) **4** and (b) **4**-d_2 in deoxygenated hexanes solution at 25 °C, recorded 256-320 ns (-○-) and 8.58-8.69 μs (···□···) after the laser pulse. The inset shows transient growth/decay profiles recorded at 470 and 380 nm.

Computational Studies.

All calculations were carried out using the Gaussian09 suite of programs.[S2]

Table S1. Comparison of calculated standard enthalpies and free energies of the $GeMe_2$/1,3-butadiene π-complex (**18**), 1,1-dimethyl-2-vinylgermirane (**19**), and the transition state for their interconversion (**T_{19}**).

	$\Delta H°$ (kcal mol^{-1})			$\Delta G°$ (kcal mol^{-1})		
Method	**18**	**T_{19}**	**19**	**18**	**T_{19}**	**19**
B3LYP/6-31G(*d,p*)^{C,H}/6-311G(*d,p*)^{Ge} [a]	-5.2	-3.3	-7.9	+5.7	+8.7	+3.2
B2PLYP/6-311G(*d,p*) [b]	-8.5	-7.6	-12.7	+3.4	+5.2	-0.9
PW91PW91/6-311+G(*2d,p*) [b]	-15.1	-14.3	-16.8	-3.6	-2.0	-5.5
PBE0/cc-pVTZ	[c]	[c]	-20.8	[c]	[c]	-8.3
G4	-13.0	-14.3	-20.2	-0.8	-0.9	-7.8
CCSD(T)/cc-pVTZ [a]	-12.1	-14.6	-22.2	-1.2	-2.7	-11.1

a. Ref. S3. The CCSD(T)/cc-pVTZ energies are single-point values based on the corresponding B3LYP/6-31G(d,p)^{C,H}/6-311G(d,p)^{Ge} geometry and frequencies.
b. Frequencies unscaled.
c. All attempts to optimize the structure resulted in structure **19**.

Table S2. Comparison of Experimental UV-vis Absorption Maxima of Germylenes, the Lewis Acid-Base Complexes of GeH_2 and $GeMe_2$ with MeOH and THF, and germiranes **20** and **21** with Those Calculated at the TDPW91PW91/6-311+G(*2d,p*), TDB2PLYP/6-311G(*d,p*), and TDPBE0/cc-pVTZ Levels of Theory.[a]

	λ_{max} (nm)			
Species	exptl	TDPW91	TDPBE0	TDB2PLYP
GeH_2	515 [b]	515	506	507
GeHMe	485 [b]	512	503	494
$GeMe_2$	480 [b] (470) [c]	495	482	474
$GeMe_2$-MeOH	295 [c]	382	323	305
$GeMe_2$-THF	300 [c]	361	317	299
GeH_2-MeOH	≤ 295 [d]	368	332	314
$GeMe_2$-THF	290 [d]	343	319	303

a. All calculations were carried out on geometries optimized at the PW91PW91/6-311+G(*2d,p*) level of theory.
b. gas phase; refs. S4 (GeH_2), S5 (GeHME) , and S6 ($GeMe_2$).
c. In hexanes solution; refs. S1 and S7.
d. In neat MeOH or THF; this work.

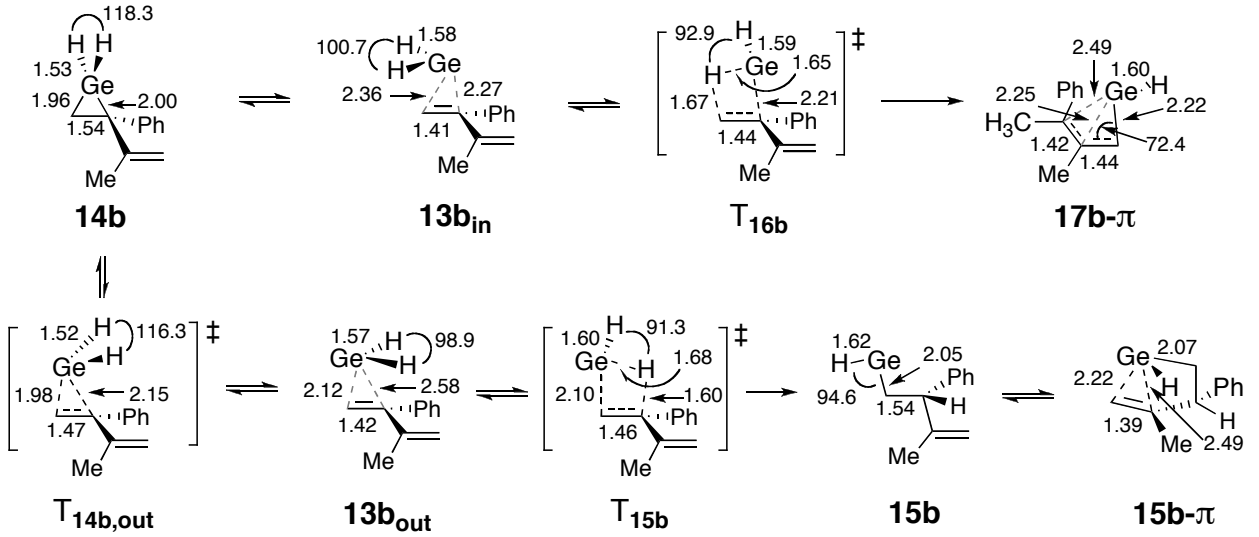

Figure S14. Calculated structures and selected geometric parameters; series b (reaction at C^3=C^4 bond).

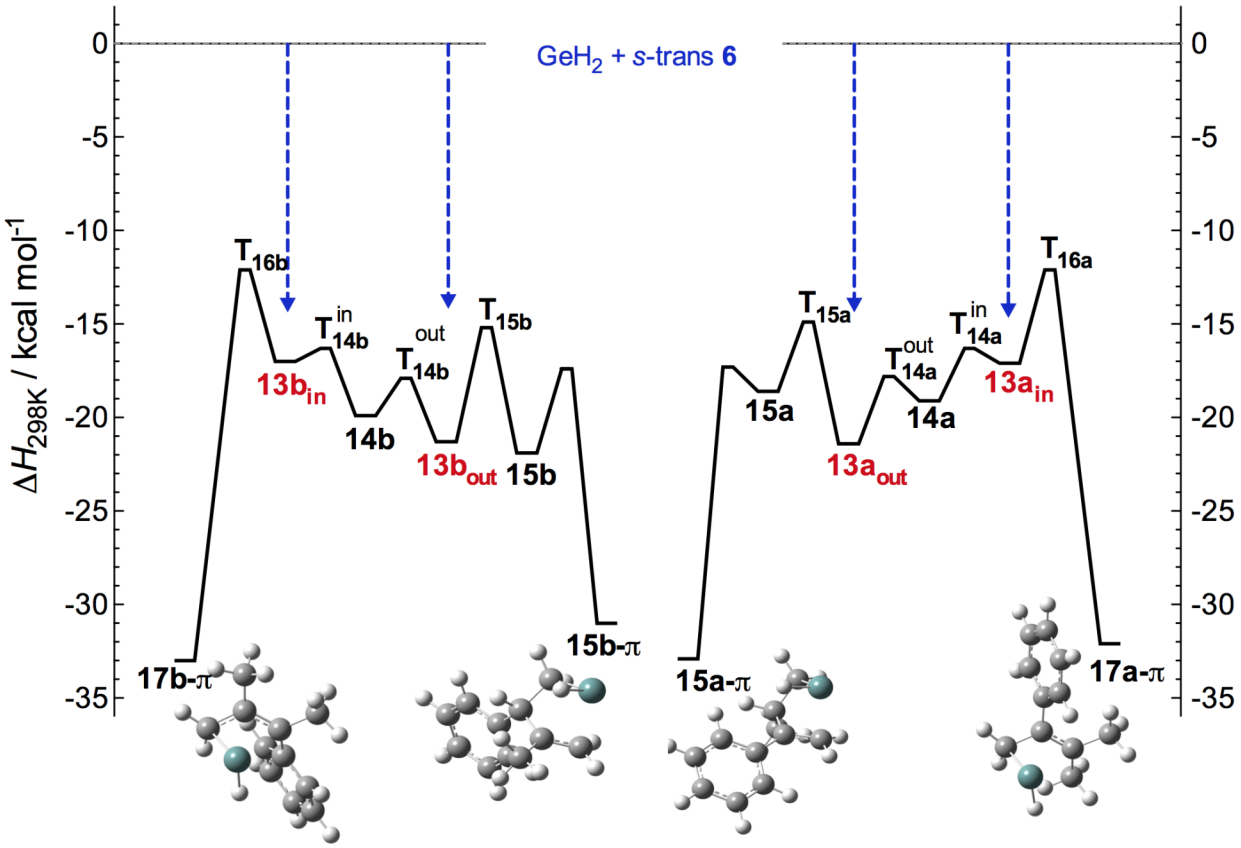

Figure S15. Partial standard enthalpy surface for the reactions of GeH_2 with 2-methyl-3-phenyl-1,3-butadiene (**6**), calculated at the PW91PW91/6-311+G(*2d,p*) level of theory relative to GeH_2 and *s*-trans **6**.

Calculated Structural Parameters and Thermochemical Data

GeH_2

```
 Zero-point correction=                           0.010472 (Hartree/Particle)
 Thermal correction to Energy=                    0.013358
 Thermal correction to Enthalpy=                  0.014302
 Thermal correction to Gibbs Free Energy=        -0.010760
 Sum of electronic and zero-point Energies=          -2078.243197
 Sum of electronic and thermal Energies=             -2078.240311
 Sum of electronic and thermal Enthalpies=           -2078.239367
 Sum of electronic and thermal Free Energies=        -2078.264429

---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1         32           0        0.000000    0.000000    0.066711
      2          1           0        0.000000    1.135755   -1.067383
      3          1           0        0.000000   -1.135755   -1.067383
 ---------------------------------------------------------------------
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s-trans 2-methyl-3-phenyl-1,3-butadiene (**6**)

```
 Zero-point correction=                           0.189191 (Hartree/Particle)
 Thermal correction to Energy=                    0.199615
 Thermal correction to Enthalpy=                  0.200560
 Thermal correction to Gibbs Free Energy=         0.153168
 Sum of electronic and zero-point Energies=           -426.103357
 Sum of electronic and thermal Energies=              -426.092933
 Sum of electronic and thermal Enthalpies=            -426.091989
 Sum of electronic and thermal Free Energies=         -426.139381

---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -1.044487    0.574808   -0.188184
      2          6           0       -1.406667    1.793478   -0.643360
      3          6           0       -2.047228   -0.431493    0.227142
      4          6           0       -1.694007   -1.553055    0.885215
      5          6           0       -3.498153   -0.152769   -0.074553
      6          6           0        0.408132    0.245715   -0.094561
      7          6           0        0.951800   -0.852602   -0.781389
      8          6           0        2.319465   -1.120245   -0.730036
      9          6           0        3.169562   -0.302191    0.018128
     10          6           0        2.641334    0.788432    0.710138
     11          6           0        1.273207    1.059958    0.652225
     12          1           0       -0.655615    2.518386   -0.955260
     13          1           0       -2.449146    2.097850   -0.721010
     14          1           0       -2.448074   -2.276457    1.196376
     15          1           0       -0.658593   -1.772805    1.140044
     16          1           0       -3.658069    0.017314   -1.149441
     17          1           0       -4.128335   -0.992168    0.242111
     18          1           0       -3.851025    0.748680    0.448837
     19          1           0        0.293828   -1.491894   -1.371127
     20          1           0        2.724424   -1.970564   -1.280185
     21          1           0        4.238014   -0.515537    0.062019
     22          1           0        3.295348    1.429527    1.302501
     23          1           0        0.859501    1.907463    1.200539
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"out" GeH_2-**6** π-complex; $C^1=C^2$ (**13a**$_{out}$)

```
 Zero-point correction=                           0.204435 (Hartree/Particle)
 Thermal correction to Energy=                    0.217519
 Thermal correction to Enthalpy=                  0.218463
 Thermal correction to Gibbs Free Energy=         0.164371
 Sum of electronic and zero-point Energies=          -2504.379492
 Sum of electronic and thermal Energies=             -2504.366408
 Sum of electronic and thermal Enthalpies=           -2504.365463
 Sum of electronic and thermal Free Energies=        -2504.419555
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	1.983582	-1.332816	-0.157253
2	1	0	3.099926	-0.455674	-0.835772
3	1	0	0.874498	-1.261685	-1.268809
4	6	0	1.178261	1.003644	0.401512
5	6	0	1.220485	-0.055710	1.344189
6	6	0	2.339850	1.966188	0.347471
7	6	0	-0.038164	1.332450	-0.350821
8	6	0	-0.091423	2.393039	-1.192697
9	6	0	-1.292364	0.546048	-0.134696
10	6	0	-1.864315	-0.180202	-1.189003
11	6	0	-3.065974	-0.868389	-1.012378
12	6	0	-3.716265	-0.840081	0.222113
13	6	0	-3.159957	-0.115330	1.278376
14	6	0	-1.957560	0.570180	1.101377
15	1	0	0.291703	-0.536677	1.649203
16	1	0	1.987803	-0.019438	2.118020
17	1	0	3.212471	1.559552	0.871005
18	1	0	2.645246	2.211802	-0.676399
19	1	0	2.051551	2.910762	0.839649
20	1	0	-1.023466	2.655909	-1.690358
21	1	0	0.775405	3.017115	-1.401404
22	1	0	-1.351541	-0.206685	-2.151209
23	1	0	-3.493263	-1.431543	-1.842851
24	1	0	-4.654471	-1.378144	0.360624
25	1	0	-3.667738	-0.076879	2.242819
26	1	0	-1.538209	1.150665	1.924917

Transition state; **$13a_{out} \rightarrow 14a$** **($T_{14a,out}$)**

Zero-point correction=	0.204043 (Hartree/Particle)
Thermal correction to Energy=	0.216455
Thermal correction to Enthalpy=	0.217399
Thermal correction to Gibbs Free Energy=	0.164882
Sum of electronic and zero-point Energies=	-2504.373174
Sum of electronic and thermal Energies=	-2504.360761
Sum of electronic and thermal Enthalpies=	-2504.359817
Sum of electronic and thermal Free Energies=	-2504.412334

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.073168	1.308180	-0.318901
2	6	0	0.045146	2.447925	-1.047111
3	6	0	1.307987	0.785922	0.300650
4	6	0	1.246322	-0.214645	1.402712
5	1	0	-0.888338	2.800701	-1.482799
6	1	0	0.933014	3.053457	-1.221417
7	1	0	2.016059	-0.154740	2.173228
8	1	0	0.273061	-0.526874	1.779695
9	32	0	1.788551	-1.252671	-0.178451
10	1	0	0.711241	-1.677889	-1.174908
11	1	0	3.216116	-1.091673	-0.707478
12	6	0	2.526918	1.688047	0.289444
13	1	0	2.809908	1.996210	-0.725351
14	1	0	2.331746	2.605160	0.873044
15	1	0	3.395912	1.187252	0.736216
16	6	0	-1.219089	0.576523	-0.127417
17	6	0	-1.897890	0.616402	1.101138
18	6	0	-1.808001	-0.122030	-1.191813
19	6	0	-3.125268	-0.027798	1.262289
20	1	0	-1.468335	1.180971	1.930520
21	6	0	-3.035551	-0.769075	-1.031931
22	1	0	-1.295232	-0.147693	-2.154386
23	6	0	-3.696164	-0.727138	0.196447
24	1	0	-3.641943	0.024021	2.221494
25	1	0	-3.477521	-1.305880	-1.872330
26	1	0	-4.654790	-1.231444	0.321872

2-methyl-2-(1-phenylethenyl)germirane (**14a**)

```
 Zero-point correction=                           0.204243 (Hartree/Particle)
 Thermal correction to Energy=                    0.217137
 Thermal correction to Enthalpy=                  0.218081
 Thermal correction to Gibbs Free Energy=         0.164323
 Sum of electronic and zero-point Energies=          -2504.375702
 Sum of electronic and thermal Energies=             -2504.362808
 Sum of electronic and thermal Enthalpies=           -2504.361864
 Sum of electronic and thermal Free Energies=        -2504.415623
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	1.683777	-1.241944	-0.121291
2	6	0	0.103894	1.340184	-0.323389
3	6	0	0.073516	2.540035	-0.936280
4	6	0	1.358081	0.724489	0.185096
5	6	0	2.617900	1.563191	0.071231
6	6	0	-1.189138	0.604237	-0.146693
7	6	0	-1.951832	0.761028	1.020577
8	6	0	-3.172359	0.100147	1.171458
9	6	0	-3.650845	-0.729863	0.155791
10	6	0	-2.905255	-0.887927	-1.013470
11	6	0	-1.684246	-0.226565	-1.162596
12	6	0	1.295875	-0.153574	1.451039
13	1	0	-0.866723	2.949174	-1.304307
14	1	0	0.968123	3.141724	-1.090320
15	1	0	3.143132	-1.617399	-0.393178
16	1	0	0.588834	-2.155716	-0.665045
17	1	0	2.527144	2.477143	0.683619
18	1	0	2.817891	1.867402	-0.964643
19	1	0	3.496810	1.012058	0.432280
20	1	0	-1.588912	1.422377	1.808945
21	1	0	-3.754222	0.239634	2.083398
22	1	0	-4.604553	-1.245579	0.272151
23	1	0	-3.277208	-1.524679	-1.817205
24	1	0	-1.109257	-0.341090	-2.082621
25	1	0	0.315153	-0.307175	1.900478
26	1	0	2.089373	0.012051	2.181175

Transition state; **$13a_{out} \rightarrow 15a$** **($T_{15a}$)**

Zero-point correction=	0.203184 (Hartree/Particle)
Thermal correction to Energy=	0.215577
Thermal correction to Enthalpy=	0.216521
Thermal correction to Gibbs Free Energy=	0.163177
Sum of electronic and zero-point Energies=	-2504.368462
Sum of electronic and thermal Energies=	-2504.356070
Sum of electronic and thermal Enthalpies=	-2504.355126
Sum of electronic and thermal Free Energies=	-2504.408470

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.124317	1.395281	-0.370433
2	6	0	-0.276574	2.590186	-0.971229
3	6	0	1.193578	0.975283	0.206468
4	6	0	1.187472	0.065711	1.338922
5	1	0	-1.253553	2.899080	-1.341396
6	1	0	0.548567	3.285785	-1.111467
7	1	0	1.938686	0.247791	2.107643
8	1	0	0.218650	-0.265079	1.711622
9	32	0	1.980751	-1.292252	-0.063590
10	1	0	1.552201	-0.001092	-1.041849
11	1	0	3.469239	-0.722939	0.112437
12	6	0	2.333499	1.969845	0.115331
13	1	0	2.564805	2.252379	-0.919189
14	1	0	2.056892	2.883863	0.665137
15	1	0	3.239752	1.551475	0.564429
16	6	0	-1.320680	0.517412	-0.188561
17	6	0	-1.429512	-0.729943	-0.822584
18	6	0	-2.386242	0.957796	0.612717
19	6	0	-2.572821	-1.512862	-0.658017
20	1	0	-0.619318	-1.086320	-1.458597
21	6	0	-3.528274	0.172939	0.778723
22	1	0	-2.307836	1.923199	1.114666
23	6	0	-3.624586	-1.066545	0.144336
24	1	0	-2.642130	-2.476127	-1.164586
25	1	0	-4.343657	0.531067	1.408327
26	1	0	-4.515579	-1.681647	0.273645

1-(2-methyl-3-phenyl-3-butenyl)germylene (**15a**)

Zero-point correction=	0.206360	(Hartree/Particle)
Thermal correction to Energy=	0.219806	
Thermal correction to Enthalpy=	0.220750	
Thermal correction to Gibbs Free Energy=	0.164099	
Sum of electronic and zero-point Energies=	-2504.375335	
Sum of electronic and thermal Energies=	-2504.361889	
Sum of electronic and thermal Enthalpies=	-2504.360945	
Sum of electronic and thermal Free Energies=	-2504.417596	

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.288527	-0.307832	-0.369619
2	1	0	-1.218149	-0.422446	-1.469338
3	1	0	-0.694567	-1.144469	0.036336
4	6	0	-0.734218	1.052070	0.088035
5	1	0	-1.402883	1.844462	-0.290881
6	6	0	0.634254	1.333163	-0.525772
7	6	0	0.815283	2.357163	-1.371536
8	1	0	-0.004010	3.034592	-1.621495
9	1	0	1.783920	2.553156	-1.832482
10	1	0	-3.172414	-2.127936	-0.527534
11	32	0	-3.238192	-0.616059	0.018616
12	6	0	-0.739471	1.138866	1.622535
13	1	0	-1.767097	1.014419	1.999655
14	1	0	-0.122441	0.347720	2.071383
15	1	0	-0.368504	2.110453	1.975879
16	6	0	1.764255	0.404627	-0.220066
17	6	0	2.449683	0.457569	1.004909
18	6	0	2.178456	-0.540232	-1.172730
19	6	0	3.512431	-0.408213	1.267824
20	1	0	2.164492	1.201961	1.748665
21	6	0	3.239560	-1.408347	-0.909336
22	1	0	1.659153	-0.587754	-2.130806
23	6	0	3.908638	-1.347362	0.313810
24	1	0	4.038958	-0.342158	2.220800
25	1	0	3.545114	-2.133229	-1.664909
26	1	0	4.738507	-2.023735	0.520671

Transition state; **15a → 15a-π** ($TS_{15a<>15a-\pi}$)

Zero-point correction=	0.206428 (Hartree/Particle)
Thermal correction to Energy=	0.218987
Thermal correction to Enthalpy=	0.219931
Thermal correction to Gibbs Free Energy=	0.166013
Sum of electronic and zero-point Energies=	-2504.371578
Sum of electronic and thermal Energies=	-2504.359018
Sum of electronic and thermal Enthalpies=	-2504.358074
Sum of electronic and thermal Free Energies=	-2504.411992

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.298334	-0.115465	-0.636879
2	1	0	0.685213	-1.012560	-0.437908
3	1	0	1.278240	-0.031153	-1.738731
4	6	0	0.725986	1.149206	0.051928
5	1	0	1.500861	1.577919	0.712212
6	6	0	-0.436478	0.802997	0.976811
7	6	0	-0.338297	0.993104	2.300694
8	1	0	0.561530	1.424958	2.743322
9	1	0	-1.154129	0.734798	2.976656
10	1	0	3.175842	-1.891758	-1.118047
11	32	0	3.173485	-0.618225	-0.131725
12	6	0	0.386772	2.231296	-0.987250
13	1	0	1.293464	2.507366	-1.545475
14	1	0	-0.352292	1.871557	-1.716256
15	1	0	-0.005296	3.140336	-0.509934
16	6	0	-1.665188	0.175976	0.404288
17	6	0	-2.577772	0.907174	-0.374687
18	6	0	-1.948271	-1.175801	0.661855
19	6	0	-3.730621	0.304727	-0.880023
20	1	0	-2.399218	1.965780	-0.561761
21	6	0	-3.098351	-1.780779	0.151554
22	1	0	-1.255636	-1.753014	1.276370
23	6	0	-3.992630	-1.042653	-0.624311
24	1	0	-4.432338	0.894736	-1.470957
25	1	0	-3.296037	-2.832166	0.364127
26	1	0	-4.892615	-1.512281	-1.022299

1-(2-methyl-3-phenyl-3-butenyl)germylene π-complex (**15a-π**)

```
Zero-point correction=                           0.208829 (Hartree/Particle)
Thermal correction to Energy=                    0.221114
Thermal correction to Enthalpy=                  0.222058
Thermal correction to Gibbs Free Energy=         0.169645
Sum of electronic and zero-point Energies=      -2504.397058
Sum of electronic and thermal Energies=         -2504.384773
Sum of electronic and thermal Enthalpies=       -2504.383828
Sum of electronic and thermal Free Energies=    -2504.436242
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.324448	0.896215	-0.627631
2	1	0	-3.149820	1.269683	-0.005350
3	1	0	-2.566347	1.104717	-1.675432
4	6	0	-0.957773	1.469987	-0.209375
5	1	0	-0.411515	1.740786	-1.122656
6	6	0	-0.179697	0.328991	0.469634
7	6	0	-0.873969	-0.437460	1.421996
8	1	0	-1.691268	0.021129	1.982755
9	1	0	-0.370243	-1.257096	1.932488
10	1	0	-0.895167	-1.338452	-1.327160
11	32	0	-2.054596	-1.109842	-0.263928
12	6	0	-1.010525	2.718972	0.682853
13	1	0	-1.522241	3.538489	0.158194
14	1	0	-1.566363	2.514629	1.609587
15	1	0	-0.002795	3.062383	0.959813
16	6	0	1.236434	0.083427	0.159244
17	6	0	1.801678	0.410177	-1.091139
18	6	0	2.098426	-0.441885	1.146020
19	6	0	3.156013	0.215734	-1.343091
20	1	0	1.161849	0.781832	-1.890914
21	6	0	3.453782	-0.637402	0.892758
22	1	0	1.702407	-0.668228	2.135879
23	6	0	3.991310	-0.310112	-0.353404
24	1	0	3.562353	0.464747	-2.323946
25	1	0	4.096521	-1.037263	1.677820
26	1	0	5.052315	-0.462297	-0.552588

"in" GeH_2-**6** π-complex; $C^1=C^2$ (**13a$_{in}$**)

Zero-point correction=	0.203800 (Hartree/Particle)
Thermal correction to Energy=	0.217060
Thermal correction to Enthalpy=	0.218005
Thermal correction to Gibbs Free Energy=	0.163373
Sum of electronic and zero-point Energies=	-2504.372753
Sum of electronic and thermal Energies=	-2504.359493
Sum of electronic and thermal Enthalpies=	-2504.358549
Sum of electronic and thermal Free Energies=	-2504.413180

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.091116	1.251482	-0.434544
2	6	0	0.145862	2.236697	-1.349072
3	6	0	1.284980	0.858610	0.373191
4	6	0	1.135465	0.183929	1.597946
5	1	0	-0.748108	2.525187	-1.900453
6	1	0	1.062403	2.779998	-1.572768
7	1	0	1.957255	0.161343	2.308805
8	1	0	0.163926	-0.160744	1.940077
9	32	0	1.775760	-1.254957	-0.160460
10	1	0	3.013353	-1.503219	0.791021
11	1	0	0.677060	-2.136797	0.542367
12	6	0	2.572544	1.629054	0.145209
13	1	0	2.856148	1.663244	-0.913015
14	1	0	2.444451	2.663603	0.500771
15	1	0	3.398386	1.177803	0.708671
16	6	0	-1.212897	0.559221	-0.191657
17	6	0	-2.005308	0.880096	0.921370
18	6	0	-1.684846	-0.397207	-1.101550
19	6	0	-3.237971	0.257178	1.119890
20	1	0	-1.657731	1.636688	1.626716
21	6	0	-2.917259	-1.022286	-0.901521
22	1	0	-1.073864	-0.650269	-1.968996
23	6	0	-3.695757	-0.698570	0.210407
24	1	0	-3.845574	0.523487	1.985572
25	1	0	-3.269134	-1.764733	-1.618627
26	1	0	-4.658471	-1.186186	0.366552

Transition state; **13a$_{in}$ → 14a** (**T$_{14a,in}$**)

Zero-point correction=	0.203466 (Hartree/Particle)
Thermal correction to Energy=	0.216028
Thermal correction to Enthalpy=	0.216972
Thermal correction to Gibbs Free Energy=	0.163886
Sum of electronic and zero-point Energies=	-2504.370882
Sum of electronic and thermal Energies=	-2504.358320
Sum of electronic and thermal Enthalpies=	-2504.357375
Sum of electronic and thermal Free Energies=	-2504.410461

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.122925	1.305429	-0.349703
2	6	0	0.140398	2.436610	-1.078111
3	6	0	1.351847	0.755710	0.293743
4	6	0	1.254304	-0.028866	1.524509
5	1	0	-0.779009	2.822472	-1.516973
6	1	0	1.050180	3.008124	-1.254621
7	1	0	2.082059	0.027717	2.228494
8	1	0	0.275891	-0.239370	1.948797
9	32	0	1.671873	-1.243090	-0.170582
10	1	0	3.056033	-1.730664	0.316916
11	1	0	0.526973	-2.245672	0.065201
12	6	0	2.641597	1.529168	0.093930
13	1	0	2.850159	1.725618	-0.964470
14	1	0	2.572694	2.494789	0.621778
15	1	0	3.494421	0.982555	0.516410
16	6	0	-1.181004	0.595997	-0.153762
17	6	0	-1.951100	0.806668	0.999937
18	6	0	-1.675690	-0.263422	-1.145304
19	6	0	-3.182263	0.169116	1.160377
20	1	0	-1.586348	1.489046	1.769150
21	6	0	-2.906604	-0.902889	-0.984244
22	1	0	-1.088099	-0.425465	-2.050041
23	6	0	-3.661597	-0.690716	0.170019
24	1	0	-3.771519	0.349080	2.060298
25	1	0	-3.277062	-1.566816	-1.766180
26	1	0	-4.623170	-1.189359	0.295529

Transition state; **13a$_{in}$ → 19a-π (T$_{16a}$)**

Zero-point correction=	0.203354 (Hartree/Particle)
Thermal correction to Energy=	0.215901
Thermal correction to Enthalpy=	0.216845
Thermal correction to Gibbs Free Energy=	0.163485
Sum of electronic and zero-point Energies=	-2504.364149
Sum of electronic and thermal Energies=	-2504.351603
Sum of electronic and thermal Enthalpies=	-2504.350658
Sum of electronic and thermal Free Energies=	-2504.404018

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.074162	1.247815	-0.469432
2	6	0	0.108332	2.250567	-1.366998
3	6	0	1.271741	0.833622	0.320533
4	6	0	1.075356	0.156320	1.571373
5	1	0	-0.789436	2.529293	-1.917020
6	1	0	1.015900	2.812489	-1.582108
7	1	0	1.852973	0.223568	2.330378
8	1	0	0.063244	-0.008908	1.939813
9	32	0	1.802861	-1.260612	-0.140307
10	1	0	3.265058	-1.071651	0.482611
11	1	0	1.127114	-1.493235	1.343092
12	6	0	2.519533	1.692556	0.176198
13	1	0	2.887762	1.723190	-0.857505
14	1	0	2.299272	2.728690	0.479511
15	1	0	3.330109	1.309106	0.806616
16	6	0	-1.224245	0.541253	-0.227310
17	6	0	-2.097242	0.982707	0.779466
18	6	0	-1.606187	-0.555938	-1.012750
19	6	0	-3.317788	0.341727	0.998672
20	1	0	-1.818670	1.847284	1.384791
21	6	0	-2.827345	-1.197445	-0.793978
22	1	0	-0.940674	-0.901389	-1.804161
23	6	0	-3.684510	-0.753412	0.213804
24	1	0	-3.986625	0.703227	1.780727
25	1	0	-3.110452	-2.046115	-1.417767
26	1	0	-4.637977	-1.254603	0.383365

1-(3-methyl-2-phenyl-2-butenyl)germylene π-complex (**19a-π**)

```
 Zero-point correction=                           0.207648 (Hartree/Particle)
 Thermal correction to Energy=                    0.220747
 Thermal correction to Enthalpy=                  0.221691
 Thermal correction to Gibbs Free Energy=         0.167311
 Sum of electronic and zero-point Energies=          -2504.396514
 Sum of electronic and thermal Energies=             -2504.383415
 Sum of electronic and thermal Enthalpies=           -2504.382470
 Sum of electronic and thermal Free Energies=        -2504.436850
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.383608	0.425499	0.541496
2	6	0	-0.979015	-0.409016	1.591172
3	6	0	-1.112726	1.352917	-0.203110
4	6	0	-0.518793	2.099157	-1.368177
5	1	0	-0.268360	-1.026321	2.139719
6	1	0	-1.772931	0.011530	2.207727
7	1	0	-1.218998	2.106286	-2.216380
8	1	0	-0.361306	3.155331	-1.089545
9	32	0	-1.735925	-1.281015	-0.193949
10	1	0	-3.152068	-0.590875	0.095279
11	1	0	0.437617	1.692393	-1.707917
12	6	0	-2.405083	1.960386	0.287081
13	1	0	-2.855018	1.423909	1.126258
14	1	0	-2.195679	2.997174	0.606365
15	1	0	-3.151354	2.022852	-0.516180
16	6	0	1.061219	0.147138	0.234044
17	6	0	2.008618	0.534750	1.195165
18	6	0	1.513422	-0.473870	-0.939100
19	6	0	3.371259	0.328795	0.979593
20	1	0	1.667885	1.006700	2.118259
21	6	0	2.877040	-0.685867	-1.151852
22	1	0	0.786750	-0.809646	-1.679868
23	6	0	3.810636	-0.282281	-0.196600
24	1	0	4.091402	0.643829	1.735578
25	1	0	3.208830	-1.176297	-2.067709
26	1	0	4.875032	-0.450050	-0.363496

"out" GeH_2-**6** π-complex; C^3=C^4 (**13b$_{out}$**)

Zero-point correction=	0.204253 (Hartree/Particle)
Thermal correction to Energy=	0.217469
Thermal correction to Enthalpy=	0.218413
Thermal correction to Gibbs Free Energy=	0.163910
Sum of electronic and zero-point Energies=	-2504.379466
Sum of electronic and thermal Energies=	-2504.366250
Sum of electronic and thermal Enthalpies=	-2504.365306
Sum of electronic and thermal Free Energies=	-2504.419808

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	-1.888438	-1.400797	-0.299370
2	1	0	-2.182125	-0.307409	-1.395592
3	1	0	-0.558989	-1.994785	-0.896269
4	6	0	-0.361385	0.532920	0.455863
5	6	0	-1.138651	-0.270990	1.333272
6	6	0	-0.867179	1.834150	-0.005936
7	6	0	-0.045954	2.765857	-0.543681
8	6	0	-2.315886	2.177312	0.245229
9	6	0	1.060130	0.165313	0.206153
10	6	0	1.896122	-0.146644	1.290992
11	6	0	3.238356	-0.474849	1.092157
12	6	0	3.770050	-0.496992	-0.196602
13	6	0	2.949995	-0.184944	-1.285733
14	6	0	1.612700	0.146018	-1.086785
15	1	0	-0.616535	-1.031489	1.915908
16	1	0	-1.999496	0.163631	1.839253
17	1	0	-0.435854	3.744260	-0.823777
18	1	0	1.017178	2.592454	-0.693441
19	1	0	-2.526095	2.261209	1.322525
20	1	0	-2.992515	1.413371	-0.162654
21	1	0	-2.566067	3.139203	-0.216719
22	1	0	1.493475	-0.113755	2.304364
23	1	0	3.869472	-0.710345	1.949809
24	1	0	4.816535	-0.758870	-0.355088
25	1	0	3.353732	-0.213449	-2.298422
26	1	0	0.967525	0.358572	-1.939626

Transition state; **$13b_{out} \rightarrow 14b$** **($T_{14b,out}$)**

Zero-point correction=	0.204071 (Hartree/Particle)
Thermal correction to Energy=	0.216465
Thermal correction to Enthalpy=	0.217409
Thermal correction to Gibbs Free Energy=	0.165139
Sum of electronic and zero-point Energies=	-2504.373138
Sum of electronic and thermal Energies=	-2504.360744
Sum of electronic and thermal Enthalpies=	-2504.359799
Sum of electronic and thermal Free Energies=	-2504.412069

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.993408	1.693170	-0.097823
2	6	0	-0.222340	2.617082	-0.710007
3	6	0	-0.475387	0.365321	0.315696
4	6	0	-1.173851	-0.388748	1.393631
5	1	0	-0.642248	3.582582	-0.990938
6	1	0	0.828045	2.446896	-0.936773
7	1	0	-0.562121	-1.025868	2.032584
8	1	0	-2.005548	0.078075	1.920531
9	32	0	-1.704235	-1.324134	-0.257997
10	1	0	-2.769633	-0.691034	-1.156577
11	1	0	-0.675364	-2.227573	-0.938213
12	6	0	-2.425742	2.038273	0.238156
13	1	0	-3.135700	1.276416	-0.117169
14	1	0	-2.573152	2.133981	1.325244
15	1	0	-2.703702	2.995347	-0.217960
16	6	0	0.994395	0.109591	0.155637
17	6	0	1.580121	-0.062023	-1.109552
18	6	0	1.835756	0.079605	1.279095
19	6	0	2.952811	-0.258947	-1.246940
20	1	0	0.937974	-0.053232	-1.991948
21	6	0	3.210970	-0.126459	1.146522
22	1	0	1.409640	0.230934	2.272583
23	6	0	3.775674	-0.295211	-0.117363
24	1	0	3.382579	-0.396691	-2.239999
25	1	0	3.842213	-0.149241	2.035875
26	1	0	4.848548	-0.458246	-0.223667

2-phenyl-2-(1-methylethenyl)germirane (**14b**)

```
 Zero-point correction=                           0.203961 (Hartree/Particle)
 Thermal correction to Energy=                    0.216937
 Thermal correction to Enthalpy=                  0.217881
 Thermal correction to Gibbs Free Energy=         0.164322
 Sum of electronic and zero-point Energies=          -2504.377031
 Sum of electronic and thermal Energies=             -2504.364056
 Sum of electronic and thermal Enthalpies=           -2504.363112
 Sum of electronic and thermal Free Energies=        -2504.416670
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	1.677113	-1.252297	-0.367846
2	6	0	0.550605	0.274749	0.278024
3	6	0	1.029126	1.689053	0.074938
4	6	0	1.762323	2.078320	-0.975840
5	6	0	0.621243	2.652250	1.162709
6	6	0	-0.923593	0.057140	0.118187
7	6	0	-1.630927	-0.932999	0.824271
8	6	0	-3.000232	-1.122304	0.626901
9	6	0	-3.704253	-0.322926	-0.272817
10	6	0	-3.018232	0.669957	-0.977755
11	6	0	-1.651197	0.854018	-0.787966
12	6	0	1.290234	-0.492109	1.391455
13	1	0	2.099066	3.111167	-1.079145
14	1	0	2.042156	1.378061	-1.763526
15	1	0	1.017104	3.658637	0.979422
16	1	0	-0.475173	2.714783	1.235329
17	1	0	0.980865	2.309147	2.145002
18	1	0	-1.116895	-1.573978	1.540210
19	1	0	-3.519000	-1.900356	1.188693
20	1	0	-4.774118	-0.469138	-0.422537
21	1	0	-3.552981	1.307008	-1.683742
22	1	0	-1.125963	1.626267	-1.351891
23	1	0	0.707701	-1.047539	2.126908
24	1	0	2.124265	0.054134	1.835158
25	1	0	3.068983	-1.023172	-0.961458
26	1	0	0.905786	-2.502404	-0.790001

Transition state; **$13b_{out} \rightarrow 15b$ (T_{15b})**

Zero-point correction=	0.203406 (Hartree/Particle)
Thermal correction to Energy=	0.215766
Thermal correction to Enthalpy=	0.216710
Thermal correction to Gibbs Free Energy=	0.164269
Sum of electronic and zero-point Energies=	-2504.368855
Sum of electronic and thermal Energies=	-2504.356495
Sum of electronic and thermal Enthalpies=	-2504.355551
Sum of electronic and thermal Free Energies=	-2504.407993

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.823374	1.839559	-0.037859
2	6	0	0.087337	2.770356	-0.371041
3	6	0	-0.413329	0.440822	0.320740
4	6	0	-1.171895	-0.247262	1.359392
5	1	0	-0.226418	3.789973	-0.595887
6	1	0	1.153305	2.555370	-0.410270
7	1	0	-0.608857	-0.929960	1.993938
8	1	0	-1.942564	0.316774	1.881762
9	32	0	-1.937638	-1.336435	-0.265744
10	1	0	-1.057472	-0.130296	-1.031689
11	1	0	-0.678378	-2.319947	-0.289614
12	6	0	-2.291502	2.167053	0.019681
13	1	0	-2.482680	3.158132	-0.407843
14	1	0	-2.883952	1.425020	-0.538295
15	1	0	-2.670757	2.167099	1.052282
16	6	0	1.030926	0.076462	0.136383
17	6	0	1.607434	-0.026195	-1.138912
18	6	0	1.853820	-0.103516	1.257591
19	6	0	2.961437	-0.313939	-1.289952
20	1	0	0.975333	0.100627	-2.019409
21	6	0	3.212480	-0.389540	1.107838
22	1	0	1.429981	-0.004008	2.257296
23	6	0	3.770849	-0.497974	-0.165196
24	1	0	3.386565	-0.404305	-2.290092
25	1	0	3.835057	-0.525808	1.992734
26	1	0	4.830166	-0.727699	-0.283086

1-(3-methyl-2-phenyl-3-butenyl)germylene (**15b**)

Zero-point correction=	0.207360 (Hartree/Particle)
Thermal correction to Energy=	0.220261
Thermal correction to Enthalpy=	0.221206
Thermal correction to Gibbs Free Energy=	0.166794
Sum of electronic and zero-point Energies=	-2504.380028
Sum of electronic and thermal Energies=	-2504.367126
Sum of electronic and thermal Enthalpies=	-2504.366182
Sum of electronic and thermal Free Energies=	-2504.420593

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.203909	-1.781631	0.264248
2	1	0	0.562361	-2.735031	-0.150467
3	1	0	0.329284	-1.827558	1.353558
4	6	0	0.995702	-0.615737	-0.360183
5	1	0	0.975739	-0.764395	-1.454812
6	6	0	2.463087	-0.571049	0.047203
7	6	0	3.430356	-0.792990	-0.853297
8	1	0	3.198325	-1.005761	-1.898299
9	1	0	4.484736	-0.780481	-0.572789
10	1	0	-2.336354	-1.865021	1.209709
11	32	0	-1.762076	-1.499440	-0.255847
12	6	0	2.769527	-0.274750	1.490296
13	1	0	2.337032	-1.037014	2.155967
14	1	0	3.851252	-0.241611	1.667961
15	1	0	2.338023	0.691400	1.794696
16	6	0	0.291058	0.719472	-0.121828
17	6	0	-0.860838	0.810396	0.680112
18	6	0	0.725410	1.878583	-0.779807
19	6	0	-1.577413	2.012444	0.793174
20	1	0	-1.137021	-0.017758	1.352497
21	6	0	0.021812	3.075450	-0.662249
22	1	0	1.620703	1.830013	-1.402443
23	6	0	-1.138417	3.146046	0.119036
24	1	0	-2.467671	2.052312	1.421265
25	1	0	0.372650	3.961793	-1.192527
26	1	0	-1.687772	4.083791	0.202558

Transition state; **15b → 15b-π** ($TS_{15b<>15b-\pi}$)

```
 Zero-point correction=                           0.206167 (Hartree/Particle)
 Thermal correction to Energy=                    0.218767
 Thermal correction to Enthalpy=                  0.219711
 Thermal correction to Gibbs Free Energy=         0.166133
 Sum of electronic and zero-point Energies=          -2504.372670
 Sum of electronic and thermal Energies=             -2504.360070
 Sum of electronic and thermal Enthalpies=           -2504.359126
 Sum of electronic and thermal Free Energies=        -2504.412704
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.234321	-0.055819	-0.749503
2	1	0	-1.704493	0.725458	-1.373328
3	1	0	-0.797895	-0.759463	-1.477117
4	6	0	-0.186969	0.529981	0.231986
5	1	0	-0.528884	0.333411	1.262556
6	6	0	-0.102218	2.051958	0.117622
7	6	0	-0.554328	2.828248	1.111718
8	1	0	-0.966186	2.400801	2.027449
9	1	0	-0.524233	3.916731	1.042666
10	1	0	-3.435769	-1.376203	-1.308887
11	32	0	-2.774803	-1.013609	0.115462
12	6	0	0.484445	2.634486	-1.138776
13	1	0	-0.021302	2.251102	-2.038830
14	1	0	0.404379	3.728359	-1.141464
15	1	0	1.546774	2.365219	-1.237840
16	6	0	1.192785	-0.115508	0.128071
17	6	0	1.781921	-0.461291	-1.096479
18	6	0	1.926378	-0.348679	1.300207
19	6	0	3.060647	-1.020750	-1.147362
20	1	0	1.238939	-0.293911	-2.028160
21	6	0	3.202151	-0.911489	1.255917
22	1	0	1.485349	-0.083623	2.263506
23	6	0	3.775984	-1.249466	0.028887
24	1	0	3.498164	-1.280925	-2.112136
25	1	0	3.748019	-1.090014	2.183212
26	1	0	4.771988	-1.691476	-0.010122

1-(3-methyl-2-phenyl-3-butenyl)germylene π-complex (**15b-π**)

```
Zero-point correction=                           0.208189 (Hartree/Particle)
Thermal correction to Energy=                    0.220737
Thermal correction to Enthalpy=                  0.221681
Thermal correction to Gibbs Free Energy=         0.166807
Sum of electronic and zero-point Energies=      -2504.394298
Sum of electronic and thermal Energies=         -2504.381750
Sum of electronic and thermal Enthalpies=       -2504.380806
Sum of electronic and thermal Free Energies=    -2504.435681
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.783225	-1.390918	-0.089383
2	1	0	-0.390835	-1.621192	-1.089648
3	1	0	-0.767474	-2.312673	0.502602
4	6	0	-0.008436	-0.239799	0.592904
5	1	0	-0.058414	-0.427771	1.676871
6	6	0	-0.833843	1.026194	0.350936
7	6	0	-1.452732	1.220056	-0.879870
8	1	0	-1.073139	0.725147	-1.775335
9	1	0	-2.038331	2.123503	-1.050958
10	1	0	-2.793865	-0.187832	1.273792
11	32	0	-2.657512	-0.543690	-0.277919
12	6	0	-0.938895	2.042788	1.445062
13	1	0	-1.080008	1.579659	2.429440
14	1	0	0.007829	2.610421	1.487750
15	1	0	-1.749630	2.760147	1.265949
16	6	0	1.468697	-0.129214	0.237125
17	6	0	1.957267	0.778576	-0.711385
18	6	0	2.381846	-0.999364	0.853739
19	6	0	3.316007	0.814378	-1.037204
20	1	0	1.271756	1.472423	-1.199970
21	6	0	3.736497	-0.970603	0.527802
22	1	0	2.019443	-1.710832	1.599271
23	6	0	4.210172	-0.061217	-0.422123
24	1	0	3.675337	1.531859	-1.776219
25	1	0	4.427516	-1.655705	1.020810
26	1	0	5.270068	-0.034329	-0.676560

"in" GeH_2-**6** π-complex; C^3=C^4 (**13b$_{in}$**)

Zero-point correction=	0.203720 (Hartree/Particle)
Thermal correction to Energy=	0.216937
Thermal correction to Enthalpy=	0.217881
Thermal correction to Gibbs Free Energy=	0.163832
Sum of electronic and zero-point Energies=	-2504.372644
Sum of electronic and thermal Energies=	-2504.359426
Sum of electronic and thermal Enthalpies=	-2504.358482
Sum of electronic and thermal Free Energies=	-2504.412531

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.093761	1.653943	-0.166885
2	6	0	-0.346344	2.528993	-0.862593
3	6	0	-0.483227	0.446292	0.471612
4	6	0	-1.062269	-0.113973	1.627040
5	1	0	-0.802631	3.422374	-1.289081
6	1	0	0.722048	2.393597	-1.016718
7	1	0	-0.490150	-0.797314	2.247757
8	1	0	-1.998445	0.259003	2.031825
9	32	0	-1.576489	-1.367856	-0.305893
10	1	0	-0.851345	-2.512234	0.502843
11	1	0	-2.981735	-1.343499	0.416585
12	6	0	0.975262	0.173300	0.216762
13	6	0	1.464484	-0.134011	-1.062599
14	6	0	1.888436	0.266790	1.277266
15	6	0	2.824936	-0.350746	-1.271635
16	1	0	0.759267	-0.222037	-1.890222
17	6	0	3.252032	0.050423	1.068803
18	1	0	1.526082	0.527827	2.272472
19	6	0	3.724524	-0.260421	-0.205941
20	1	0	3.184258	-0.600170	-2.270545
21	1	0	3.945558	0.128600	1.906706
22	1	0	4.788387	-0.434493	-0.369915
23	6	0	-2.562194	1.908675	0.056944
24	1	0	-3.174386	1.043894	-0.237716
25	1	0	-2.779015	2.112991	1.116657
26	1	0	-2.891536	2.777264	-0.524705

Transition state; **$13b_{in} \rightarrow 14b$ ($TS_{14b,in}$)**

```
Zero-point correction=                           0.203520 (Hartree/Particle)
Thermal correction to Energy=                    0.216093
Thermal correction to Enthalpy=                  0.217037
Thermal correction to Gibbs Free Energy=         0.164117
Sum of electronic and zero-point Energies=          -2504.370893
Sum of electronic and thermal Energies=             -2504.358320
Sum of electronic and thermal Enthalpies=           -2504.357376
Sum of electronic and thermal Free Energies=        -2504.410296
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.048610	1.654451	-0.132981
2	6	0	-0.245782	2.576375	-0.693694
3	6	0	-0.506505	0.355948	0.380025
4	6	0	-1.137341	-0.287849	1.531772
5	1	0	-0.656721	3.526607	-1.035165
6	1	0	0.823759	2.422250	-0.820407
7	1	0	-0.515774	-0.900536	2.179843
8	1	0	-2.000124	0.176854	2.002632
9	32	0	-1.598833	-1.295893	-0.291125
10	1	0	-0.941042	-2.633636	0.114852
11	1	0	-3.129212	-1.280107	-0.073624
12	6	0	0.965301	0.105468	0.175908
13	6	0	1.504297	-0.153258	-1.093458
14	6	0	1.839066	0.184633	1.269727
15	6	0	2.875998	-0.328580	-1.264328
16	1	0	0.827150	-0.231408	-1.945812
17	6	0	3.214221	0.009053	1.100635
18	1	0	1.436440	0.398744	2.260594
19	6	0	3.737321	-0.248559	-0.166288
20	1	0	3.274670	-0.538018	-2.257561
21	1	0	3.877142	0.074288	1.964174
22	1	0	4.809979	-0.393134	-0.298720
23	6	0	-2.518613	1.934799	0.048453
24	1	0	-3.141910	1.151416	-0.407412
25	1	0	-2.794185	1.987971	1.112338
26	1	0	-2.783653	2.892394	-0.414344

Transition state; **$13b_{in} \rightarrow 17b\text{-}\pi$ (T_{16b})**

Zero-point correction=	0.202931 (Hartree/Particle)
Thermal correction to Energy=	0.215527
Thermal correction to Enthalpy=	0.216471
Thermal correction to Gibbs Free Energy=	0.163504
Sum of electronic and zero-point Energies=	-2504.364252
Sum of electronic and thermal Energies=	-2504.351656
Sum of electronic and thermal Enthalpies=	-2504.350712
Sum of electronic and thermal Free Energies=	-2504.403679

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.071253	1.650733	-0.198691
2	6	0	-0.317652	2.521769	-0.893249
3	6	0	-0.499953	0.403693	0.403954
4	6	0	-1.098909	-0.109035	1.608229
5	1	0	-0.765805	3.420671	-1.316504
6	1	0	0.748399	2.373923	-1.054051
7	1	0	-0.500246	-0.738527	2.263411
8	1	0	-1.899274	0.446971	2.094561
9	32	0	-1.625310	-1.365633	-0.292494
10	1	0	-0.495029	-2.374801	0.204089
11	1	0	-2.275893	-1.221497	1.216851
12	6	0	0.968856	0.145648	0.197057
13	6	0	1.484626	-0.203668	-1.060744
14	6	0	1.870163	0.304880	1.259637
15	6	0	2.850558	-0.405162	-1.246573
16	1	0	0.796783	-0.327149	-1.899820
17	6	0	3.239625	0.095518	1.079817
18	1	0	1.495932	0.609701	2.238391
19	6	0	3.734990	-0.260550	-0.173943
20	1	0	3.226621	-0.686382	-2.230892
21	1	0	3.920445	0.220415	1.922684
22	1	0	4.803435	-0.424241	-0.317073
23	6	0	-2.538675	1.923972	0.023107
24	1	0	-3.157226	1.052734	-0.244320
25	1	0	-2.755433	2.166489	1.075268
26	1	0	-2.867043	2.775149	-0.584400

1-(*Z*-2-methyl-3-phenyl-2-butenyl)germylene π-complex (**17b-π**)

```
 Zero-point correction=                           0.207770 (Hartree/Particle)
 Thermal correction to Energy=                    0.220929
 Thermal correction to Enthalpy=                  0.221873
 Thermal correction to Gibbs Free Energy=         0.167696
 Sum of electronic and zero-point Energies=          -2504.398126
 Sum of electronic and thermal Energies=             -2504.384966
 Sum of electronic and thermal Enthalpies=           -2504.384022
 Sum of electronic and thermal Free Energies=        -2504.438199
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.263111	0.970402	-0.349644
2	6	0	-1.306593	0.332484	-1.635995
3	6	0	-0.286734	0.648571	0.624536
4	6	0	-0.421657	1.143289	2.049947
5	1	0	-2.113720	0.623783	-2.305867
6	1	0	-0.392596	-0.010274	-2.113431
7	1	0	0.166907	0.516678	2.730829
8	1	0	-0.024213	2.168610	2.145187
9	32	0	-1.776932	-1.205065	-0.110670
10	1	0	-0.370794	-1.840328	-0.516478
11	1	0	-1.456965	1.145407	2.408234
12	6	0	1.112859	0.283137	0.239730
13	6	0	1.856950	-0.655970	0.975429
14	6	0	1.764537	0.965332	-0.801353
15	6	0	3.187469	-0.923204	0.666511
16	1	0	1.372043	-1.209467	1.781343
17	6	0	3.099023	0.698239	-1.114023
18	1	0	1.219145	1.722039	-1.366766
19	6	0	3.816575	-0.249150	-0.384471
20	1	0	3.736140	-1.668786	1.243283
21	1	0	3.580653	1.242224	-1.927703
22	1	0	4.858172	-0.459744	-0.628212
23	6	0	-2.462414	1.815906	0.022511
24	1	0	-2.866598	1.587060	1.015297
25	1	0	-2.159718	2.875037	0.027543
26	1	0	-3.268069	1.695635	-0.710891

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