Supporting Information

Trans- and *cis*-Selective Lewis Acid-Catalyzed Hydrogermylation of Alkynes

Todd Schwier and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago

845 West Taylor St., Chicago, Illinois 60607-7061

General Information.....	S2
Preparation of Starting Materials.....	S3
Preparation of Aryl Alkynes.....	S3
General Procedure for Hydrogermylation of Alkynes.....	S5
Characterization Data for Vinylgermanes.....	S6
Procedure for Halodegermylation of Acrylate Derivatives.....	S10
Assignment of Regiochemistry of Stilbenes 3fb and 3gb	S10
Spectral Charts.....	S13

General Information

NMR spectra were recorded on Bruker DPX-400 (400 MHz) and DRX-500 (500 MHz) instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, NP-5MS). The same GC system with FID (30 m x 0.25 mm capillary column, HP-5) was used for capillary GLC analyses. HR EI MS analysis was performed on a JEOL GCmate II mass spectrometer. Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 63-200 μ m). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. All manipulations were conducted under an argon or nitrogen atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous dichloromethane and THF (BHT-free) was purchased from Aldrich, degassed with argon, and dried by passage through activated alumina on an Innovative Technology PureSolv system. Triethylamine and diisopropylamine were purchased from Aldrich, degassed with argon, and stored over calcium hydride. $\text{B}(\text{C}_6\text{F}_5)_3$ is commercially available, but for our purpose it was prepared according to the known procedure.¹ Compounds **1a**,² **1f**,³ and **1g** are known compounds and were prepared by the method reported. The preparation of alkynes **1i**, **1j**, **1k**, and **1l** is described below. Commercially available alkynes and propiolates were purchased and used without further purification. Trimethylgermane, triethylgermane, and triphenylgermane were purchased from Gelest. Tributylgermane was purchased from Alfa Aesar. Products **5**⁴ and **6l**⁵ are known and their spectral data agreed with the literature. The spectral data for vinylgermanes **3** and **4**, as well as previously unreported **1b**, **1i**, **1k**, **1l**, and **6o**, are provided below. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiment.

-
- (1) (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, 2, 245. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, 5, 218.
 (2) Crisp, G. T.; Turner, P. D.; Stephens, K. A. *J. Organomet. Chem.* **1998**, 570, 219.
 (3) Rubin, M.; Trofimov, A.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, 127, 10243.
 (4) (a) For X=Br, see: Weiss, H. M.; Touchette, K. M.; Angell, S.; Khan, J. *Org. Biomol. Chem.* **2003**, 1, 2152. (b) for X=I, see: Shen, Y.; Gao, S. *J. Chem. Soc., Perkin Trans 1* **1995**, 11, 1331.
 (5) Rossi, R.; Carpita, A.; Bellina, F.; Cossi, P. *J. Organomet. Chem.* **1993**, 451, 33.

Preparation of Starting Materials

d-1i: Potassium carbonate (55 mg, 0.4 mmol) and tetrabutylammonium iodide (100 mg, 0.27 mmol) were dissolved in deuterium oxide (3.4 mL, 200 mmol). A solution of ethyl propiolate (2 mL, 20 mmol) in dichloromethane (5 mL) was added and the reaction was stirred for 12 hours. The reaction was diluted with dichloromethane (10 mL) and the organic phase was separated, dried (MgSO₄), and filtered. The dichloromethane was distilled off, and the deuterated propiolate was purified by distillation. Recovery 1.0g (10.2 mmol, 51%) 94% deuterium-incorporated. ¹H NMR (500.13 MHz, CDCl₃) δ 4.25 (q, *J*=7.34 Hz, 2H), 1.32 (t, *J*=7.15 Hz, 3H); ¹³C NMR (125.76 MHz, CDCl₃) δ 152.7, 74.5, 74.3, 74.1, 62.4 (-), 14.0 (+).

1b: To a stirred solution of B(C₆F₅)₃ (17 mg, 33 μmol) in anhydrous dichloromethane (500 μL) was added triethylsilane (114 μL, 0.716 mmol) followed by addition of 1-(1-hexynyl)-4-methoxybenzene (128 mg, 0.680 mmol) **1a** in dichloromethane (500 μL). After the vigorous gas evolution had subsided, the reaction was stirred a further 5 minutes and then quenched by filtration through a short column (silica gel, CH₂Cl₂ as an eluent). Purification by column chromatography gave **1b** as a colorless oil. Yield 196 mg (0.679 mmol, 99.9%). ¹H NMR (500.13 MHz, CDCl₃) δ 7.27 (ddd, *J*=8.99, 2.57, 2.38 Hz, 2H), 6.76 (ddd, *J*=8.99, 2.57, 2.38 Hz, 2H), 2.39 (t, *J*=6.97 Hz, 2H), 1.55 - 1.61 (m, 2H), 1.44 - 1.51 (m, *J*=14.86, 7.34, 7.34, 7.15 Hz, 2H), 0.99 (t, *J*=7.89 Hz, 9H), 0.95 (t, *J*=7.34 Hz, 3H), 0.73 (q, *J*=8.19 Hz, 6 H); ¹³C NMR (125.76 MHz, CDCl₃) δ 155.2, 132.9 (+, 2C), 119.9 (+, 2C), 116.8, 88.9, 80.3, 31.0 (-), 22.0 (-), 19.1 (-), 13.7 (+), 6.6 (+), 5.0 (-); GC/MS *m/z* 288 (M⁺, 100%), 259 (M⁺-C₂H₅, 64.50%), 231 (M⁺-C₄H₉, 43.00%), 203 (21.99%), 115 (61.19%). HRMS Calcd for C₁₈H₂₈OSi 288.1909. Found 288.1903.

Preparation of Aryl Alkynes

1i: PdCl₂(PPh₃)₂ (84 mg, 0.12 mmol) and CuI (46 mg, 0.24 mmol) were combined and dissolved in anhydrous triethylamine (10 mL). 1-bromo-3-iodobenzene (0.8 mL, 6.3 mmol) and 1-hexyne (1.0 mL, 8.9 mmol) were added sequentially and the reaction was warmed to 40°C and stirred for 10 hours. Upon consumption of aryl iodide, the reaction mixture was poured into 2M HCl_(aq)

(100 mL) and diluted with diethyl ether (100 mL). The organic phase was washed with 2M HCl_(aq) (2 x 50 mL), saturated NaHCO_{3(aq)} (50 mL), and brine (50mL). The organic phase was separated, dried (MgSO₄), filtered, and concentrated. Purification by column chromatography (silica gel, 10:1 hexanes/benzene) gave **1i** (1.434 g, 6.0 mmol, 96%) as a light yellow oil. ¹H NMR (500.13 MHz, CDCl₃) δ 7.55 (s, 1 H), 7.40 (d, *J*=8.07 Hz, 1H), 7.32 (d, *J*=7.70 Hz, 1H), 7.14 (t, *J*=7.89 Hz, 1H), 2.41 (t, *J*=7.06 Hz, 2H), 1.55 - 1.63 (m, 2H), 1.44 - 1.54 (m, 2H), 0.96 (t, *J*=7.34 Hz, 3H); ¹³C NMR (125.76 MHz, CDCl₃) δ 134.4 (+), 130.6 (+), 130.1 (+), 129.6 (+), 126.2, 122.0, 92.0, 79.2, 30.7 (-), 22.1 (-), 19.1 (-), 13.7 (+); GC/MS *m/z* 238 (⁸¹Br-M⁺, 24.46%), 236 (⁷⁹Br-M⁺, 22.48%), 223 (18.04%), 221 (21.03%), 195 (42.60%), 193 (40.64%), 142 (100%).

1j: PdCl₂(PPh₃)₂ (84 mg, 0.12 mmol) and CuI (46 mg, 0.24 mmol) were combined and dissolved in anhydrous diisopropylamine (10 mL). 1,2-diiodobenzene (784 μL, 6.0 mmol) and 1-hexyne (0.68 mL, 6.04 mmol) were added sequentially. After stirring for 10 hours, the reaction mixture was poured into 2M HCl_(aq) (100 mL) and diluted with diethyl ether (100 mL). The organic phase was washed with 2M HCl_(aq) (2 x 50 mL), saturated NaHCO_{3(aq)} (50 mL), and brine (50mL). The organic phase was separated, dried (MgSO₄), filtered, and concentrated. Purification by column chromatography (silica gel, 50:1 hexanes/benzene) gave **1j** (1.44 g, 5.1 mmol, 85%) as a light yellow oil. ¹H NMR (500.13 MHz, CDCl₃) δ 7.82 (d, *J*=8.07 Hz, 1H), 7.40 (dd, *J*=7.70, 1.28 Hz, 1H), 7.24 - 7.28 (m, 1 H), 6.95 (td, *J*=7.70, 1.47 Hz, 1H), 2.48 (t, *J*=6.97 Hz, 2H), 1.61 - 1.68 (m, 2H), 1.55 (dq, *J*=14.92, 7.25 Hz, 2H), 0.97 (t, *J*=7.24 Hz, 3H); ¹³C NMR (125.76 MHz, CDCl₃) δ 138.6 (+), 132.44 (+), 130.5, 128.7 (+), 127.7 (+), 101.1, 94.8, 82.9, 30.6 (-), 22.1 (-), 19.3 (-), 13.7 (+); GC/MS *m/z* 284 (M⁺, 84.01%), 269 (24.69%), 241 (39.05%), 142 (94.21%), 115 (100%).

1k: PdCl₂(PPh₃)₂ (140 mg, 0.2 mmol) and CuI (76 mg, 0.4 mmol) were combined and dissolved in anhydrous triethylamine (10 mL). 2-bromofuran (891 μL, 10 mmol) and 1-hexyne (1.5 mL, 13 mmol) were added sequentially. After stirring at 60°C for 12 hours, the reaction mixture was poured into 2M HCl_(aq) (100 mL) and diluted with diethyl ether (100 mL). The organic phase was washed with 2M HCl_(aq) (2 x 50 mL), saturated NaHCO_{3(aq)} (50 mL), and brine (50mL). The organic phase was separated, dried (MgSO₄), filtered, and concentrated. Purification by column chromatography (silica gel, 10:1 hexanes/CH₂Cl₂) gave **1k** (1.05 g, 7.1 mmol, 71%) as a light

brown oil. ^1H NMR (500.13 MHz, CDCl_3) δ 7.32 (dd, $J=1.83, 0.73$ Hz, 1H), 6.46 (d, $J=3.30$ Hz, 1H), 6.35 (dd, $J=3.30, 2.02$ Hz, 1H), 2.44 (t, $J=7.06$ Hz, 2H), 1.55 - 1.62 (m, 2H), 1.42 - 1.51 (m, 2H), 0.94 (t, $J=7.24$ Hz, 3H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 142.6 (+), 137.7, 113.6 (+), 110.6 (+), 94.8, 70.9, 30.5 (-), 22.0 (-), 19.2 (-), 13.6 (+); GC/MS m/z 148 (M^+ , 97.22), 133 (54.10%), 119 (45.76%), 105 (100%), 91 (43.99%), 77 (64.82%).

11: 4-bromophenylboronic acid (0.90g, 4.5 mmol) and pinacol (0.58 g, 4.95 mmol) were dissolved in anhydrous diethyl ether (10 mL). After stirring overnight the reaction was diluted with diethyl ether (50 mL) and washed with water (2 x 25 mL). The organic phase was separated, dried (MgSO_4), filtered, and concentrated to give the pinacol ester as a white solid, which was used without further purification. The pinacol ester (1.28 g, 4.5 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (70 mg, 0.1 mmol), and CuI (38 mg, 0.2 mmol) were combined and dissolved in anhydrous triethylamine (10 mL). 1-hexyne (0.68 mL, 5.4 mmol) was added and the reaction was warmed to 60°C . After stirring at 60°C for 12 hours, the reaction mixture was poured into 2M $\text{HCl}_{(\text{aq})}$ (100 mL) and diluted with diethyl ether (100 mL). The organic phase was washed with 2M $\text{HCl}_{(\text{aq})}$ (2 x 50 mL), saturated $\text{NaHCO}_{3(\text{aq})}$ (50 mL), and brine (50mL). The organic phase was separated, dried (MgSO_4), filtered, and concentrated. Purification by column chromatography (silica gel, 40:1:4 hexanes/ $\text{EtOAc}/\text{CH}_2\text{Cl}_2$) gave **11** (1.00 g, 3.5 mmol, 78%) as a light brown oil which solidified upon standing to a dark brown solid. ^1H NMR (500.13 MHz, CDCl_3) δ 7.73 (d, $J=8.25$ Hz, 2H), 7.40 (d, $J=8.07$ Hz, 2H), 2.42 (t, $J=7.06$ Hz, 2H), 1.56 - 1.64 (m, 2H), 1.44 - 1.53 (m, 2H), 1.34 (s, 12H), 0.96 (t, $J=7.34$ Hz, 3H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 134.5 (+), 130.8 (+), 126.9, 92.0, 83.9, 80.8, 30.8 (-), 24.9 (+, 4C), 22.0 (-), 19.2 (-), 13.7 (+); GC/MS m/z 284 (M^+ , 49.50%), 269 (33.35%), 241 (10.21%), 185 (100%), 169 (50.58%), 141 (69.23%).

Typical Procedure for $\text{B}(\text{C}_6\text{F}_5)_3$ -Catalyzed Hydrogermylation

To a stirred solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (5 mg, 5 mol%) in anhydrous dichloromethane (200 μL) was added triethylgermane (0.24 mmol, 38.6 mg, 38 μL) followed by addition of 1-(1-hexynyl)-4-methoxybenzene (0.2 mmol, 37.7 mg) **1a**. The reaction was stirred at room temperature and the reaction progress was monitored by GC/MS analysis. Once the reaction was complete (2- 4 h for

1a), the mixture was filtered through a short column (silica gel, CH₂Cl₂ as an eluent) and concentrated. Purification by column chromatography gave **3ab**. Yield 64.9 mg (0.186 mmol, 93%). Reactions were run on scales between 0.2 mmol and 1 mmol without notable change in yields.

3ab: ¹H NMR (500.13 MHz, CDCl₃) δ 7.12 (s, 1H), 7.08-7.11 (m, 2H), 6.82 (d, *J*=8.80 Hz, 2H), 3.80 - 3.84 (m, 3H), 2.24 (t, *J*=7.70 Hz, 2H), 1.34 - 1.44 (m, 4H), 0.90 - 0.97 (m, 12H), 0.68 (q, *J*=7.95 Hz, 6H); ¹³C NMR (125.76 MHz, CDCl₃) δ 158.4, 143.9, 139.2 (+), 133.2, 129.4 (+, 2C), 113.1 (+, 2C), 55.2 (+), 39.4 (-), 32.6 (-), 22.5 (-), 14.1 (+), 9.1 (+, 3C), 5.7 (-, 3C); GC/MS *m/z* 350 (M⁺, 1.9%), 321 (M⁺-C₂H₅, 100%), 189 (M⁺-Et₃Ge, 27.0%), 147 (63.4%), 103 (52.9%). HRMS Calcd for C₁₇H₂₇GeO (M⁺-C₂H₅) 321.1274. Found 321.1276.

3ca: ¹H NMR (500.13 MHz, CDCl₃) δ 7.26 - 7.30 (m, 2H), 7.22 (t, *J*=7.15 Hz, 1H), 7.17 (d, *J*=7.34 Hz, 2H), 7.14 (s, 1H), 2.01 (d, *J*=1.47 Hz, 3H), 0.09 (s, 9 H); ¹³C NMR (125.76 MHz, CDCl₃) δ 142.5, 140.3, 139.2 (+), 128.5 (+, 2C), 127.8 (+, 2C), 126.5 (+), 25.5 (+), -0.4 (+, 3C); GC/MS *m/z* 236 (M⁺, 4.12%), 221 (M⁺-CH₃, 100%), 115 (95.46%), 105 (68.89%).

3cb: ¹H NMR (500.13 MHz, CDCl₃) δ 7.28 (t, *J*=7.34 Hz, 2H), 7.21 - 7.24 (m, 2H), 7.18 (d, *J*=6.97 Hz, 2H), 2.01 (s, 3H), 0.93 (t, *J*=7.89 Hz, 9H), 0.67 (dq, *J*=8.07, 0.73 Hz, 6H); ¹³C NMR (125.76 MHz, CDCl₃) δ 140.5, 140.4, 140.0 (+), 128.3 (+, 2C), 127.7 (+, 2C), 126.5 (+), 26.6 (+), 9.0 (+, 3C), 5.2 (-, 3C); GC/MS *m/z* 249 (M⁺-C₂H₅, 100%), 221 (15.14%), 189 (25.58%), 115 (52.94%). HRMS Calcd for C₁₃H₁₉Ge (M⁺-C₂H₅) 249.0699. Found 249.0683.

3cc: ¹H NMR (500.13 MHz, CDCl₃) δ 7.24 - 7.29 (m, 2H), 7.14 - 7.23 (m, 4H), 1.99 (d, *J*=1.83 Hz, 3H), 1.18 - 1.24 (m, 12H), 0.81 - 0.85 (m, 9H), 0.62 - 0.67 (m, 6H); ¹³C NMR (125.76 MHz, CDCl₃) δ 141.0, 140.5, 139.7 (+), 128.3 (+, 2C), 127.7 (+, 2C), 126.5 (+), 27.4 (-, 3C), 26.5 (-, 3C), 13.7 (+, 3C), 13.7 (-, 3C); GC/MS *m/z* 305 (M⁺-C₄H₉, 100%), 249 (M⁺-C₈H₁₇, 40.15%), 191 (94.50%), 151 (40.41%), 115 (36.74%). HRMS Calcd for C₁₇H₂₇Ge (M⁺-C₄H₉) 305.1324. Found 305.1328.

3cd: ^1H NMR (500.13 MHz, CDCl_3) δ 7.56 (s, 1H), 7.49 - 7.53 (m, 6H), 7.29 - 7.37 (m, 9H), 7.10 (d, $J=7.34$ Hz, 2H), 6.90 (t, $J=7.34$ Hz, 1H), 6.85 (t, $J=7.34$ Hz, 2H), 2.11 (d, $J=1.83$ Hz, 3H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 143.1 (+), 138.0, 137.0 (3C), 135.2 (+, 6C), 134.9, 128.7 (+, 3C), 128.6 (+, 2C), 128.1 (+, 6C), 27.9 (+); GC/MS m/z 345 ($\text{M}^+-\text{C}_6\text{H}_5$, 3.27%), 305 (Ph_3Ge^+ , 55.26%), 267 (5.39%), 228 (38.72%), 192 (100%), 151 (51.39%), 115 (74.36%). HRMS Calcd for $\text{C}_{27}\text{H}_{24}\text{Ge}$ 422.1090. Found 422.1058.

3db: ^1H NMR (500.13 MHz, CDCl_3) δ 5.91 (t, $J=7.34$ Hz, 1H), 2.00 - 2.06 (m, 4H), 1.33 (dq, $J=7.38$, 3.77 Hz, 4H), 1.25 - 1.30 (m, 4H), 1.03 (t, $J=7.89$ Hz, 9H), 0.87 - 0.93 (m, 6H), 0.85 (q, $J=8.07$ Hz, 6H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 140.4 (+), 138.8, 38.6 (-), 32.9 (-), 32.5 (-), 32.1 (-), 22.6 (-), 22.4 (-), 14.1 (+), 14.1 (+), 9.1 (+, 3C), 5.4 (-, 3C); GC/MS m/z 271 ($\text{M}^+-\text{C}_2\text{H}_5$, 68.96%), 243 ($\text{M}^+-\text{C}_4\text{H}_9$, 6.01%), 133 (100%), 103 (68.48%). HRMS Calcd for $\text{C}_{14}\text{H}_{29}\text{Ge}$ ($\text{M}^+-\text{C}_2\text{H}_5$) 271.1481. Found 271.1470.

3eb: ^1H NMR (500.13 MHz, CDCl_3) δ 7.30 - 7.39 (m, 8H), 7.20 - 7.27 (m, 3H), 0.92 (t, $J=7.89$ Hz, 9H), 0.68 (q, $J=7.70$ Hz, 6H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 147.4, 146.9, 143.3 (+), 140.0, 128.3 (+, 2C), 128.0 (+, 2C), 127.9 (+, 2C), 127.1 (+, 3C), 125.7 (+, 1C), 9.1 (+, 3C), 6.3 (-, 3C); GC/MS m/z 311 ($\text{M}^+-\text{C}_2\text{H}_5$, 100%), 283 (13.27%), 253 (8.32%), 178 (84.56%), 151 (60.87%), 133 (34.33%), 105 (34.15%). HRMS Calcd for $\text{C}_{20}\text{H}_{26}\text{Ge}$ 340.1246. Found 340.1259.

3fb: ^1H NMR (500.13 MHz, CDCl_3) δ 7.33 (t, $J=7.52$ Hz, 2H), 7.26 - 7.30 (m, 3H), 7.18 - 7.25 (m, 3H), 6.90 (d, $J=8.44$ Hz, 2H), 3.86 (s, 3H), 0.92 (t, $J=7.89$ Hz, 9H), 0.69 (q, $J=7.70$ Hz, 6H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 158.9, 147.5, 145.5, 143.0 (+), 132.5, 129.5 (+, 2C), 127.9 (+, 2C), 127.2 (+, 2C), 125.6 (+), 113.3 (+, 2C), 55.3 (+), 9.1 (+, 3C), 6.3 (-, 3C); GC/MS m/z 370 (M^+ , 8.54%), 341 ($\text{M}^+-\text{C}_2\text{H}_5$, 100%), 313 ($\text{M}^+-\text{C}_4\text{H}_9$, 7.79%), 285 (8.18%), 210 (35.68%), 165 (95.75%), 105 (64.04%). HRMS Calcd for $\text{C}_{21}\text{H}_{28}\text{GeO}$ 370.1352. Found 370.1349.

3gb: ^1H NMR (500.13 MHz, CDCl_3) δ 7.58 (d, $J=7.70$ Hz, 2H), 7.28 - 7.37 (m, 8H), 0.89 (t, $J=7.89$ Hz, 9H), 0.65 (q, $J=7.70$ Hz, 6H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 151.2, 146.0, 144.3, 139.4, 128.2, 128.0, 127.7, 127.4, 124.9 (+, q, $J=3.70$ Hz, 2C), 9.0, 6.2; ^{19}F NMR (470.59 MHz, CDCl_3) δ -63.7; GC/MS m/z 408 (M^+ , 0.14%), 379 ($\text{M}^+-\text{C}_2\text{H}_5$, 67.35%), 351 ($\text{M}^+-\text{C}_4\text{H}_9$, 5.65%),

321 (3.62%), 247 (9.29%), 227 (100%), 178 (25.61%), 151 (26.61%). HRMS Calcd for $C_{21}H_{25}F_3Ge$ 408.1120. Found 408.1107.

3hb: 1H NMR (500.13 MHz, $CDCl_3$) δ 7.48 (d, $J=14.31$ Hz, 1H), 7.25 - 7.34 (m, 5H), 5.94 (dd, $J=14.12$, 2.02 Hz, 1H), 0.98 (t, $J=7.89$ Hz, 9H), 0.77 (dq, $J=8.07$, 1.83 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 145.8 (+), 140.4, 131.0 (+), 128.0 (+, 2C), 127.7 (+, 2C), 127.2 (+), 9.0 (+, 3C), 6.0 (-, 3C); GC/MS m/z 264 (M^+ , 1.44%), 235 ($M^+-C_2H_5$, 100%), 207 ($M^+-C_4H_9$, 32.65%), 177 (43.18%), 151 (69.49%), 103 ($C_8H_7^+$, 43.17%). HRMS Calcd for $C_{14}H_{22}Ge$ ($M^+-C_2H_5$) 235.0542. Found 235.0539.

3ib: 1H NMR (500.13 MHz, $CDCl_3$) δ 7.34 - 7.38 (m, 2H), 7.07 - 7.18 (m, 3H), 2.27 (td, $J=7.40$, 1.28 Hz, 2H), 1.35 - 1.46 (m, 4H), 0.92 - 0.98 (m, 12H), 0.69 (q, $J=7.89$ Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 147.2, 142.7, 138.0 (+), 131.3 (+), 129.5 (+), 129.2 (+), 127.0 (+), 121.8, 39.3 (-), 32.3 (-), 22.5 (-), 14.1 (+), 9.1 (+, 3C), 5.7 (-, 3C); GC/MS m/z 369 ($M^+-C_2H_5$, 100%), 341 (6.29%), 129 (31.27%). HRMS Calcd for $C_{16}H_{24}GeBr$ ($M^+-C_2H_5$) 369.0273. Found 369.0257.

3jb: 1H NMR (500.13 MHz, $CDCl_3$) δ 7.48 (d, $J=14.31$ Hz, 1H), 7.25 - 7.34 (m, 5H), 5.94 (dd, $J=14.12$, 2.02 Hz, 1H), 0.98 (t, $J=7.89$ Hz, 9H), 0.77 (dq, $J=8.07$, 1.83 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 146.0, 144.3, 143.2 (+), 138.3 (+), 129.8 (+), 128.4 (+), 127.5 (+), 100.5, 38.5 (-), 32.1 (-), 22.7 (-), 14.1 (+), 9.1 (+, 3C), 5.4 (-, 3C); GC/MS m/z 417 ($M^+-C_2H_5$, 100%), 389 (2.52%), 290 (7.25%), 261 (52.14%). HRMS Calcd for $C_{16}H_{24}GeI$ ($M^+-C_2H_5$) 417.0134. Found 417.0126.

3kb: 1H NMR (500.13 MHz, $CDCl_3$) δ 7.48 (d, $J=14.31$ Hz, 1H), 7.25 - 7.34 (m, 5H), 5.94 (dd, $J=14.12$, 2.02 Hz, 1H), 0.98 (t, $J=7.89$ Hz, 9H), 0.77 (dq, $J=8.07$, 1.83 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.1, 144.4, 140.8 (+), 126.5 (+), 111.3 (+), 108.1 (+), 39.9 (-), 32.8 (-), 22.5 (-), 14.1 (+), 9.2 (+, 3C), 5.8 (-, 3C); GC/MS m/z 310 (M^+ , 0.54%), 281 ($M^+-C_2H_5$, 100%), 253 (2.86%), 133 (51.55%), 105 (57.77%). HRMS Calcd for $C_{14}H_{23}GeO$ ($M^+-C_2H_5$) 281.0691. Found 281.0957.

3lb: ^1H NMR (500.13 MHz, CDCl_3) δ 7.48 (d, $J=14.31$ Hz, 1H), 7.25 - 7.34 (m, 5H), 5.94 (dd, $J=14.12$, 2.02 Hz, 1H), 0.98 (t, $J=7.89$ Hz, 9H), 0.77 (dq, $J=8.07$, 1.83 Hz, 6H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 145.8, 143.5, 139.7 (+), 134.2 (+, 2C), 127.7 (+, 2C), 83.70 (2C), 39.5 (-), 32.4 (-), 24.9 (+, 4C), 22.5 (-), 14.1 (+), 9.1 (+, 3C), 5.7 (-, 3C); GC/MS m/z 417 ($\text{M}^+-\text{C}_2\text{H}_5$, 100%), 317 (77.94%), 289 (27.49%), 133 (76.75%), 105 (64.91%). HRMS Calcd for $\text{C}_{22}\text{H}_{36}\text{BGeO}_2$ ($\text{M}^+-\text{C}_2\text{H}_5$) 417.2020. Found 417.2017.

4mb: ^1H NMR (500.13 MHz, CDCl_3) δ 6.81 (dd, $J=2.57$, 1.10 Hz, 1H), 5.87 (dd, $J=2.75$, 1.28 Hz, 1H), 4.20 (dq, $J=7.09$, 1.10 Hz, 2H), 1.30 (td, $J=7.15$, 1.47 Hz, 3H), 1.02 (dt, $J=7.89$, 1.10 Hz, 9H), 0.91 (dq, $J=6.97$, 1.10 Hz, 6H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 169.7, 143.1, 137.9 (-), 60.5 (-), 14.3 (+), 8.8 (+, 3C), 4.4 (-, 3C); GC/MS m/z 231 ($\text{M}^+-\text{C}_2\text{H}_5$, 56.77%), 215 (5.69%), 187 (100%), 133 (64.43%), 103 (43.00%). HRMS Calcd for $\text{C}_9\text{H}_{17}\text{GeO}_2$ ($\text{M}^+-\text{C}_2\text{H}_5$) 231.0440. Found 231.0429.

4na: ^1H NMR (500.13 MHz, CDCl_3) δ 6.21 (q, $J=6.79$ Hz, 1H), 4.19 (q, $J=7.34$ Hz, 2H), 1.99 (d, $J=6.60$ Hz, 3H), 1.30 (t, $J=6.97$ Hz, 3H), 0.26 (s, 9 H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 170.1, 144.9 (+), 137.4, 60.0 (-), 17.6 (+), 14.4 (+), -1.6 (+, 3C); GC/MS m/z 217 (M^+-CH_3 , 39.03%), 187 (18.66%), 173 (100%), 119 (67.02%), 105 (48.47%). HRMS Calcd for $\text{C}_8\text{H}_{15}\text{GeO}_2$ (M^+-CH_3) 217.0284. Found 217.0294.

4ob: ^1H NMR (500.13 MHz, CDCl_3) δ 5.99 (t, $J=7.15$ Hz, 1H), 3.70 (s, 3H), 2.34 (q, $J=7.58$ Hz, 2H), 1.39 - 1.46 (quintet, $J=7.24$ Hz, 2H), 1.26 - 1.33 (m, 4H), 1.01 (t, $J=7.52$ Hz, 9H), 0.82 - 0.90 (m, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 171.3, 150.5 (+), 133.3, 51.0 (+), 31.7 (-), 31.4 (-), 28.9 (-), 22.5 (-), 14.0 (+), 8.7 (+, 3C), 4.4 (-, 3C); GC/MS m/z 287 ($\text{M}^+-\text{C}_2\text{H}_5$, 100%), 255 (62.91%), 163 (26.06%), 133 (32.98%), 105 (40.98%). HRMS Calcd for $\text{C}_{13}\text{H}_{25}\text{GeO}_2$ ($\text{M}^+-\text{C}_2\text{H}_5$) 287.1066. Found 287.1054.

4pa: ^1H NMR (500 MHz, CDCl_3) δ 7.29 - 7.35 (m, 4H), 7.25 - 7.28 (m, 1H), 6.73 (s, 1H), 4.21 (q, $J=6.97$ Hz, 2H), 1.23 (t, $J=7.15$ Hz, 3H), 0.39 (s, 9 H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 172.0, 139.6, 139.5 (+), 136.5, 128.5 (+, 2C), 128.3 (+), 128.1 (+, 2C), 60.4 (-), 14.2 (+), -1.8 (+, 3C); GC/MS m/z 279 (M^+-CH_3 , 69.78%), 249 (16.75%), 235 (87.53%), 149 (28.73%), 131

(27.53%), 119 (100%), 105 (88.14%), 103 (91.30%), 89 (52.38%). HRMS Calcd for $C_{13}H_{17}GeO_2$ ($M^+ - CH_3$) 279.0440. Found 279.0428.

4pb: 1H NMR (500.13 MHz, $CDCl_3$) δ 7.29 - 7.34 (m, 4H), 7.24 - 7.28 (m, 1H), 6.69 (s, 1H), 4.19 (q, $J=6.97$ Hz, 2H), 1.22 (t, $J=7.15$ Hz, 3H), 1.10 (t, $J=7.70$ Hz, 9H), 0.98 (dq, $J=8.07$, 1.10 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 172.3, 140.2 (+), 137.4, 136.6, 128.3 (+, 2C), 128.1 (+), 128.1 (+, 2C), 60.4 (-), 14.1 (+), 8.7 (+, 3C), 4.5 (-, 3C); GC/MS m/z 307 ($M^+ - C_2H_5$, 68.97%), 291 (9.03%), 263 (100%), 133 (86.32%), 115 (41.86%), 103 (72.48%). HRMS Calcd for $C_{15}H_{21}GeO_2$ ($M^+ - C_2H_5$) 307.0753. Found 307.0736.

Typical Procedure for Halodegermylation of Acrylate Derivatives

NIS (47 mg, 0.21 mmol) and $AlCl_3$ (28 mg, 0.21 mmol) were dissolved in dichloromethane (200 μ L) and cooled to 0°C. A solution of **4ob** (63.0 mg) in dichloromethane (50 μ L) was added slowly. After one hour, conc. $NH_{3(aq)}$ (30 μ L) was injected and the reaction was filtered through a short column (florisil, CH_2Cl_2 as an eluent). Purification by column chromatography gave **6o**. Yield 49.7 mg (88%).

6o: 1H NMR (500 MHz, $CDCl_3$) δ 6.92 (t, $J=7.70$ Hz, 1H), 3.79 (s, 3H), 2.46 (q, $J=7.34$ Hz, 2H), 1.41 (quintet, $J=7.34$ Hz, 2H), 1.27 - 1.32 (m, 4H), 0.89 (t, $J=6.97$ Hz, 3 H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 164.3, 157.1 (+), 83.5, 53.0 (+), 33.5 (-), 31.3 (-), 28.4 (-), 22.4 (-), 14.0 (+); GC/MS m/z 282 (M^+ , 100%), 239 (80.23%), 213 (52.46%), 181 (29.81%), 127 (27.96%), 95 (81.92%). HRMS Calcd for $C_9H_{15}IO_2$ 282.0117. Found 282.0116.

Assignment of Regiochemistry of Stilbenes **3fb** and **3gb**

2D NMR analysis of **3fb** and **3gb** failed to unambiguously establish the regiochemistry. Reduction of the compounds **3fb** and **3gb** was effected by hydrogenation over Pd/C in MeOH. Subsequent 2D NMR analysis provided a clear assignment of the regiochemistry of the products.

7: A solution of **3fb** (55 mg, 0.15 mmol) in MeOH (200 μ L) was added to 20% Pd/C (16 mg, 0.03 mmol). The reaction was stirred under an atmosphere of H₂ for several hours and the reaction progress was monitored by GC analysis. Upon full consumption of starting material, the suspension was filtered through a short column (silica gel, CH₂Cl₂ as an eluent), concentrated, and purified by column chromatography to give 50 mg (75% yield of **7**) of an inseparable 3:1 mixture of **7** and 1-methoxy-4-(2-phenylethyl)benzene, product of degermylation. ¹H NMR (500.13 MHz, CDCl₃) δ 7.21 (t, J =6.97 Hz, 2H, **A**), 7.05 - 7.09 (m, 3H, **BC**), 7.01 (d, J =8.44 Hz, 2H, **D**), 6.73 (d, J =8.80 Hz, 2H, **E**), 3.74 (s, 3H, **F**), 3.04 - 3.23 (m, 2H, **G**), 2.74 (dd, J =11.37, 4.40 Hz, 1H, **H**), 1.00 (t, J =7.89 Hz, 9H, **I**), 0.76 (q, J =8.19 Hz, 6H, **J**); ¹³C NMR (125.76 MHz, CDCl₃) δ 157.6 (**1**), 144.3 (**2**), 134.4 (**3**), 129.3 (+, 2C, **4**), 128.1 (+, 2C, **5**), 127.6 (+, 2C, **6**), 124.2 (+, **7**), 113.5 (+, 2C, **8**), 55.2 (+, **9**), 36.8 (+, **10**), 36.0 (-, **11**), 9.1 (+, 3C, **12**), 3.3 (-, 3C, **13**); ¹H-¹³C HMQC NMR (500.13 MHz, 125.76 MHz, CDCl₃) **A**₅, **B**₆, **C**₇, **D**₄, **E**₈, **F**₉, **G**₁₁, **H**₁₀, **I**₁₂, **J**₁₃; ¹H-¹³C HMBC NMR (500.13 MHz, 125.76 MHz, CDCl₃) **A**₂₋₅₋₇, **B**₆₋₇₋₁₀, **C**₅, **D**₁₋₄₋₈₋₁₁, **E**₁₋₃₋₈, **F**₁₋₉, **G**₂₋₃₋₄, **H**₂₋₃₋₅, **I**₁₃, **J**₁₀₋₁₂ GC/MS m/z 372 (M⁺, 2.53%), 343 (M⁺-C₂H₅, 4.69%), 210 (M⁺-Et₃GeH, 94.77%), 161 (53.34%), 133 (100%), 103 (40.93%).

8: A solution of **3gb** (61 mg, 0.15 mmol) in MeOH (200 μ L) was added to 20% Pd/C (16 mg, 0.03 mmol). The reaction was stirred under an atmosphere of H₂ for several hours and the reaction progress was monitored by GC analysis. Upon full consumption of starting material, the suspension was filtered through a short column (silica gel, CH₂Cl₂ as an eluent), concentrated, and purified by column chromatography. Yield 61 mg (0.15 mmol, 100%). ¹H NMR (500.13 MHz, CDCl₃) δ 7.45 (d, J =8.07 Hz, 2H, **A**), 7.19 (t, J =7.34 Hz, 2H, **B**), 7.16 (d, J =8.07 Hz, 2H, **C**), 7.10 - 7.14 (m, 1H, **D**), 7.07 - 7.10 (m, J =6.97 Hz, 2H, **E**), 3.14 - 3.27 (m, 2H, **F**), 2.88 (dd, J =11.74, 4.40 Hz, 1H, **G**), 1.01 (t, J =7.89 Hz, 9H, **H**), 0.78 (q, J =7.95 Hz, 6H, **I**); ¹³C NMR (125.76 MHz, CDCl₃) δ 148.9 (**1**), 141.9 (**2**), 128.6 (+, 2C, **3**), 128.4 (+, 2C, **4**), 127.7 (+, 2C, **5**), 126.6 (q, J =33.29 Hz, **6**), 126.1 (+, **7**), 125.3 (+, q, J =3.70 Hz, 2C, **8**), 124.8 (q, J =271.88 Hz, **9**), 36.9 (+, **10**), 36.7 (-, **11**), 9.2 (+, 3C, **12**), 3.5 (-, 3C, **13**); ¹⁹F NMR (470.59 MHz, CDCl₃) δ -51.2; GC/MS m/z 381 (M⁺-C₂H₅, 1.36%), 248 (5.7%), 230 (100%).

¹H Spectrum of **1k** ¹³C Spectrum of **1k**

¹H Spectrum of **3cc** ¹³C spectrum of **3cc**

¹H Spectrum of **4na** ¹³C spectrum of **4na**

¹H Spectrum of **6o** ¹³C Spectrum of **6o**

¹H Spectrum of **8** ¹³C spectrum of **8**