

## Supporting Information for

**Substituent Effects on the Reactions of Diarylgermylenes and Tetraaryldigermenes with Acetic Acid and Other Lewis Bases in Hydrocarbon Solvents**

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**Figure S1.** Concentration vs. time plots for (a) **1a-d**, (b) **4a-d**, and (c) 2,3-dimethyl-1,3-butadiene (DMB) from photolysis of **1a-d** (0.02 M) in cyclohexane-*d*<sub>12</sub> containing 0.2 M MeOH. [**a** (○ - H), **b** (□ - CH<sub>3</sub>), **c** (● - F), **d** (■ - CF<sub>3</sub>)] S3

**Figure S2.** Representative <sup>1</sup>H NMR spectra from photolysis of **1d** in C<sub>6</sub>D<sub>12</sub> containing MeOH (0.2 M) and Si<sub>2</sub>Me<sub>6</sub> (as internal integration standard). S4

**Figure S3.** <sup>1</sup>H NMR spectrum of the crude reaction mixture from photolysis of **1b** in hexane containing HOAc (0.4 M), after evaporation of the solvent and re-dissolution in CDCl<sub>3</sub>. The peaks marked with an asterisk, which are due to residual **1b**, illustrate the degree of conversion. S5

**Figure S4.** Transient UV/vis absorption spectra from laser flash photolysis of dry, deoxygenated solutions of **1b** (0.003 M) at 25°C, (a) in hexane 30-100 ns (○) and 3.49-3.52 μs (●) after the laser pulse and (b) in hexane containing 15 mM THF 198-224 ns (○) and 3.43-3.48 μs (●) after the laser pulse. The insets show transient absorption profiles recorded at 350, 440 and 500 nm. S6

**Figure S5.** Transient UV/vis absorption spectra from laser flash photolysis of dry, deoxygenated solutions of **1c** (0.003 M) at 25°C, (a) in hexane 35-100 ns (○) and 3.56-3.58 μs (●) after the laser pulse and (b) in hexane containing 7.3 mM THF 326-352 ns (○) and 3.27-3.30 μs (●) after the laser pulse. The insets show transient absorption profiles recorded at 345, 440 and 500 nm. S6

**Figure S6.** Growth/decay profiles recorded at 440 nm and 500 nm by laser flash photolysis of optically matched (at 248 nm) solutions of **1a-d** (ca. 0.003 M) in dry, deoxygenated hexanes at 25 °C. The traces shown in red are the corrected 500 nm decays, obtained by scaled subtraction of the 440 nm trace from the 500 nm one; the solid lines are the best fits of the data to second order decay kinetics. S7

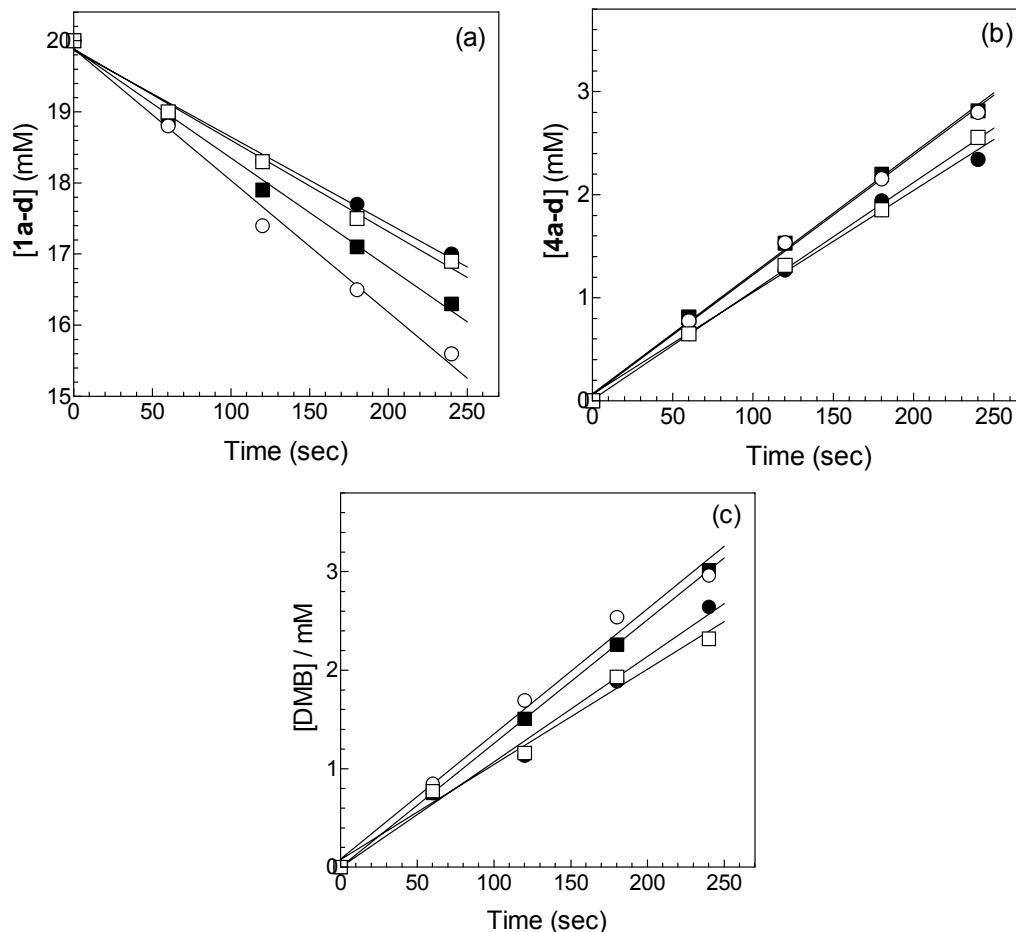
**Figure S7.** Raw growth decay/profiles recorded at (a) 440 nm and (b) 500 nm by laser flash photolysis of a ca. 0.003 M solution of **1b** in hexane containing various concentrations of AcOH between 0 and 3 mM. S8

**Figure S8.** (a) Plots of  $k_{\text{decay}}$  and  $\Delta A_0/\Delta A_{\text{res}}$  for quenching of GePh<sub>2</sub> (**2a**) by THF in hexane solution at 60 °C. (b) Corrected 500 nm transient decay trace for GePh<sub>2</sub> in hexane containing 2.0 mM THF at 60°C, illustrating the procedure used for extraction of  $k_{\text{decay}}$  and  $\Delta A_{\text{res}}$  values. The solid red line is the fit of the data to two first order exponential decays, from which  $k_{\text{decay}}$  was obtained, while the solid black line is the value of  $\Delta A_{\text{res}}$ , estimated as the break point in the bimodal decay. The  $\Delta A_0$  value used for calculation of  $\Delta A_0/\Delta A_{\text{res}}$  values at each concentration was taken from the corrected 500 nm decay in the absence of added THF. S8

**Synthesis and Characterization of Compounds** S9

**References** S14

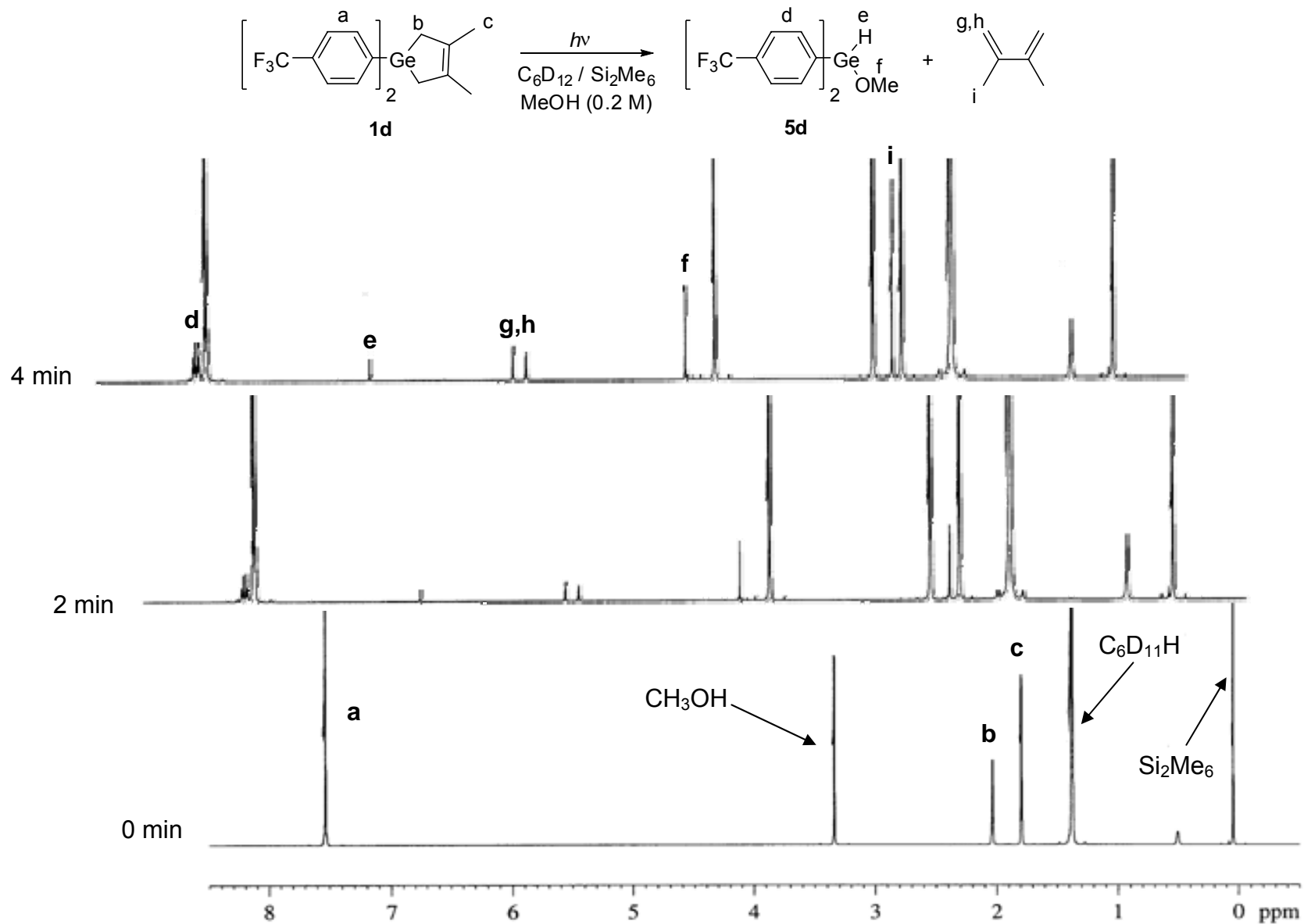
**Figure S1.** Concentration vs. time plots for (a) **1a-d**, (b) **4a-d**, and (c) 2,3-dimethyl-1,3-butadiene (DMB) from photolysis of **1a-d** (0.02 M) in cyclohexane- $d_{12}$  containing 0.2 M MeOH [**a** ( $\circ$  - H), **b** ( $\square$  -  $\text{CH}_3$ ), **c** ( $\bullet$  - F), **d** ( $\blacksquare$  -  $\text{CF}_3$ )]. The integrals due to the methoxy protons in **4a-d** were used to estimate the concentrations of these products at the various photolysis times monitored.



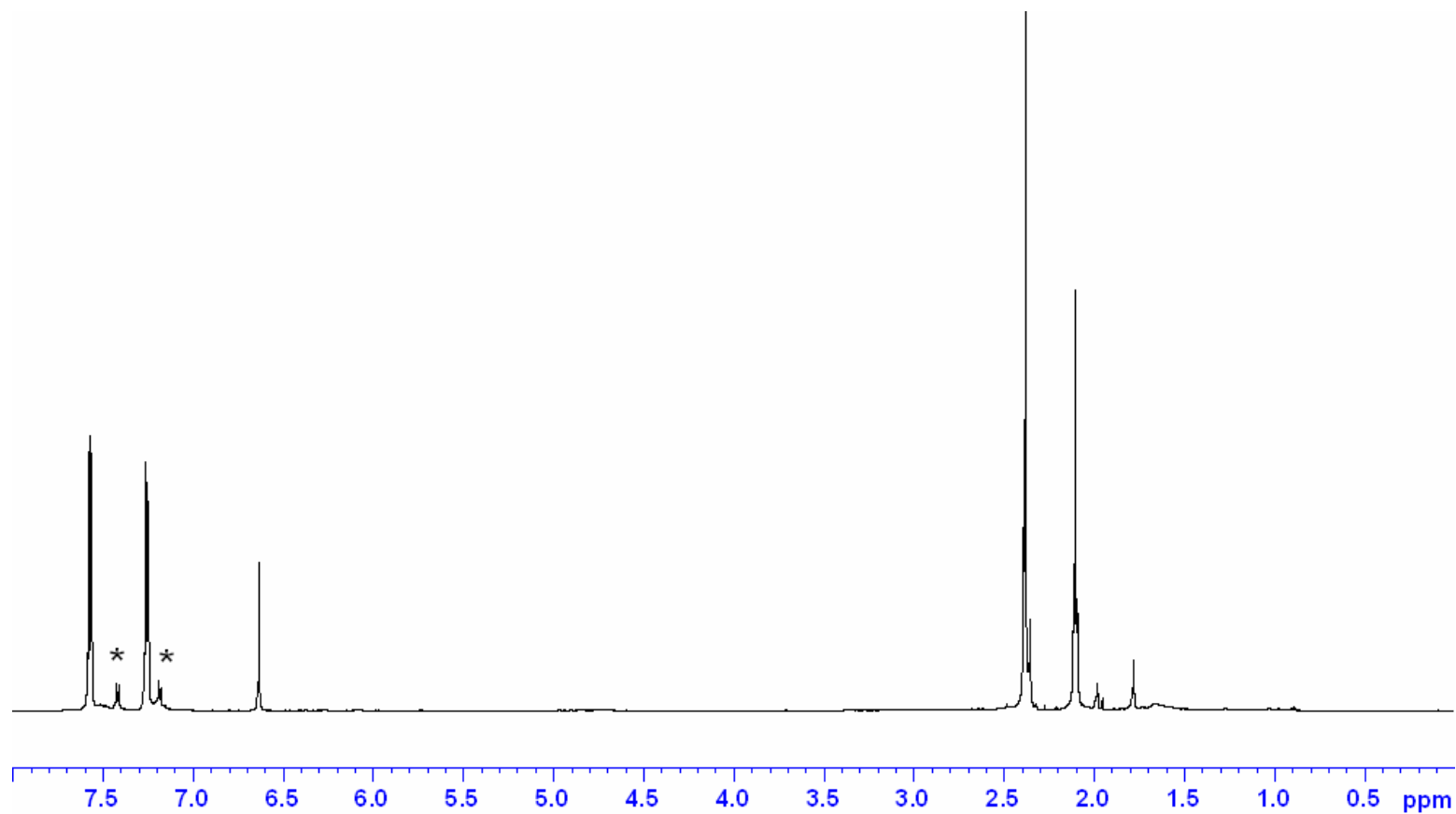
The slopes of the plots of Fig. S1b are listed below, with errors given as one standard deviation from the least squares analyses. Quantum yields for formation of **4b-d** were then calculated from the slopes relative to that for formation of **4a** from **1a** and the reported quantum yield for the latter reaction ( $\Phi = 0.55 \pm 0.07$ ).

<b>4a</b>	( $\circ$ - H)	$0.01163 \pm 0.00034 \text{ mM s}^{-1}$	$\Phi = 0.55 \pm 0.07$
<b>4b</b>	( $\square$ - $\text{CH}_3$ )	$0.01053 \pm 0.00021 \text{ mM s}^{-1}$	$\Phi = 0.50 \pm 0.09$
<b>4c</b>	( $\bullet$ - F)	$0.00988 \pm 0.00048 \text{ mM s}^{-1}$	$\Phi = 0.47 \pm 0.10$
<b>4d</b>	( $\blacksquare$ - $\text{CF}_3$ )	$0.01168 \pm 0.00037 \text{ mM s}^{-1}$	$\Phi = 0.55 \pm 0.10$

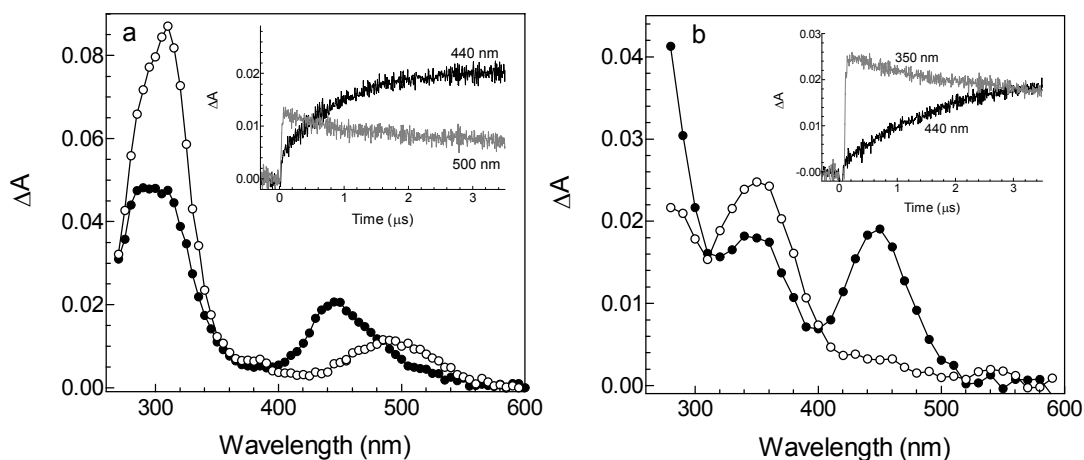
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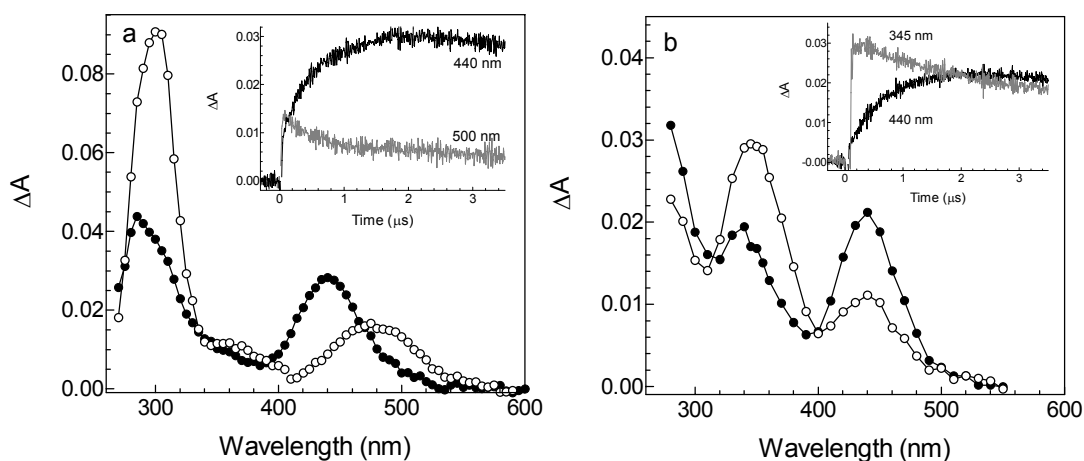
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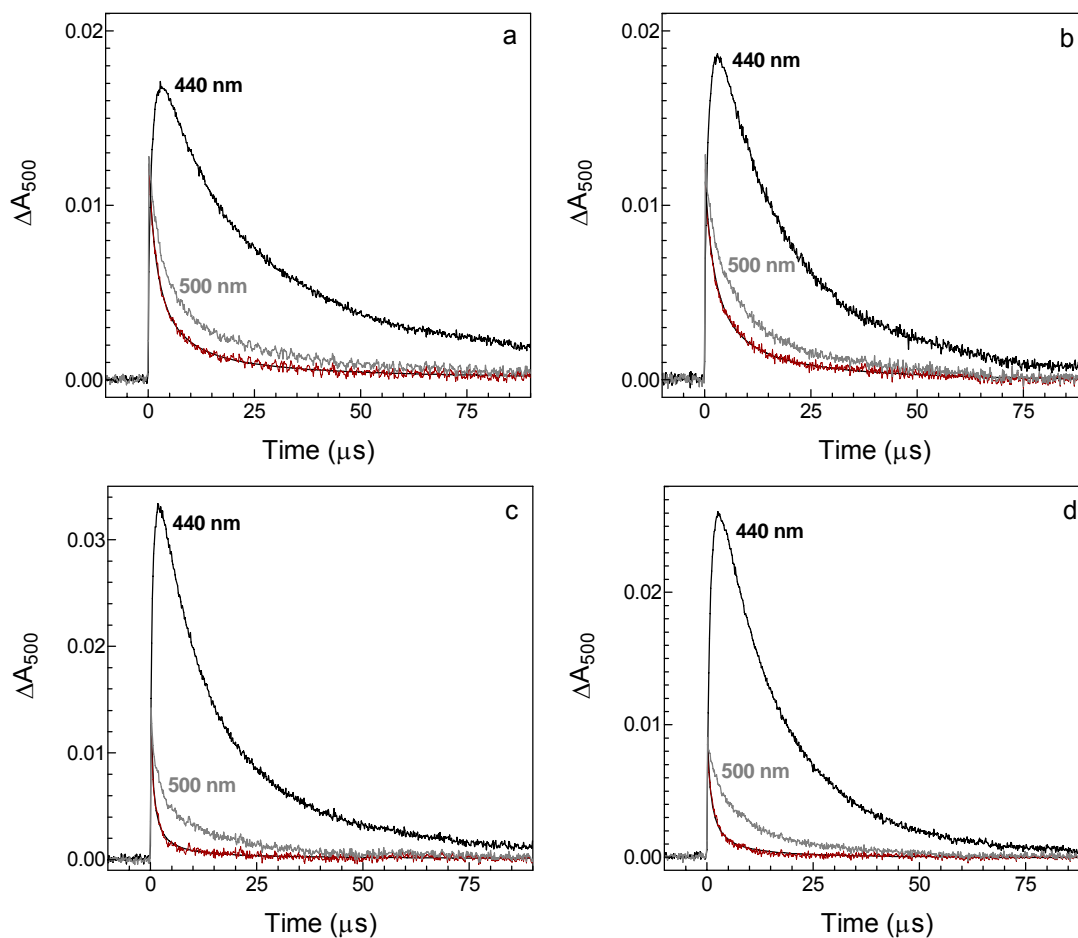
**Figure S4.** Transient UV/vis absorption spectra from laser flash photolysis of dry, deoxygenated solutions of **1b** (0.003 M) at 25°C, (a) in hexane 30-100 ns ( $\circ$ ) and 3.49-3.52  $\mu$ s ( $\bullet$ ) after the laser pulse and (b) in hexane containing 15 mM THF 198-224 ns ( $\circ$ ) and 3.43-3.48  $\mu$ s ( $\bullet$ ) after the laser pulse. The insets show transient absorption profiles recorded at 350, 440 and 500 nm.



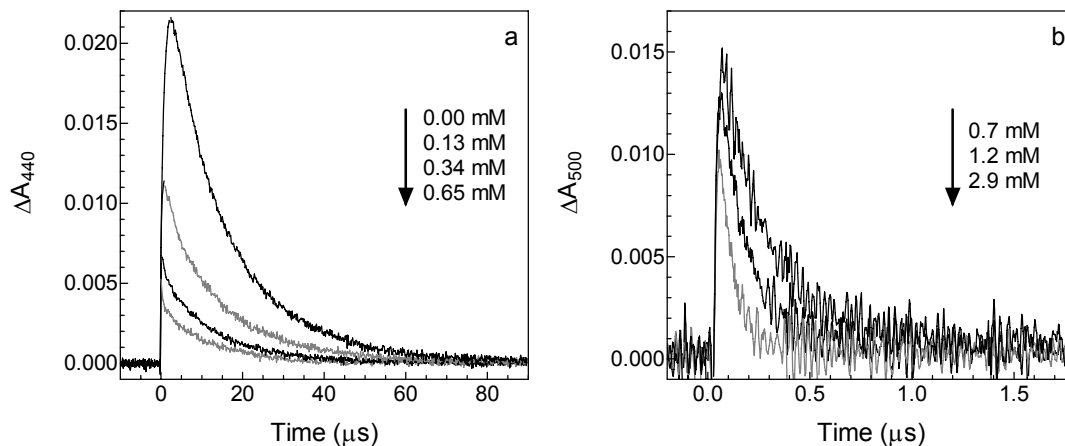
**Figure S5.** Transient UV/vis absorption spectra from laser flash photolysis of dry, deoxygenated solutions of **1c** (0.003 M) at 25°C, (a) in hexane 35-100 ns ( $\circ$ ) and 3.56-3.58  $\mu$ s ( $\bullet$ ) after the laser pulse and (b) in hexane containing 7.3 mM THF 326-352 ns ( $\circ$ ) and 3.27-3.30  $\mu$ s ( $\bullet$ ) after the laser pulse. The insets show transient absorption profiles recorded at 345, 440 and 500 nm.



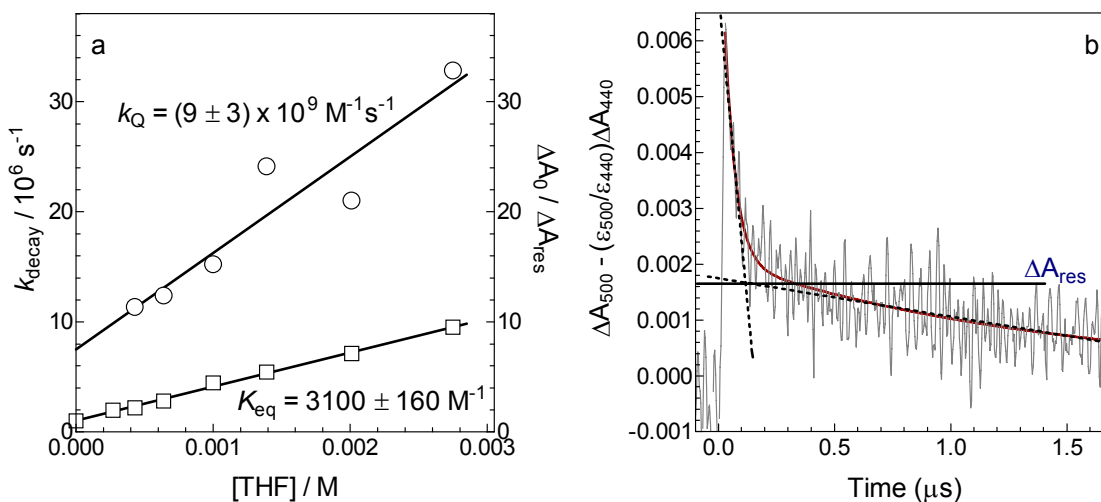
**Figure S6.** Growth/decay profiles recorded at 440 nm and 500 nm by laser flash photolysis of optically matched (at 248 nm) solutions of **1a-d** (ca. 0.003 M) in dry, deoxygenated hexanes at 25 °C. The traces shown in red are the corrected 500 nm decays, obtained by scaled subtraction of the 440 nm trace from the 500 nm one; the solid lines are the best fits of the data to second order decay kinetics.



**Figure S7.** Raw growth decay/profiles recorded at (a) 440 nm and (b) 500 nm by laser flash photolysis of a ca. 0.003 M solution of **1b** in hexane containing various concentrations of AcOH between 0 and 3 mM.



**Figure S8.** (a) Plots of  $k_{\text{decay}}$  and  $\Delta A_0/\Delta A_{\text{res}}$  for quenching of GePh<sub>2</sub> (**2a**) by THF in hexane solution at 60 °C. (b) Corrected 500 nm transient decay trace for GePh<sub>2</sub> in hexane containing 2.0 mM THF at 60°C, illustrating the procedure used for extraction of  $k_{\text{decay}}$  and  $\Delta A_{\text{res}}$  values. The solid red line is the fit of the data to two first order exponential decays, from which  $k_{\text{decay}}$  was obtained, while the solid black line is the value of  $\Delta A_{\text{res}}$ , estimated as the break point in the bimodal decay. The  $\Delta A_0$  value used for calculation of  $\Delta A_0/\Delta A_{\text{res}}$  values at each concentration was taken from the corrected 500 nm decay in the absence of added THF.



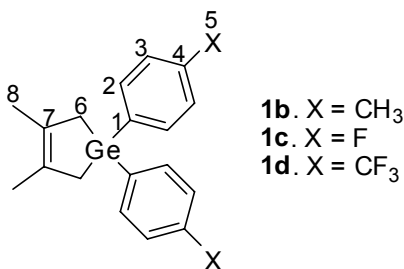


## Synthesis and Characterization of Compounds

NMR spectra were recorded on Bruker AV200, DRX500, or AV600 spectrometers using the solvent ( $\text{CDCl}_3$  unless otherwise noted) peak as a reference. Mass spectra were recorded on a Micromass TofSpec 2E mass spectrometer using electron impact (70 eV) or chemical ionization ( $\text{NH}_3$  reagent gas, positive ion mode). Infrared spectra were recorded as thin-films on sodium chloride plates using a Bio-Rad FTS-40 FTIR spectrometer. Melting points were recorded using a Mettler FP82 hot stage mounted on a polarizing microscope and are uncorrected. Combustion analyses were performed by Guelph Chemical Laboratories Ltd., Guelph ON. Column chromatography was carried out using acid washed 230-400 mesh silica gel (Silicycle).

All synthetic preparations were carried out in conventional glassware under an atmosphere of dry nitrogen. 1,1-Dichloro-3,4-dimethylgermacyclopent-3-ene,<sup>1</sup> 3,4-dimethyl-1,1-diphenylgermacyclopent-3-ene (**1a**),<sup>1</sup> and hexamesitylcyclotrigermane (**4**)<sup>2</sup> were prepared as previously described.

The 1,1-diaryl-3,4-dimethylgermacyclopent-3-enes **1b-d** were prepared by an analogous method to the preparation of **1a**, and purified by column chromatography (silica gel, hexanes) and multiple recrystallizations from hexanes. They were identified on the basis of the following spectroscopic data ( $m/z$  values marked with \* indicate ions containing  $^{74}\text{Ge}$ ):



*3,4-Dimethyl-1,1-di-(4-methylphenyl)-1-germacyclopent-3-ene* (**1b**; mp 81.4 – 83.7 °C).  $^1\text{H}$  NMR,  $\delta$  = 1.78 (s, 6H,  $\text{C}^8\text{H}_3$ ), 1.98 (s, 4H,  $\text{C}^6\text{H}_2$ ), 2.36 (s, 6H,  $\text{C}^5\text{H}_3$ ), 7.19 (d, 4H,  $J = 7.8$  Hz,  $\text{C}^3\text{H}$ ), 7.42

(d, 4H,  $J = 7.8$  Hz,  $C^2H$ );  $^{13}C$  NMR,  $\delta = 19.55$  (C8), 21.56 (C5), 25.80 (C6), 129.11 (C2), 130.91 (C7), 134.32 (C3), 134.91 (C1), 138.69 (C4); IR,  $\nu$  ( $cm^{-1}$ ) = 2914 (m,br), 1911 (w), 1497 (m), 1440 (m,br), 1264 (m), 1171 (m), 1157 (m), 1087 (m), 799 (s), 742 (m), 667 (m); MS,  $m/z$  (I) = 338.1\* (38), 256.0\* (100), 181.1 (94), 164.9\* (46), 139.0\* (15); HRMS, calc for  $C_{20}H_{24}Ge$ : 338.1090, found: 338.1078; Anal., calc. for  $C_{20}H_{24}Ge$ , C 71.28, H 7.18; found, C 70.91, H 6.99.

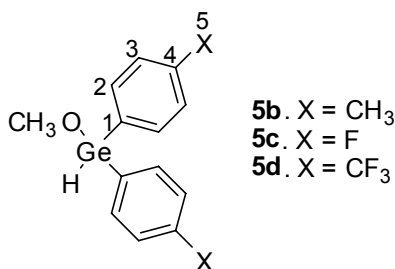
*1,1-Di-(4-fluorophenyl)-3,4-dimethyl-1-germacyclopent-3-ene (1c; mp 83.1 – 84.8°C)*.  $^1H$  NMR,  $\delta = 1.80$  (s, 6H,  $C^8H_3$ ), 2.00 (s, 4H,  $C^6H_2$ ), 7.07 (dd, 2H,  $J = 9, 9$  Hz,  $C^3H$ ), 7.46 (dd, 2H,  $J = 9, 6$  Hz,  $C^2H$ );  $^{13}C$  NMR,  $\delta = 19.51$  (C8), 25.82 (C6), 115.55 (d,  $^2J_{C-F} = 20$  Hz, C3), 130.87 (C7), 133.40 (C1), 136.00 (d,  $^3J_{C-F} = 7$  Hz, C2), 163.81 (d,  $^1J_{C-F} = 248$  Hz, C4); IR,  $\nu$  ( $cm^{-1}$ ) = 2911 (m,br), 1893 (w), 1587 (s), 1496 (m), 1230 (m), 1162 (m), 1086 (m), 821 (m), 743 (m), 670 (w); MS,  $m/z$  (I) = 346.1\* (50), 262.0\* (58), 169.0\* (100), 152.1 (88), 92.9\* (70); HRMS, Calc. for  $C_{18}H_{18}F_2Ge$ , 346.0588; found, 346.0564; Anal. calc. for  $C_{18}H_{18}F_2Ge$ , C 62.68, H 5.26; found, C 63.07, H 5.56.

*3,4-Dimethyl-1,1-bis-(4-trifluoromethylphenyl)-1-germacyclopent-3-ene (1d, mp 59.2 – 60.0 °C)*;  $^1H$  NMR,  $\delta = 1.80$  (s, 6H,  $C^8H_3$ ), 2.06 (s, 4H,  $C^6H_2$ ), 7.62 (s, 8H, all ArH);  $^{13}C$  NMR,  $\delta = 19.46$  (C8), 25.44 (C6), 124.28 (q,  $^1J_{C-F} = 272$  Hz, C5), 124.96 (C3), 130.86 (C7), 131.38 (q,  $^2J_{C-F} = 32$  Hz, C4), 134.60 (C2), 142.66 (C1); IR,  $\nu$  ( $cm^{-1}$ ) = 2915 (m,br), 1925 (w), 1607 (m), 1394 (m), 1325 (s), 1167 (s), 1129 (s), 1058 (s), 1019 (m), 826 (m), 690 (m); MS:  $m/z$  (I) = 446.1\* (19), 271.1 (69), 252.1 (77), 219.0 (46), 126.0 (26); HRMS, Calc. for  $C_{20}H_{18}F_6Ge$ , 446.0524; found 446.0501; Anal. calc. for  $C_{20}H_{18}F_6Ge$ , C 53.99, H 4.08; found, C 54.06, H 4.02.

Steady state photolysis experiments with **1a-d** were carried out in quartz tubes (7 x 90 mm) or quartz NMR tubes on 0.5-1.0 mL aliquots of the appropriate solutions of the compounds (0.02 – 0.035 M) in dry hexanes or  $C_6D_{12}$ , and employed a Rayonet<sup>®</sup> photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round apparatus and two RPR-2537

lamps (254 nm). The tubes were sealed with rubber septa and deoxygenated with a stream of dry argon for ca. 20 minutes, and then the appropriate amount of MeOH or HOAc was added via syringe.

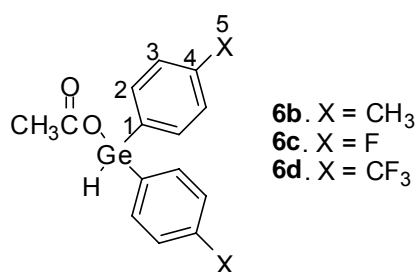
Solutions of **1a-d** in  $C_6D_{12}$  containing MeOH (0.2 M) and a trace of  $Si_2Me_6$  as internal standard were irradiated in parallel, monitoring the solutions by  $^1H$  NMR spectroscopy in 1 minute time intervals to ~20% conversion (4 min). DMB and methoxygermanes **5b-d** were the only products detectable from **1b-d** in >5% yield relative to consumed starting material in all cases. Identification of **5b-d** was made on the basis of comparisons of their  $^1H$  NMR spectra to that of **5a**.<sup>1</sup> Attempted GC/MS analysis of the product mixtures afforded complex mixtures of germanium-containing compounds in addition to unreacted **1**, but high resolution mass spectra of the photolyzed solutions without prior GC separation showed ions corresponding to the  $M^+$  or  $(M-1)^+$  ions of the three products. Quantum yields for formation of **5b-d** were determined from the slopes of concentration vs. time plots constructed from the NMR data (see Supporting Information), relative to that for formation of **5a** from **1a** ( $\Phi = 0.55 \pm 0.07$ ).<sup>1</sup> The  $^1H$  NMR and HRMS data for **5b-d** are as follows.



**5b:**  $^1H$  NMR ( $C_6D_{12}$ ),  $\delta = 2.30$  (s, 6H,  $C^5H_3$ ), 3.50 (s, 3H,  $OCH_3$ ), 6.05 (s, H,  $GeH$ ), 7.10 (d, 4H,  $J = 7.8$  Hz,  $C^3H$ ), 7.39 (d, 4H,  $J = 7.8$  Hz,  $C^2H$ ); HRMS, calc. for  $C_{15}H_{18}GeO$  ( $M^+$ ), 288.0570; found, 288.0572. **5c:**  $^1H$  NMR ( $C_6D_{12}$ ),  $\delta = 3.53$  (s, 3H,  $OCH_3$ ), 6.10 (s, H,  $GeH$ ), 7.00 (m, 4H,  $C^3H$ ), 7.44 (m, 4H,  $C^2H$ ). HRMS, calc. for  $C_{13}H_{11}F_2GeO$  ( $M-H$ ), 294.9990; found, 294.9986. **5d:**  $^1H$  NMR ( $C_6D_{12}$ ),  $\delta = 3.53$  (s, 3H,  $OCH_3$ ), 6.10 (s, H,  $GeH$ ), 7.00 (m, 4H,  $C^3H$ ), 7.44 (m,

4H,  $C^2H$ ); HRMS, calc. for  $C_{15}H_{11}F_6GeO$  (M-H), 394.9926; found, 394.9929.

Solutions of **1b-d** in hexanes containing HOAc (0.4 M) were irradiated for two hours in parallel, and the solvent and excess HOAc were removed under high vacuum to afford yellow oils, the  $^1H$  NMR spectra of which showed high conversion (> 80%) of the starting material to a single product major product (>90 %). These products were unstable towards silica gel chromatography or GC/MS and thus could not be isolated. Compounds **6b-d** were thus identified on the basis of the following spectroscopic data, obtained on the crude reaction mixtures.



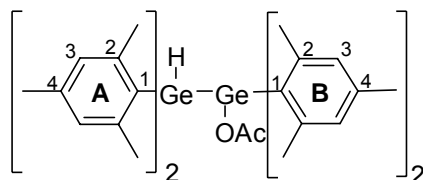
**6b:**  $^1H$  NMR,  $\delta$  = 2.11 (s, 3H, OAc), 2.38 (s, 6H,  $C^5H_3$ ), 6.63 (s, 1H, GeH), 7.25 (d, 4H,  $J$  = 7.9 Hz,  $C^3H$ ), 7.57 (d, 4H,  $J$  = 7.5 Hz,  $C^2H$ );  $^{13}C$  NMR,  $\delta$  = 21.68 (C5), 22.15 (COCH<sub>3</sub>), 129.47 (C2), 129.86 (C1), 134.60 (C3), 140.80 (C4), 174.64 (C=O); IR,  $\nu$  ( $cm^{-1}$ ) = 2087  $cm^{-1}$  (m), 2041 (w), 1700 (s); HRMS, calc. for  $C_{16}H_{17}GeO_2$  (M-H), 316.0519; found, 316.0512. **6c:**  $^1H$  NMR,  $\delta$  = 2.12 (s, 3H, OAc), 6.65 (s, H, GeH), 7.13-7.18 (m, 4H,  $C^3H$ ), 7.64-7.67 (m, 4H,  $C^2H$ );  $^{13}C$  NMR,  $\delta$  = 22.00 (COCH<sub>3</sub>), 116.13 (d,  $^2J_{C-F}$  = 20 Hz, C3), 128.49 (C1), 136.70 (d,  $^3J_{C-F}$  = 7 Hz, C2), 164.70 (d,  $^1J_{C-F}$  = 251 Hz, C4), 174.66 (C=O); IR,  $\nu$  ( $cm^{-1}$ ) = 2049  $cm^{-1}$  (m, br), 1699 (s); HRMS, calc. for  $C_{14}H_{11}F_2GeO_2$  (M-H), 322.9939; found, 322.9997. **6d:**  $^1H$  NMR,  $\delta$  = 2.16 (s, 3H, OAc), 6.75 (s, H, GeH), 7.70 (d, 4H,  $J$  = 8.4 Hz,  $C^3H$ ), 7.79 (d, 4H,  $J$  = 8.4 Hz,  $C^2H$ );  $^{13}C$  NMR,  $\delta$  = 21.81 (COCH<sub>3</sub>), 123.95 (q,  $^1J_{C-F}$  = 272 Hz, C5), 125.47 (C2), 133.03 (q,  $^2J_{C-F}$  = 32 Hz, C4), 135.00 (C3), 137.85 (C1), 174.74 (C=O); IR,  $\nu$  ( $cm^{-1}$ ) = 2101  $cm^{-1}$  (m, br), 1702 (s); HRMS, calc. for  $C_{16}H_{11}F_6GeO_2$  (M-H), 422.9875; found, 422.9908.

Photolysis of 0.03 M solutions of **1a** in  $C_6D_{12}$  containing  $Et_2NH$  or  $EtOAc$  (0.3 M) and a

trace of  $\text{Si}_2\text{Me}_6$  was carried out to ~50% conversion, with periodic monitoring by NMR. The spectra showed the characteristic resonances of DMB and broad baseline absorption in the  $\delta$  6.5 – 8 chemical shift range.

Tetramesityldigermene (**3e**) was synthesized according to the procedure of Baines and co-workers.<sup>3</sup> A solution of hexamesitylcyclotrigermane (**4**; 18 mg,  $1.9 \times 10^{-5}$  mol) in dry toluene (15 mL) was placed in a 15 × 150 mm quartz tube and sealed with a rubber septum. Triethylsilane (0.05 mL,  $3.1 \times 10^{-4}$  mol) was then injected via syringe and the solution was deoxygenated with a fine stream of argon for 30 min. It was then placed in a Pyrex dewar containing 3:1 2-propanol/methanol, cooled to  $<-50^\circ\text{C}$  with dry ice, and photolysed with 12 × RPR3500 lamps in a Rayonet<sup>®</sup> photochemical reactor for three hours. Addition of acetic acid (0.2 mL,  $3.5 \times 10^{-3}$  mol) to the cold solution caused no change in the characteristic yellow color due to **3e**, so was removed from the dewar and allowed to warm to room temperature. The solution turned colorless after ca. 10 minutes at  $\sim 20^\circ\text{C}$ . The solvent and excess HOAc were removed under vacuum to yield a pale yellow oil.  $^1\text{H}$  NMR of the crude mixture showed two products present, in addition to residual starting material and  $\text{Mes}_2\text{Ge}(\text{H})(\text{SiEt}_3)$ , the product resulting from the trapping of  $\text{Mes}_2\text{Ge}$  with triethylsilane. The mixture was purified using column chromatography (silica; 1:1 dichloromethane:hexanes). Residual **4** (2 mg) was recovered, followed by 1-hydroxy-1,1,2,2-tetramesityldigermene (**7f**; 2 mg),<sup>4</sup> formed from traces of water present in the system. The major product was a colorless oil which was identified as 1-acetoxy-1,1,2,2-tetramesityldigermene (**7e**, 8 mg,  $1.2 \times 10^{-5}$  mol, 63%) on the basis of the following spectroscopic data:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ),  $\delta$  = 1.88 (s, 3H, OAc), 2.06 (s, 6H, *p*- $\text{CH}_3$  A), 2.08 (s, 6H, *p*- $\text{CH}_3$  B), 2.36 (s, 12H, *o*- $\text{CH}_3$  A), 2.40 (s, 12H, *o*- $\text{CH}_3$  B), 6.32 (s, H, GeH), 6.70 (s, 4H, ArH A), 6.72 (s, 4H, ArH B);  $^{13}\text{C}$  ( $\text{CDCl}_3$ ):  $\delta$  = 21.12 (*p*- $\text{CH}_3$ , A&B - there are two overlapping signals here that can be resolved in benzene- $d_6$ ), 23.37 ( $\text{COCH}_3$ ), 23.80 (*o*- $\text{CH}_3$  A),

24.52 (*o*-CH<sub>3</sub> B), 128.63 (C3 A), 129.42 (C3 B), 134.51 (C1 A), 136.76 (C1 B), 138.39 (C4 A), 138.92 (C4 B), 142.83 (C2 A), 143.77 (C2 B), 172.01 (COCH<sub>3</sub>); IR,  $\nu$  (cm<sup>-1</sup>) = 2964 (s, br), 2922 (s, br), 2077 (w), 2034 (w), 1710 (s), 1698 (s), 1602 (m), 1448 (m, br), 1264 (s), 1017 (m), 847 (m); MS (CI),  $m/z$  (I) = 682.2\* (9), 621.1\* (90), 563.1\* (17), 503.1\* (11), 431.2\* (17), 371.1\* (95), 312.1\* (48), 253.0\* (32), 192.0\* (100); HRMS, Calc. for C<sub>38</sub>H<sub>48</sub>O<sub>2</sub>Ge<sub>2</sub>, 682.2061; found, 682.2087. Several other minor products were also present that were not identified.



Addition of Et<sub>2</sub>NH (0.25 mL, 0.25 M) to a similarly prepared solution of **3e** in THF at -50 °C, followed by standing for 2 days at 4 °C, caused no visual change in the solution. Similar results were obtained when a solution of **3e** was treated with *n*-butylamine (0.13 M) under similar conditions.

## References

- (1) Leigh, W. J.; Harrington, C. R.; Vargas-Baca, I. *J. Am. Chem. Soc.* **2004**, *126*, 16105.
- (2) Tsumuraya, T.; Kabe, Y.; Ando, W. *J. Organomet. Chem.* **1994**, *482*, 131.
- (3) Samuel, M. S.; Jennings, M. C.; Baines, K. M. *J. Organomet. Chem.* **2001**, *636*, 130.
- (4) Baines, K. M.; Cooke, J. A.; Dixon, C. E.; Liu, H.; Netherton, M. R. *Organometallics* **1994**, *13*, 631.