Supplementary Information

Di- and Trivalent Organogermanium Reactive Intermediates. Kinetics and Mechanisms of Some Reactions of Diphenylgermylene and Tetraphenyldigermene in Solution.

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Figure SI-1. Transient absorption spectra of Ph_2Ge-amine complexes in hexane solution at 23 ^oC. The spectra were recorded 2.8-3.1 μs, 1.65-1.78 μs, and 4.4-5.1 μs after the laser pulse for solutions containing 0.13 mM n-$BuNH_2$ (black), 0.66 mM Et_2NH (blue), and 5.0 mM Et_3N (red), respectively. The species decayed with mixed order kinetics under these conditions, with lifetimes of 50-200 μs.

Figure SI-2. Plot of $(\Delta A_{500,0} - \Delta A_{500,res})/(\Delta A_{500,res})$ ("*span/plateau*") vs. [isoprene] in hexane solution at 23 ^oC (see Eqn. 7 in the paper). The $\Delta A_{500,0}$ and $\Delta A_{500,res}$ used are the best-fit values of the initial and residual transient absorbances from non-linear least squares analysis of the ΔA_{500} vs. time data of Figure 5(a) to a single exponential decay.

Figure SI-3. Reversible scavenging of Ph_2Ge by 4,4-dimethyl-1-pentene (DMP). Raw transient growth/decay profiles recorded at **(a)** 500 nm and **(b)** 440 nm on the same time scale in the presence of DMP at the concentrations listed in (a); **(c)** 440 nm data from a different experiment, recorded over a longer time scale; (**d**) the data of (a) after subtraction of the data from (b) scaled by 0.15, and fit to a single exponential decay.

Figure SI-4. **(a)** plots of k_{decay} (from Fig. SI-3d) and $\Delta A_{440,0}/\Delta A_{440,Q}$ (from Fig. SI-3c) vs [Q]; **(b)** plot of *span*/*plateau* values vs. [DMP], from the fits of the data in Fig. SI-3d.

Figure SI-5. Kinetic simulations of reversible scavenging for $k_Q = 5 \times 10^9$ $M^{-1}s^{-1}$ and $K_{eq} = 5000$ M^{-1}: **(a)** germylene decay profiles; **(b)** digermene growth/decay curves; **(c)** plots of k_{decay} vs [Q] and $\Delta A_{digerm,0}/\Delta A_{digerm,Q}$ vs [Q], where the (germylene) k_{decay} values were determined by non-linear least squares fitting of the simulated data of (a) to a single exponential decay and ΔA_{digerm} values are the maxima in the digermene growth/decay curves of (b); **(d)** plot of *span*/*plateau* values vs. [IP], from the fits of the data in (a).

Figure SI-6. Transient absorption spectra and decay profiles of the transient products from reaction of Ph_2Ge with (**a**) 4,4-dimethyl-1-pentene (DMP; 100 mM) and (**b**) 3,3-dimethyl-1-butyne (TBE; 2.5 mM) in deoxygenated hexane solution at 23 ^oC.

Figure SI-7. 600 MHz ^{1}H NMR spectra of product mixtures from steady state photolyses of **1a** (0.05 M) in deoxygenated C_6D_{12} solution containing **(a)** 0.05 M DMP and **(b)** 0.05 M TBE.

Figure SI-1. Transient absorption spectra of Ph_2Ge-amine complexes in hexane solution at 23 ^oC. The spectra were recorded 2.8-3.1 μs, 1.65-1.78 μs, and 4.4-5.1 μs after the laser pulse for deoxygenated solutions containing 0.003 M **1a** and 0.13 mM n-$BuNH_2$ (black), 0.66 mM Et_2NH (blue), and 5.0 mM Et_3N (red), respectively. The species decayed with mixed order kinetics under these conditions, with lifetimes of 50-200 μs. The band at 440 nm in the spectrum of the Ph_2Ge-NEt_3 complex is due to tetraphenyldigermene (**2a**).

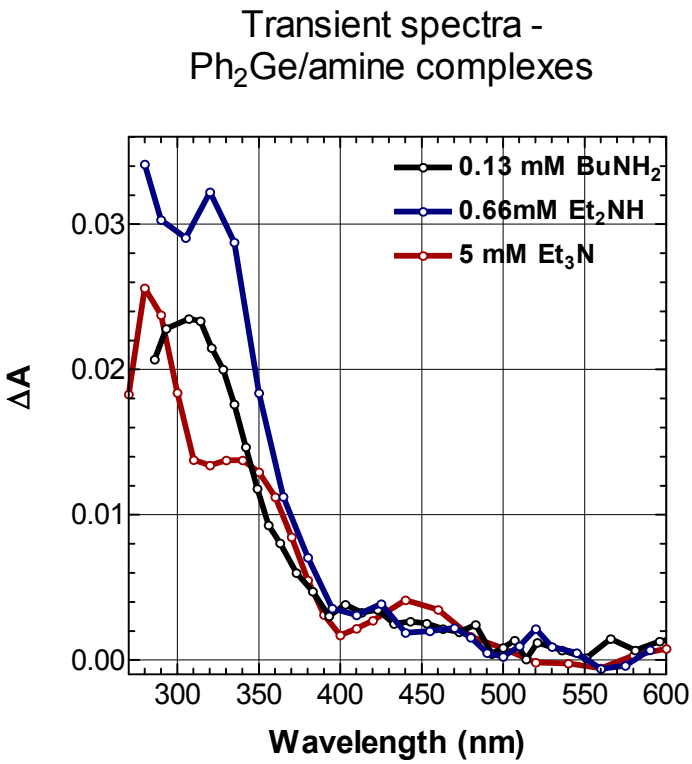


Figure SI-2. Plot of $(\Delta A_{500,0} - \Delta A_{500,res})/(\Delta A_{500,res})$ ("*span/plateau*") vs. [isoprene] in hexane solution at 23 ^{o}C (see Eqn. 7 in the paper). The $\Delta A_{500,0}$ and $\Delta A_{500,res}$ used are the best-fit values of the initial and residual transient absorbances from non-linear least squares analysis of the ΔA_{500} vs. time data of Figure 5(a) to a single exponential decay.

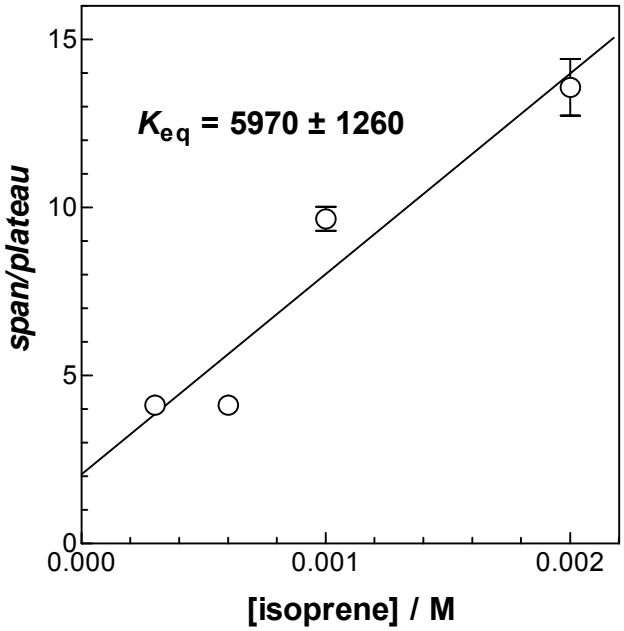


Figure SI-3. Reversible scavenging of Ph_2Ge by 4,4-dimethyl-1-pentene (DMP). Raw transient growth/decay profiles recorded at **(a)** 500 nm and **(b)** 440 nm on the same time scale in the presence of DMP at the concentrations listed in (a); **(c)** 440 nm data from a different experiment, recorded over a longer time scale; (**d**) the data of (a) after subtraction of the data from (b) scaled by 0.15, and fit to a single exponential decay.

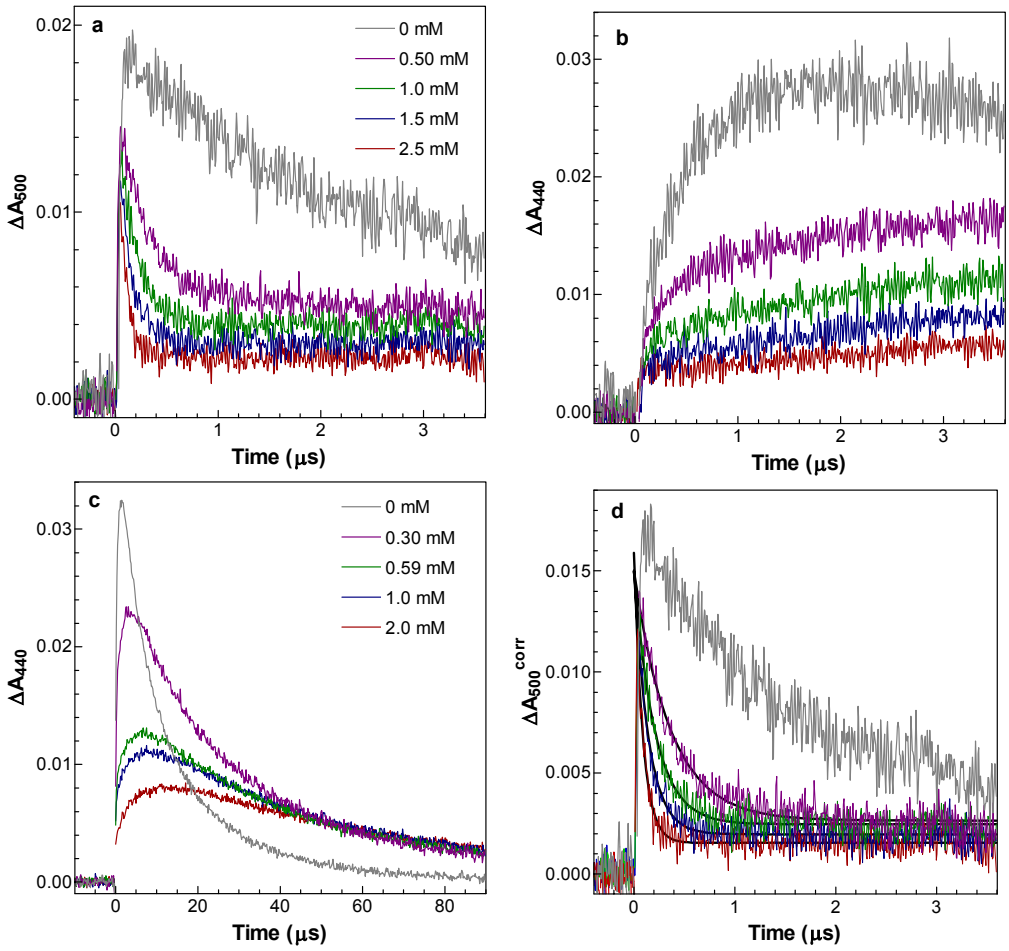


Figure SI-4. **(a)** Plots of k_{decay} (from Fig. SI-3d) and $\Delta A_{440,0}/\Delta A_{440,Q}$ (from Fig. SI-3c) vs [Q]; **(b)** plot of *span*/*plateau* values vs. [DMP], from the fits of the data in Fig. SI-3d.

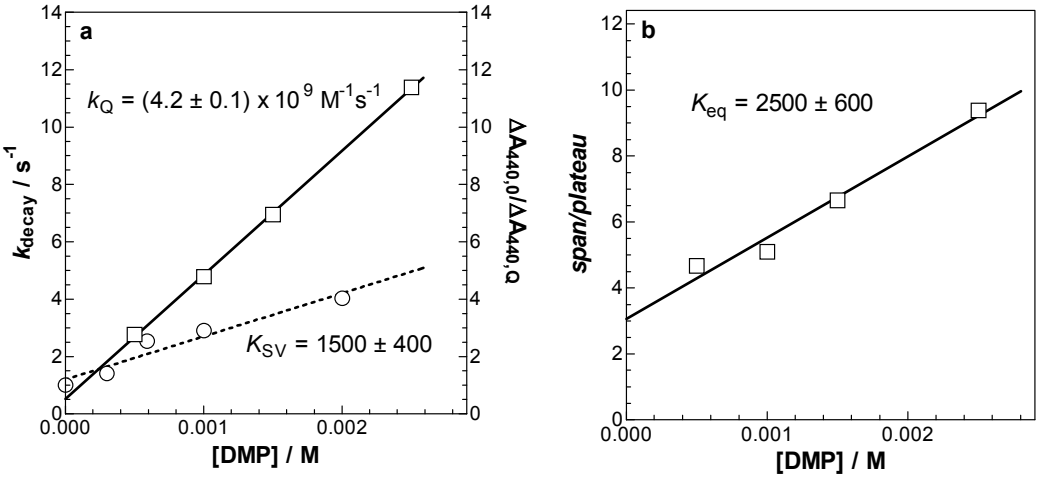
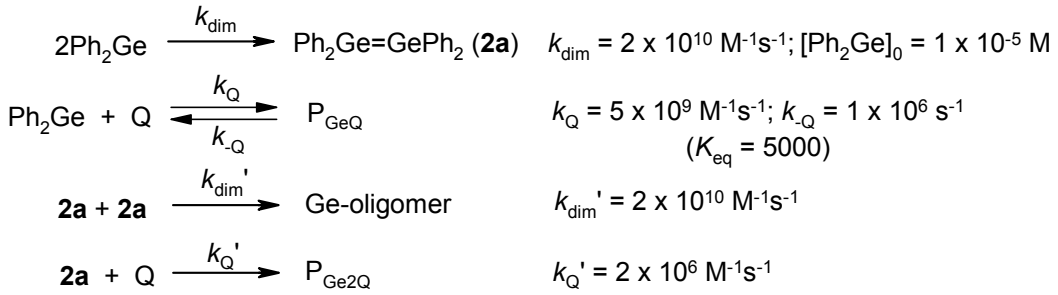
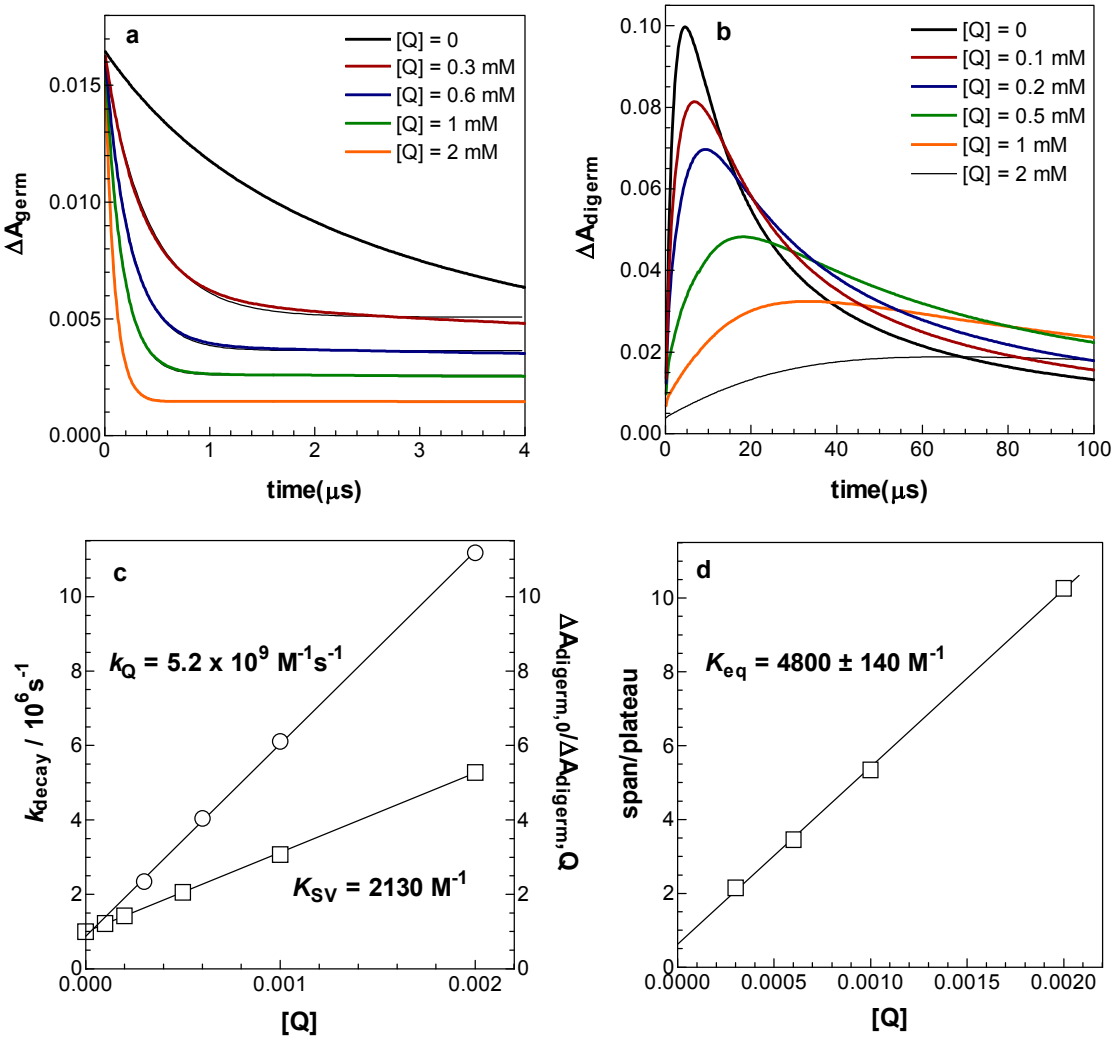


Figure SI-5. Simulation of (a) germylene decay profiles and (b) digermene growth/decay curves for reversible germylene scavenging according to the following scheme:





Fitting each set of the simulated data of (a) to a first-order exponential decay (as with the experimental data) returns the decay rate constants plotted in (c); the slope agrees well with the original k_Q value used in the simulation. Figure (d) shows a plot of the *span/plateau* values returned by the fits of the decay data in (a); again, the slope agrees well with the original K_{eq} value used in the simulation.

Figure SI-6. Transient absorption spectra of the transient products from reaction of Ph_2Ge with (**a**) 4,4-dimethyl-1-pentene (DMP) and (**b**) 3,3-dimethyl-1-butyne (TBE). The spectra were recorded by laser flash photolysis of deoxygenated 0.003 M hexane solutions of **1a** in the presence of 100 mM and 2.5 mM DMP and TBE, respectively. The Inserts show representative decay traces recorded at or near the absorption maxima, using neutral density filters to reduce the laser intensity; the solid lines represent the best fits of the data to a first order exponential decay.

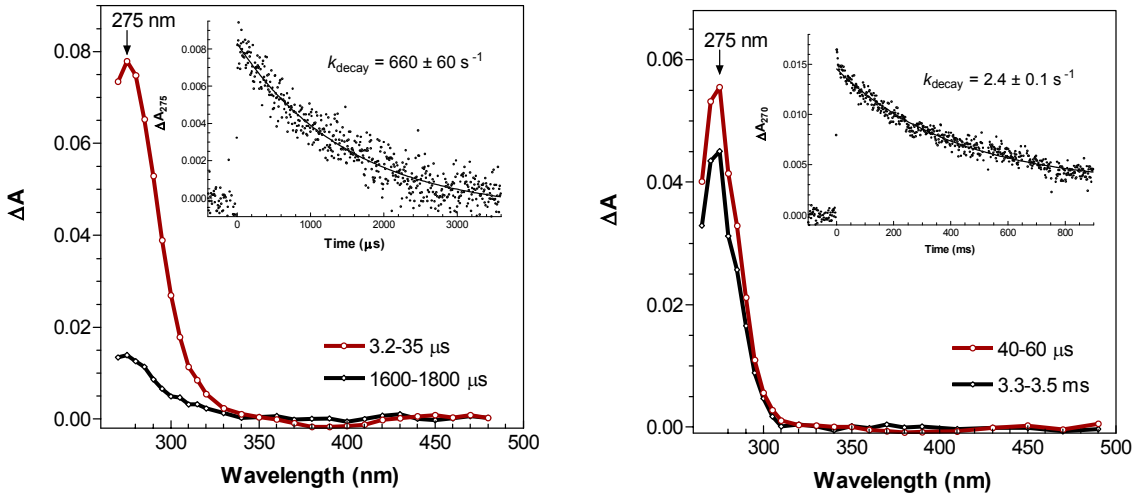


Figure SI-7. **(a)** 600 MHz ^{1}H NMR spectra of product mixtures from steady state photolyses of **1a** (0.05 M) in deoxygenated C_6D_{12} solution containing 0.05 M DMP before and after 15 minutes photolysis with 6 RPR-2537 lamps.

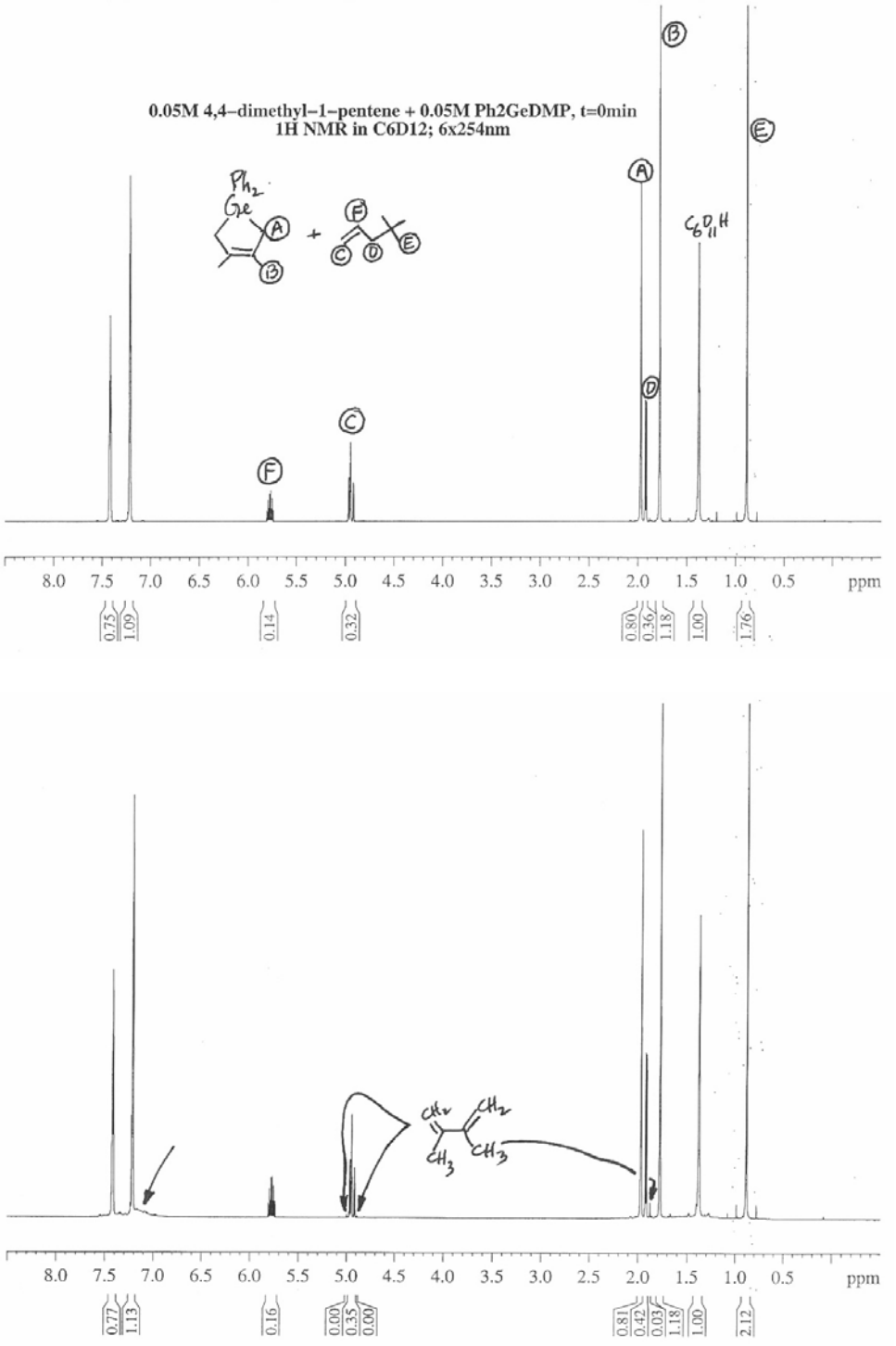


Figure SI-7. **(b)** 600 MHz ^{1}H NMR spectra of product mixtures from steady state photolyses of **1a** (0.05 M) in deoxygenated C_6D_{12} solution containing 0.05 M TBE before and after 15 minutes photolysis with 6 RPR-2537 lamps. The peak labeled "Product 1" in the second spectrum is due to the primary product of the reaction, while that labeled "Product 2" is a secondary product. A peak tentatively assigned to a third relatively minor product is also labeled.