**Radical-mediated Silyl- and Germynesulfonylation of Vinyl and (α -Fluoro)vinyl Sulfones:
Application of Tris(trimethylsilyl)silanes and Germanes in Pd-catalyzed Couplings**

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SUPPORTING INFORMATION

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General Procedures

¹H (Me₄Si) NMR spectra were determined with solutions in CDCl₃ at 400 MHz, ¹³C (Me₄Si) at 100.6 MHz, ¹⁹F (CCl₃F) at 376.4 MHz, and ³¹P (H₃PO₄) at 161.9 MHz. Mass spectra (MS) were obtained by atmospheric pressure chemical ionization (APCI) techniques unless noted otherwise. Reagent grade chemicals were used and solvents were dried by reflux over and distillation from CaH₂ (except THF//Na/benzophenone) under an argon atmosphere. Selectfluor™ fluorinating reagent (>95% active [F⁺]) was purchased from Aldrich. TLC was performed on Merck kieselgel 60-F₂₅₄ and products were detected with 254 nm light or by development of color with I₂. Merck kieselgel 60 (230-400 mesh) was used for column chromatography. Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN. Purity and identity of the products (crude and/or purified) were also established using a Hewlett-Packard (HP) GC/MS (EI) system with a HP 5973 mass selective detector [capillary column HP-5MS (30 m × 0.25 mm × 25 μm)]. Phosphonates **1a-f** were prepared as follow: **1a** and **1d** as reported;^{13c} **1b** and **1e** as described^{13c} for **1a** (using 2-mercaptopyridine instead of 2-mercaptopyrimidine) and **1d**, respectively with data as noted below; **1c** was prepared by oxidation of commercially available diethyl (phenylthiomethyl)phosphonate with Oxone.¹⁹ Fluorination^{13c} of **1c** with Selectfluor gave **1f** (92%) with data as reported.²⁰

Diethyl (Pyridin-2-ylsulfonyl)methylphosphonate (1b). Treatment^{13c} of diethyl (chloromethyl)phosphonate (1.25 mL, 1.5 g, 8.05 mmol) with 2-mercaptopyridine (0.9 g, 8.0 mmol) gave the viscous thioether, which was oxidized with Oxone (17.6 g/50% reagent, 14.3 mmol) to give **1b** (1.0g, 60% overall) as a colorless oil: ¹H NMR δ 1.04 (t, *J* = 7.1 Hz, 6H), 3.91 (“quint”, *J* = 7.2 Hz, 4H), 3.95 (d, *J* = 16.8 Hz, 2H), 7.41 (t, *J* = 6.0 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 8.52 (d, *J* = 4.2 Hz, 1H); ¹³C NMR δ 16.43 (d, *J* = 6.3 Hz), 48.95 (d, *J* = 138.0 Hz), 63.57 (d, *J* = 6.4 Hz), 122.14 (py), 128.13 (py), 138.71 (py), 150.36 (py), 157.45 (py); ³¹P NMR [¹H] δ 12.43 (s); MS *m/z* 294 (100, MH⁺). Anal. Calcd for C₁₀H₁₆NO₅PS (293.05): C, 40.95; H, 5.50; N, 4.78. Found: C, 40.88; H, 5.32; N, 5.02.

Diethyl Fluoro(pyridin-2-ylsulfonyl)methylphosphonate (1e). Fluorination^{13c} of **1b** (300 mg, 1.05 mmol) with Selectfluor (0.8 g, 2.27 mmol) gave **1e** (167 mg, 51%): mp 37-39 °C; ¹H NMR δ 1.37 (td, *J* = 7.1, 0.6 Hz, 6H), 4.33 (“quint”, *J* = 7.1 Hz, 4H), 6.09 (dd, *J* = 45.6, 6.3 Hz, 1H), 7.62 (dd, *J* = 7.7, 4.7 Hz, 1H), 8.01 (t, *J* = 7.8 Hz, 1H), 8.14 (dd, *J* = 7.8, 0.7 Hz, 1H), 8.77 (dd, *J* = 4.0, 0.6 Hz, 1H); ¹³C NMR δ 16.76 (d, *J* = 5.9 Hz), 65.62 (dd, *J* = 10.0, 6.5 Hz), 94.16 (dd, *J* = 229.1, 159.4 Hz), 124.64 (py), 128.68 (py), 138.81 (py), 151.02 (py), 155.36 (py); ¹⁹F NMR δ -197.53 (dd, ²*J*_{F-P} = 67.8 Hz, ²*J*_{F-H} = 45.2Hz); ³¹P NMR [¹H] δ 6.29 (d, ²*J*_{F-P} = 68.0 Hz); MS *m/z* 312 (100, MH⁺). Anal. Calcd for C₁₀H₁₅FNO₅PS (311.04): C, 38.59; H, 4.86; N, 4.50. Found: C, 38.95; H, 5.12; N, 4.36.

(*E/Z*)-1-Fluoro-2-phenyl-1-(pyrimidin-2-ylsulfonyl)ethene (3a). Procedure A. LHMDs (1.0 M; 1.11 mL, 1.11 mmol) was added dropwise to a stirred solution of **1d** (316 mg, 1.01 mmol) in dried THF (5 mL) under N₂ at -78 °C. After 20 minutes, **2a** (0.11 mL, 118 mg, 1.11 mmol) was added and the yellow reaction mixture was allowed to warm to -40 °C over 2 h. Glacial acetic acid (~0.1 mL) was added and volatiles were evaporated. The residue was partitioned (NaHCO₃/H₂O/EtOAc) and the organic layer was washed (brine), dried (MgSO₄), evaporated and chromatographed (15 → 30% EtOAc/hexanes) to give **3a** (232 mg, 87%; *E/Z*, 19:1): mp 147-150 °C soften, 151-152 °C dec.; ¹H NMR for **3a(E)** δ 7.20 (d, *J* = 34.3 Hz, 1H), 7.45-7.49 (m, 3H), 7.63 (t, *J* = 4.9 Hz, 1H), 7.68-7.71 (m, 2H), 9.02 (d, *J* = 4.9 Hz, 2H); ¹³C NMR δ 120.13 (ph), 124.88 (py), 128.60 (ph), 129.51 (ph), 130.94 (d, ²*J*_{C-F} = 7.5 Hz), 131.32 (ph), 151.45 (d, ¹*J*_{C-F} = 239.1 Hz), 159.49 (py), 165.09 (py); ¹⁹F NMR δ -112.30 (d, ³*J*_{F-H(cis)} = 21.0 Hz, 0.05F, *Z*), -122.62 (d, ³*J*_{F-H(trans)} = 34.0 Hz, 0.95F, *E*); MS *m/z* 265 (100, MH⁺). Anal. Calcd for C₁₂H₉FN₂O₂S (264.28): C, 54.54; H, 3.43; N, 10.60. Found: C, 54.73; H, 3.53; N, 10.40.

(*E/Z*)-1-Fluoro-4-phenyl-1-(pyrimidin-2-ylsulfonyl)-1-butene (3b). Treatment of **2b** (0.22 mL, 202 mg, 1.5 mmol) with **1d** (420 mg, 1.35 mmol) by procedure A gave **3b** (355 mg, 90%; *E/Z*, 5:2) as viscous oil. Compound **3b(E)** had: IR (neat) 2929, 1670, 1603, 1556, 1385 cm⁻¹; ¹H NMR δ 2.68 (q, *J* = 7.7 Hz, 2H), 2.82 (t, *J* = 7.7 Hz, 2H), 6.47 (dt, *J* = 32.0, 7.7 Hz, 1H), 7.19-7.30 (m, 5H), 7.60 (t, *J* = 4.8 Hz, 1H), 8.94 (d, *J* = 4.8 Hz, 2H); ¹³C NMR δ 26.74 (C3), 34.39 (C4), 122.63 (d, *J* = 6.1 Hz, C2), 124.97 (py), 126.88 (ph), 128.80 (ph), 129.01 (ph), 140.30 (ph), 152.37 (d, *J* = 295.1 Hz, C1), 159.45 (py), 164.85 (py); ¹⁹F NMR δ -125.25 (d, *J* = 33.0 Hz). Compound **3b(Z)** had: ¹H NMR δ 2.82 (t, *J* = 7.7 Hz, 2H), 2.96 (q, *J* = 7.7, 2H), 6.23 (dt, *J* = 21.1, 8.4 Hz, 1H), 7.19-7.30 (m, 5H), 7.60 (t, *J* = 4.8 Hz, 1H), 8.94 (d, *J* = 4.8 Hz, 2H); ¹³C NMR δ 26.78 (C3), 35.54 (C4), 124.48 (d, *J* = 11.8 Hz, C2), 125.04 (py), 126.8 (ph), 128.93 (ph), 128.96 (ph), 140.47 (ph), 150.58 (d, *J* = 287.4 Hz, C1), 159.48 (py), 165.13 (py); ¹⁹F NMR δ -114.31 (d, *J* = 22.6 Hz); MS *m/z* 293 (100, MH⁺). Anal. Calcd for C₁₄H₁₃FN₂O₂S (292.33): C, 57.52; H, 4.48; N, 9.58. Found: C, 57.86; H, 4.79; N, 9.31.

(*E/Z*)-1-Fluoro-2-phenyl-1-(pyrimidin-2-ylsulfonyl)propene (3d). Treatment of **2d** (0.06 mL, 64 mg, 0.53 mmol) with **1d** (150 mg, 0.48 mmol) by procedure A gave **3d** (105 mg, 80%; *E/Z*, 1:1). Compound **3d(E)** had: ¹H NMR δ 2.49 (d, *J* = 3.5 Hz, 3H), 7.34-7.38 (m, 5H), 7.58 (t, *J* = 5.0 Hz, 1H), 8.96 (d, *J* = 4.5 Hz, 2H); ¹³C NMR δ 17.76 (Me), 124.59 (py), 128.20 (ph), 128.91 (ph), 129.68 (ph), 132.56 (d, *J* = 6.2 Hz, C2), 136.32 (ph), 147.10 (d, *J* = 285.9 Hz, C1), 159.40 (py), 165.77 (py); ¹⁹F NMR δ -118.88 (q, ⁴*J*_{F-H(trans)} = 3.5 Hz, *E*). Compound **3d(Z)** had: ¹H NMR δ 2.26 (d, *J* = 4.6 Hz, 3H), 7.25-7.32 (m, 5H), 7.55 (t, *J* = 4.9 Hz, 1H), 8.92 (d, *J* = 4.9 Hz, 2H); ¹⁹F NMR δ -118.25 (q, ⁴*J*_{F-H(cis)} = 4.3 Hz, *Z*); MS 279 *m/z* (100, MH⁺). Anal. Calcd for C₁₃H₁₁FN₂O₂S•0.15C₆H₁₄ (299.84): C, 58.08; H, 4.87; N, 9.34.

Found: C, 57.86; H, 4.68; N, 9.27 (0.15 molecule of hexane was integrated on ^1H NMR).

(*E/Z*)-1-Fluoro-4-phenyl-1-(pyridin-2-ylsulfonyl)-1-butene (4b). Treatment of **2b** (0.032 mL, 29.6 mg, 0.22 mmol) with **1e** (62.2 mg, 0.2 mmol) by procedure A gave **4b** (58 mg, 100%; *E/Z*, 2:1). Compound **4b(E)** had: mp 58-60 °C; ^1H NMR δ 2.63 (qd, $J = 7.7$, 2.0 Hz, 2H), 2.84 (t, $J = 7.7$ Hz, 2H), 6.47 (dt, $J = 32.4$, 7.8 Hz, 1H), 7.19-7.34 (m, 5H), 7.61 (dd, $J = 7.1$, 4.2 Hz, 1H), 8.00 (td, $J = 7.8$, 1.7 Hz, 1H), 8.14 (d, $J = 7.85$ Hz, 1H), 8.80 (d, $J = 3.7$ Hz, 1H); ^{13}C NMR δ 26.67 (C3), 34.54 (C4), 121.03 (d, $J = 6.1$ Hz, C2), 124.22 (py), 126.85 (py), 128.33 (py), 128.75 (ph), 128.99 (ph), 138.73 (py) 140.34 (ph), 151.08 (ph), 152.97 (d, $J = 294.4$ Hz, C1), 155.84 (py); ^{19}F NMR δ -127.67 (d, $J = 33.9$ Hz). Compound **4b(Z)** had: ^1H NMR δ 2.88 (t, $J = 7.8$ Hz, 2H), 3.04 (q, $J = 7.8$ Hz, 2H), 6.10 (dt, $J = 21.4$, 8.4 Hz, 1H), 7.19-7.34 (m, 5H), 7.61 (dd, $J = 7.1$, 4.2 Hz, 1H), 8.00 (td, $J = 7.8$, 1.7 Hz, 1H), 8.11 (d, $J = 7.9$ Hz, 1H), 8.80 (d, $J = 3.7$ Hz, 1H); ^{13}C NMR δ 30.13 (C3), 35.74 (C4), 122.92 (d, $J = 12.2$ Hz, C2), 123.64 (py), 126.76 (py), 128.41 (py), 128.75 (ph), 128.96 (ph), 138.72 (py) 140.57 (ph), 151.09 (ph), 151.34 (d, $J = 286.9$ Hz, C1), 156.57 (py); ^{19}F NMR δ -116.02 (d, $J = 22.6$ Hz); MS $m/z = 292$ (100, MH^+). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{FNO}_2\text{S}$ (291.07): C, 61.84; H, 4.84; N, 4.81. Found: C, 62.48; H, 5.18; N, 4.37.

(*E/Z*)-1-Fluoro-2-phenyl-1-(phenylsulfonyl)ethene (5a). Treatment of **2a** (0.11 mL, 113 mg, 1.06 mmol) with **1f** (300 mg, 0.97 mmol) by procedure A gave **5a**^{5a} (221 mg, 86%; *E/Z*, 32:1): ^1H NMR δ 7.10 (d, $J = 34.9$ Hz, 1H), 7.39-7.41 (m, 3H), 7.57-7.63 (m, 4H), 7.70 (t, $J = 7.5$ Hz, 1H), 8.05 (d, $J = 7.5$ Hz, 2H); ^{19}F NMR δ -111.98 (d, $^3J_{\text{F-H(cis)}} = 18.8$ Hz, 0.03F, *Z*), -125.05 (d, $^3J_{\text{F-H(trans)}} = 33.9$ Hz, 0.97F, *E*).

(*E/Z*)-1-Fluoro-4-phenyl-1-(phenylsulfonyl)-1-butene (5b). Treatment of **2b** (0.160 mL, 167 mg, 1.24 mmol) with **1f** (350 mg, 1.13 mmol) by procedure A gave **5b** (324 mg, 99%; *E/Z*, 2.4:1) with data as reported.^{7b} The two isomers were separated by flash chromatography on silica gel (1/10 Et_2O /hexane). More polar **5b(E)** had: ^1H NMR δ 2.58 (qd, $J = 7.6$, 2.0 Hz, 2H), 2.82 (t, $J = 7.6$ Hz, 2H), 6.31 (dt, $J = 32.4$, 7.8 Hz, 1H), 7.16-7.31 (m, 5H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.70 (t, $J = 7.5$ Hz, 1H), 7.91 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR δ 26.31 (d, $J = 1.2$ Hz, C3), 34.52 (d, $J = 1.5$ Hz, C4), 118.09 (d, $J = 6.8$ Hz, C2), 126.89 (phSO₂), 128.75 (ph), 128.92 (ph), 129.02 (ph), 129.84 (phSO₂), 134.77 (phSO₂), 137.86 (ph), 140.35 (phSO₂), 154.81 (d, $J = 294.5$ Hz, C1); ^{19}F NMR δ -128.00 (d, $J = 33.9$ Hz); Less polar **5b(Z)** had: ^1H NMR δ 2.83 (t, $J = 7.3$ Hz, 2H), 3.03 (qd, $J = 7.3$, 1.4 Hz, 2H), 5.89 (dt, $J = 22.0$, 8.4 Hz, 1H), 7.22-7.36 (m, 5H), 7.56 (t, $J = 7.8$ Hz, 2H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR δ 26.64 (d, $J = 3.6$ Hz, C3), 35.79 (d, $J = 2.1$ Hz, C4), 120.05 (d, $J = 12.6$ Hz, C2), 126.83 (phSO₂), 128.73 (ph), 129.04 (ph, 2x), 129.80 (phSO₂), 134.81 (phSO₂), 138.56 (ph), 140.56 (phSO₂), 152.87 (d, $J = 286.0$ Hz, C1); ^{19}F NMR δ -116.00 (d, $J = 22.6$ Hz).

(*E/Z*)-1-Fluoro-1-(phenylsulfonyl)octene (5c). Treatment of **2c** (0.11 mL, 88 mg, 0.77 mmol)

with **1f** (228 mg, 0.73 mmol) by procedure A gave **5c** (183 mg, 92%; *E/Z*, 2:1). The two isomers were separated by flash chromatography on silica gel (1/10, Et₂O/hexane). Less polar **5c(Z)** had: ¹H NMR δ 0.91 (t, *J* = 6.9 Hz, 3H), 1.27-1.39 (m, 6H), 1.48 (quint, *J* = 7.3 Hz, 2H), 2.66 (dq, *J* = 1.6, 8.3 Hz, 2H), 5.87 (dt, *J* = 22.3, 8.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.71 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H); ¹³C NMR δ 14.47 (C8), 22.96 (C7), 24.84 (d, *J* = 3.5 Hz, C3), 29.18 (C6), 29.68 (d, *J* = 2.0 Hz, C4), 31.91 (C5), 121.34 (d, *J* = 12.0 Hz, C2), 128.72 (ph), 129.78 (ph), 134.79 (ph), 138.90 (ph), 152.50 (d, *J* = 285.0 Hz, C1); ¹⁹F NMR δ -117.11 (d, ³*J*_{F-H(cis)} = 22.6 Hz). More polar **5c(E)** had: IR (neat) 2929, 1668, 1343, 1165 cm⁻¹; ¹H NMR δ 0.86 (t, *J* = 6.9 Hz, 3H), 1.21-1.30 (m, 6H), 1.44 (“quint”, *J* = 7.1 Hz, 2H), 2.21 (dq, *J* = 2.3, 8.3 Hz, 2H), 6.27 (dt, *J* = 32.7, 7.9 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.68 (dt, *J* = 1.8, 7.5 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H); ¹³C NMR δ 14.39 (C8), 22.87 (C7), 24.60 (d, *J* = 1.9 Hz, C3), 28.42 (d, *J* = 1.4 Hz, C4), 29.01 (C6), 31.75 (C5), 119.19 (d, *J* = 7.0 Hz, C2), 128.90 (ph), 129.79 (ph), 134.71 (ph), 138.00 (ph), 154.47 (d, *J* = 293.0 Hz, C1); ¹⁹F NMR δ -129.40 (d, ³*J*_{F-H(trans)} = 33.9 Hz); MS *m/z* 271 (100, MH⁺). Anal. Calcd for C₁₄H₁₉FO₂S (270.36): C, 62.19; H, 7.08. Found: C, 62.56; H, 7.33.

(*E/Z*)-1-Fluoro-2-phenyl-1-(phenylsulfonyl)propene (5d). Treatment of **2d** (0.12 mL, 127 mg, 1.06 mmol) with **1f** (300 mg, 0.96 mmol) by procedure A gave **5d**^{17a} (213 mg, 80%; *E/Z*, 1.5:1; overall). *E* isomer had: ¹H NMR δ 2.56 (d, *J* = 3.7 Hz, 3H), 7.23-7.42 (m, 5H), 7.60-8.06 (m, 5H); ¹⁹F NMR δ -119.87 (q, ⁴*J*_{F-H(trans)} = 3.8 Hz, *E*). *Z*-isomer had ¹H NMR δ 2.13 (d, *J* = 4.5 Hz, 3H), 7.23-7.42 (m, 5H), 7.51-7.82 (m, 5H); ¹⁹F NMR δ -118.70 (q, ⁴*J*_{F-H(cis)} = 3.8 Hz, *Z*). Note: Careful purification on silica gel gave fractions enriched in *E* or *Z* isomers.

[(Cyclohexylidene)(fluoro)]methyl phenyl sulfone (5e). Treatment of **2e** (0.12 mL, 108 mg, 1.1 mmol) with **1f** (310 mg, 1.0 mmol) by procedure A gave **5e** (252 mg, 99%) with data as reported:²¹ ¹⁹F NMR -125.6 (s).

(*E/Z*)-6-Chloro-1-fluoro-2-methyl-1-(phenylsulfonyl)-1-hexene (5f). Treatment of **2f** (148 mg, 0.15 mL, 1.1 mmol) with **1f** (310 mg, 1.0 mmol) by procedure A [column chromatography, hexane/Et₂O (9:1)] gave **5f(Z)** (101 mg, 35%), **5f(*E/Z*)** (23 mg, 10%; *E/Z*, 1:1) and **5f(*E*)** (101 mg, 35%): MS *m/z* 293 (38, MH⁺[³⁷Cl]), 291 (100, MH⁺[³⁵Cl]). Less polar **5f(Z)** had: ¹H NMR δ 1.70 (quint, *J* = 7.7 Hz, 2H), 1.85 (d, *J* = 4.4 Hz, 3H), 1.87 (quint, *J* = 7.7 Hz, 2H), 2.69 (td, *J* = 7.7, 1.0 Hz, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 2H); ¹³C NMR δ 16.79 (d, *J* = 9.1 Hz, CH₃), 25.71 (d, *J* = 3.2 Hz, C4), 30.13 (C3), 32.36 (C5), 45.07 (C6), 128.59 (ph), 129.74 (ph), 130.35 (d, *J* = 7.9 Hz, C2), 134.58 (ph), 139.35 (ph), 149.18 (d, *J* = 279.1 Hz, C1); ¹⁹F NMR δ -120.72 (sextet, *J* = 3.8 Hz). More polar **5f(*E*)** had: ¹H NMR δ 1.57-1.67 (m, 2H), 1.68-1.77 (m, 2H), 2.22 (d, *J* = 3.3 Hz, 3H), 2.23 (quint, *J* = 3.8 Hz, 2H), 3.52 (t, *J* = 6.3 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.4

Hz, 1H), 7.97 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR δ 15.67 (CH₃), 24.34 (d, $J = 2.0$ Hz, C4), 31.80 (d, $J = 7.3$ Hz, C3), 32.10 (C5), 44.82 (C6), 128.44 (ph), 129.74 (ph), 129.89 (d, $J = 9.5$ Hz, C2), 134.56 (ph), 139.53 (ph), 149.04 (d, $J = 277.7$ Hz, C1); ^{19}F NMR δ -122.30 (sextet, $J = 3.8$ Hz). Anal. Calcd for C₁₃H₁₆ClFO₂S (290.05): C, 53.70; H, 5.55. Found: C, 54.02; H, 5.72.

(E)-2-Phenyl-1-(pyrimidin-2-ylsulfonyl)ethene (6a). Treatment of **2a** (0.38 mL, 397 mg, 3.70 mmol) with **1a** (1.0 g, 3.4 mmol) by procedure A and crystallization (MeOH) gave **6a** (688 mg, 82%) as white needle: mp 112–113 °C; ^1H NMR δ 7.22 (d, $J = 15.5$ Hz, 1H), 7.37–7.42 (m, 3H), 7.52–7.56 (m, 3H), 7.81 (d, $J = 15.5$ Hz, 1H), 8.92 (d, $J = 4.9$ Hz, 2H); ^{13}C NMR δ 123.67 (ph), 124.07 (py), 129.37 (ph), 129.60 (ph), 132.16 (C2), 132.60 (ph), 147.26 (C1), 159.16 (py), 167.08 (py); MS m/z 247 (100, MH⁺). Anal. Calcd for C₁₂H₁₀N₂O₂S (246.29): C, 58.52; H, 4.09; N, 11.37. Found: C, 58.19; H, 4.19; N, 11.21. Purification of the mother liquor on silica gel column (CHCl₃) yielded an additional amount of **6a** (142 mg, 17%) to give an overall yield of **6a** (830 mg, 99%).

(E)-4-Phenyl-1-(pyrimidin-2-ylsulfonyl)-1-butene (6b). Treatment of **2b** (0.32 mL, 296 mg, 2.2 mmol) with **1a** (588 mg, 2.0 mmol) by procedure A gave **6b** (466 mg, 85%) as a white solid: mp 60–62 °C; ^1H NMR δ 2.65 (q, $J = 7.4$ Hz, 2H), 2.83 (t, $J = 7.4$ Hz, 2H), 6.69 (d, $J = 15.3$ Hz, 1H), 7.14–7.29 (m, 6H), 7.54 (t, $J = 4.8$ Hz, 1H), 8.92 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR δ 33.96 (C3), 34.04 (C4), 124.18 (py), 126.8 (C2), 127.73 (C1), 128.78 (ph), 128.98 (ph), 140.29 (ph), 151.17 (ph), 159.29 (py), 166.84 (py); MS m/z 275 (100, MH⁺). Anal. Calcd for C₁₄H₁₄N₂O₂S (274.08): C, 61.29; H, 5.14; N, 10.21. Found: C, 61.45; H, 5.39; N 10.22.

(E)-4-Phenyl-1-(pyridin-2-ylsulfonyl)-1-butene (7b). Treatment of **2b** (0.032 mL, 30 mg, 0.22 mmol) with **1b** (59 mg, 0.2 mmol) by procedure A gave **7b** (54 mg, 100%) as a white solid: mp 96–98 °C; ^1H NMR δ 2.64 (q, $J = 7.6$ Hz, 2H), 2.83 (t, $J = 7.6$ Hz, 2H), 6.57 (d, $J = 15.2$ Hz, 1H), 7.13–7.28 (m, 6H), 7.55 (dd, $J = 7.3, 4.5$ Hz, 1H), 7.96 (td, $J = 7.8, 1.7$ Hz, 1H), 8.07 (d, $J = 7.8$ Hz, 1H), 8.75 (d, $J = 4.7$ Hz, 1H); ^{13}C NMR, δ 33.88 (C3), 34.16 (C4), 122.29 (py), 126.78 (C2), 127.50 (py), 128.75 (ph), 128.79 (C1), 128.96 (ph), 138.58 (py), 140.37 (ph), 149.33 (ph), 150.72 (py), 158.80 (py); MS m/z 274 (100, MH⁺). Anal. Calcd for C₁₅H₁₅NO₂S (273.08): C, 65.91; H, 5.53; N, 5.12. Found: C, 66.52; H, 6.45; N, 4.41.

(E)-2-Phenyl-1-(phenylsulfonyl)ethene (8a). Treatment of **2a** (0.115 mL, 120 mg, 1.13 mmol) with **1c** (300 mg, 1.03 mmol) by procedure A gave **8a** (250 mg, 100%) with data as reported:²² ^1H NMR δ 6.90 (d, $J = 15.4$ Hz, 1H), 7.39–7.42 (m, 3H), 7.48–7.50 (m, 2H), 7.56 (t, $J = 7.1$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.70 (d, $J = 15.4$ Hz, 1H), 7.97 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR δ 127.68, 128.06, 129.02, 129.52, 129.79, 131.68, 132.73, 133.85, 141.10, 142.92.

(E)-4-Phenyl-1-(phenylsulfonyl)-1-butene (8b). Treatment of **2b** (0.15 mL, 152 mg, 1.13

mmol) with **1c** (300 mg, 1.03 mmol) by procedure A gave **8b**²³ (217 mg, 78%): ¹H NMR δ 2.58 (dq, J = 1.1, 7.8 Hz, 2H), 2.80 (t, J = 7.8 Hz, 2H), 6.32 (dt, J = 15.3, 1.5 Hz, 1H), 7.03 (dt, J = 15.1, 6.9 Hz, 1H), 7.13-7.31 (m, 5H), 7.54 (t, J = 7.4 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.85 (d, J = 7.2 Hz, 2H).

(E)-1-(Phenylsulfonyl)octene (8c). Treatment of **2c** (0.30 mL, 245 mg, 2.15 mmol) with **1c** (600 mg, 2.05 mmol) by procedure A gave **8c**²⁴ (507 mg, 98%): ¹H NMR δ 0.78 (t, J = 7.1 Hz, 3H), 1.13-1.26 (m, 6H), 1.37 (quint, J = 7.5 Hz, 2H), 2.16 (dq, J = 1.3, 7.6 Hz, 2H), 6.27 (d, J = 15.1 Hz, 1H), 6.92 (dt, J = 15.1, 7.0 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.80 (d, J = 7.2 Hz, 2H); ¹³C NMR δ 14.37 (C8), 22.81 (C7), 27.87 (C6), 29.00 (C5), 31.78 & 31.80 (C3/4), 127.83 (ph), 129.61 (ph), 130.68 (C2), 133.61 (ph), 141.10 (ph), 147.71 (C1).

(Cyclohexylidene)methyl phenyl sulfone (8e). Treatment of **2e** (216 mg, 0.024 mL, 2.2 mmol) with **1c** (62 mg, 0.2 mmol) by procedure A gave **8e** (44 mg, 94%) with data as reported:²⁵ m.p. 32.5-34.0 °C. ¹H NMR δ 6.16 (s, 1H, CH).

(E/Z)-1-Fluoro-2-phenyl-1-[tris(trimethylsilyl)silyl]ethene (9a). Procedure B. Argon was bubbled through a solution of **3a** (*E/Z*, 19:1; 30 mg, 0.11 mmol) in anhydrous benzene or toluene (2 mL) for 15 min. Tris(trimethylsilyl)silane (0.095 mL, 85 mg, 0.34 mmol) and AIBN (5 mg, 0.028 mmol) were added, and degassing of oxygen was continued for another 10 min. The solution was then heated (85 °C, oil bath) for 4 h [additional AIBN (20 mg, 0.11 mmol) in degassed benzene or toluene (2 mL) was injected through a septum via a precision syringe pump or periodically by manual injection over the 4 h period]. The volatiles were evaporated, and the residue was chromatographed (hexane) to give **9a** (35 mg, 60%; *E/Z*, 24:1): IR (neat) 2950, 1622, 1397, 1246 cm⁻¹; ¹H NMR for **9a(E)** δ 0.20 (s, 27H), 5.82 (d, J = 50.4 Hz, 1H), 7.24 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.4 Hz, 2H), 7.54 (d, J = 7.3 Hz, 2H); ¹³C NMR δ 1.23 (TMS), 122.98 (ph), 127.38 (ph), 128.80 (ph), 129.11 (d, J = 31.2 Hz, C2), 134.79 (d, J = 2.2 Hz, ph), 169.17 (d, J = 298 Hz, C1); ¹⁹F NMR δ -78.51 (d, ³ $J_{\text{F-H(cis)}}$ = 38.0 Hz, 0.04F, *Z*), -89.47 (d, ³ $J_{\text{F-H(trans)}}$ = 50.4 Hz, 0.96F, *E*); MS m/z 369 (100, MH⁺). Anal. Calcd for C₁₇H₃₃FSi₄ (368.78): C, 55.37; H, 9.02. Found: C, 55.01; H, 9.25. Repeated column chromatography afforded pure *E*-isomer.

Analogous treatment of **5a** (*E/Z*, 97:3) with TTMSS (2 equiv.) by procedure B gave **9a** (90%; *E/Z*, 99:1).

(E)-1-Fluoro-4-(phenyl)-1-[tris(trimethylsilyl)silyl]-1-butene (9b). Treatment of **5b** (*E/Z*, 2.4:1; 30 mg, 0.10 mmol) with TTMSS (0.032 mL, 28 mg, 0.11 mmol) and AIBN (25 mg, 0.15 mmol) by procedure B gave **9b(E)** (21 mg, 51%): IR (neat) 2950, 1581, 1397, 1245 cm⁻¹; ¹H NMR δ 0.20 (s, 27H), 2.51 (q, J = 7.3 Hz, 2H), 2.70 (t, J = 7.4 Hz, 2H), 4.94 (dt, J = 47.8, 7.3 Hz, 1H), 7.18-7.31 (m, 5H); ¹³C NMR δ 1.14 (TMS), 26.28 (d, J = 10.1 Hz, C3), 36.15 (d, J = 1.1 Hz, C4), 123.67 (d, J = 6.5 Hz, C2), 126.21 (ph), 128.68 (ph), 128.88 (ph), 142.06 (ph), 165.64 (d, J = 284.9 Hz, C1); ¹⁹F NMR δ -98.42 (d,

$^3J_{\text{F-H(trans)}} = 47.8 \text{ Hz}$; MS m/z 397 (100, MH^+). Anal. Calcd for $\text{C}_{19}\text{H}_{37}\text{FSi}_4$ (396.84): C, 57.51; H, 9.40. Found: C, 57.53; H, 9.63.

Treatment of **5b(Z)** by procedure B (18 h. reflux, benzene, 4.5 eq TTMSS, 3 eq. AIBN) gave **9b(E)** (66%). *Cis-trans* isomerization took place within 5 hours [*E* starting material (64%) and *E* product (36%) but no *Z* starting material was observed, ^{19}F NMR]. Continued refluxing yielded **9b(E)** (66%), **5b(E)** (23%) and decomposition byproducts (11%).

Treatment of **3b** (*E/Z*, 1.9:1; 33 mg, 0.11 mmol) with TTMSS (0.11 mL, 84 mg, 0.33 mmol) and AIBN (25 mg, 0.15 mmol) by procedure B gave **9b** (36 mg, 83%; *E/Z*, 24:1): ^{19}F NMR δ -98.42 (d, $^3J_{\text{F-H(trans)}} = 47.8 \text{ Hz}$, 0.96F, *E*), -88.56 (d, $^3J_{\text{F-H(cis)}} = 33.9 \text{ Hz}$, 0.04F, *Z*).

Treatment of **4b** (*E/Z*, 2:1; 29 mg, 0.10 mmol) with TTMSS (0.10 mL, 75 mg, 0.30 mmol) and AIBN (21.3 mg, 0.13 mmol) by procedure B gave **9b** (26 mg, 66%; *E/Z*, 16:1).

(E/Z)-1-Fluoro-1-[tris(trimethylsilyl)silyl]-1-octene (9c). Treatment of **5c** (*E/Z*, 6.7:1; 29 mg, 0.09 mmol) with TTMSS (0.052 mL, 46 mg, 0.18 mmol) and AIBN (18 mg, 0.11 mmol) by procedure B gave **9c** (*E/Z*, 49:1; 15 mg, 42%): IR (neat) 2954, 1635, 1396, 1246 cm^{-1} ; ^1H NMR for **9c(E)** δ 0.23 (s, 27H), 0.91 (t, $J = 7.0 \text{ Hz}$, 3H), 1.30-1.34 (m, 8H), 2.17 (q, $J = 6.5 \text{ Hz}$, 2H), 4.94 (dt, $J = 48.2, 7.4 \text{ Hz}$, 1H); ^{13}C NMR δ 1.17 (TMS), 14.50 (C8), 24.65 (d, $J = 10.0 \text{ Hz}$, C3), 23.08, 29.16, 29.88, 32.03 (C 4/5/6/7), 125.05 (d, $J = 6.8 \text{ Hz}$, C2), 164.85 (d, $J = 283.3 \text{ Hz}$, C1); ^{19}F NMR δ -90.23 (d, $^3J_{\text{F-H(cis)}} = 35.8 \text{ Hz}$, 0.02F, *Z*), -99.83 (d, $^3J_{\text{F-H(trans)}} = 48.2 \text{ Hz}$, 0.98F, *E*). Anal. Calcd for $\text{C}_{17}\text{H}_{41}\text{FSi}_4$ (376.85): C, 54.18; H, 10.97. Found: C, 54.43; H, 11.19.

(E/Z)-1-Fluoro-2-phenyl-1-[tris(trimethylsilyl)silyl]propene (9d). Treatment of **5d** (*E/Z*, 1:2.6; 36 mg, 0.13 mmol) with TTMSS (0.080 mL, 72 mg, 0.28 mmol) and AIBN (26 mg, 0.16 mmol) by procedure B gave **9d** (*E/Z*, 1:1.9; 36 mg, 73%). More polar **9d(E)** had: IR (neat) 2953, 1591, 1405, 1248 cm^{-1} ; ^1H NMR δ 0.30 (s, 27H), 2.02 (d, $J = 3.7 \text{ Hz}$, 3H), 7.19-7.49 (m, 5H); ^{13}C NMR δ 2.00 (TMS), 20.78 (d, $J = 6.7 \text{ Hz}$, Me), 127.28 (ph), 128.44 (ph), 128.49 (ph), 130.34 (d, $J = 7.4 \text{ Hz}$, C2), 139.15 (d, $J = 6.1 \text{ Hz}$, ph), 161.77 (d, $J = 279.7 \text{ Hz}$, C1); ^{19}F NMR δ -91.41 ("s"). Less polar **9d(Z)** had: ^1H NMR δ 0.09 (s, 27H), 2.03 (d, $J = 4.6 \text{ Hz}$, 3H), 7.17-7.36 (m, 5H); ^{13}C NMR δ 1.76 (TMS), 19.05 (d, $J = 14.7 \text{ Hz}$, Me), 127.73 (ph), 129.14 (ph), 129.54 (d, $J = 2.8 \text{ Hz}$, ph), 134.39 (d, $J = 13.9 \text{ Hz}$, C2), 141.42 (d, $J = 11.6 \text{ Hz}$, ph), 162.15 (d, $J = 273.1 \text{ Hz}$, C1); ^{19}F NMR δ -84.06 (q, $J = 3.8 \text{ Hz}$); MS m/z 383 (100, MH^+). Anal. Calcd for $\text{C}_{18}\text{H}_{35}\text{FSi}_4$ (382.81): C, 56.48; H, 9.22. Found: C, 56.75; H, 9.57.

Analogous treatment of **3d** (*E/Z*, 24:1) by procedure B gave **9d(E)** (40%).

[Cyclohexylidene(fluoro)methyl]tris(trimethylsilyl)silane (9e). Treatment of **5e** (51 mg, 0.2 mmol) with TTMSS (0.2 mL, 0.6 mmol) and AIBN (42.7 mg, 0.25 mmol) by procedure B gave **9e** (54 mg, 75%): IR (neat) 2952, 1637, 1397, 1247 cm^{-1} ; ^1H NMR δ 0.24 (s, 27H), 1.55 (br s, 6H), 2.04 (br s, 2H),

2.33 (br. s 2H); ^{13}C NMR δ 1.92 (TMS), 26.34 (d, J = 14.0 Hz), 26.96, 27.54, 28.47 (d, J = 2.6 Hz), 31.25 (d, J = 8.1 Hz), 134.94 (d, J = 8.4 Hz), 156.06 (d, J = 269.9 Hz); ^{19}F NMR δ -102.03 (s); HRMS (FAB, m/z): calcd for $\text{C}_{16}\text{H}_{37}\text{FSi}_4\text{Li}$ (MLi^+), 367.2116; found 367.2110. Anal. Calcd for $\text{C}_{16}\text{H}_{37}\text{FSi}_4$ (360.81): C, 53.26; H, 10.34. Found: C, 52.94; H, 9.99.

(*E*)-2-Phenyl-1-[tris(trimethylsilyl)silyl]ethene (10a). Treatment of **6a(*E*)** (30 mg, 0.12 mmol) with TTMSS (0.102 mL, 91 mg, 0.37 mmol) and AIBN (25 mg, 0.15 mmol) by procedure B gave **10a** (21 mg, 50%) with data as reported:^{12a,26} ^1H NMR δ 0.24 (s, 27H), 6.47 (d, J = 18.8 Hz, 1H), 6.92 (d, J = 18.8 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1 H), 7.35 (t, J = 7.3 Hz, 2H), 7.41 (d, J = 7.3 Hz, 2H).

Analogous treatment of **8a(*E*)** by procedure B gave **10a** (60%).

(*E*)-4-Phenyl-1-[tris(trimethylsilyl)silyl]-1-butene (10b). Treatment of **8b(*E*)** (30 mg, 0.11 mmol) with TTMSS (0.061 mL, 55 mg, 0.22 mmol) and AIBN (25 mg, 0.15 mmol) by procedure B gave **10b** (34 mg, 81%): IR (neat) 2951, 1603, 1397, 1246 cm^{-1} ; ^1H NMR δ 0.17 (s, 27H), 2.46 ("q", J = 7.2 Hz, 2H), 2.73 (t, J = 7.3 Hz, 2H), 5.55 (dt, J = 18.2, 1.3 Hz, 1H), 6.03 (dt, J = 18.2, 6.4 Hz, 1H), 7.19-7.31 (m, 5H); ^{13}C NMR δ 1.20 (TMS), 36.12 (C4), 39.63 (C3), 122.16 (C1), 126.11 (Ar), 128.66 (Ar), 128.90 (Ar), 142.26 (Ar), 148.29 (C2); MS m/z 379 (100, MH^+). Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{Si}_4 \cdot \text{H}_2\text{O}$ (396.23): C, 57.59; H, 10.17. Found: C, 57.19; H, 10.47.

Treatment of **7b(*E*)** (27 mg, 0.10 mmol) with TTMSS (0.10 mL, 75 mg, 0.30 mmol) and AIBN (21 mg, 0.13 mmol) by procedure B also gave **10b** (22 mg, 57%).

Treatment of **6b(*E*)** (39 mg, 0.14 mmol) with TTMSS (0.14 mL, 107 mg, 0.43 mmol) and AIBN (31 mg, 0.18 mmol) by procedure B gave **10b** (16 mg, 30%).

(*E*)-1-[Tris(trimethylsilyl)silyl]-1-octene (10c). Treatment of **8c(*E*)** (38 mg, 0.15 mmol) with TTMSS (0.082 mL, 74 mg, 0.30 mmol) and AIBN (31 mg, 0.19 mmol) by procedure B gave **10c** (45 mg, 83%): IR (neat) 2955, 1603, 1396, 1245 cm^{-1} ; ^1H NMR δ 0.23 (s, 27H), 0.91 (t, J = 6.9 Hz, 3H), 1.30-1.40 (m, 8H), 2.13 (q, J = 6.9 Hz, 2H), 5.51 (d, J = 18.2 Hz, 1H), 6.01 (dt, J = 18.2, 6.5 Hz, 1H); ^{13}C NMR δ 1.21 (TMS), 14.53 (C8), 23.10, 29.09, 29.57, 32.14 (C4/5/6/7), 38.08 (C3), 120.81 (C1), 149.91 (C2); HRMS (FAB, m/z): calcd for $\text{C}_{17}\text{H}_{42}\text{Si}_4\text{Li}$ (MLi^+), 365.2524; found 365.2518. Anal. Calcd for $\text{C}_{17}\text{H}_{42}\text{Si}_4$ (358.86): C, 56.90; H, 11.80. Found: C, 56.75; H, 12.11.

[(Cyclohexylidene)methyl]tris(trimethylsilyl)silane (10e). Treatment of **8e** (47 mg, 0.2 mmol) with TTMSS (0.2 mL, 0.6 mmol) and AIBN (42 mg, 0.25 mmol) by procedure B gave **10e** (47 mg, 68%); ^1H NMR δ 0.19 (s, 27H), 1.57 (br s, 6H), 2.20 (br s, 2H), 2.24 (br s, 2H), 5.10 (s, 1H), ^{13}C NMR δ 1.59 (TMS), 26.74, 28.71, 29.21, 36.39, 41.00, 110.89 (CH), 159.75 (C). HRMS (FAB, m/z): calcd for $\text{C}_{16}\text{H}_{38}\text{Si}_4\text{Li}$ (MLi^+), 349.2211; found 349.2206. Anal. Calcd for $\text{C}_{16}\text{H}_{38}\text{Si}_4$ (342.81): C, 56.06; H, 11.17. Found: C, 56.25; H, 11.47.

(E)-1-Fluoro-2-phenyl-1-[tris(trimethylsilyl)germyl]ethene (11a). Procedure C. Argon was bubbled through a solution of **5a(E)** (45 mg, 0.17 mmol) in anhydrous benzene or toluene (2 mL) for 15 min. (TMS)₃GeH (0.054 mL, 50 mg, 0.17 mmol) and AIBN (5 mg, 0.03 mmol) were added, and degassing of oxygen was continued for another 10 min. and then the solution was refluxed for 6 h. The volatiles were evaporated, and the residue was chromatographed in hexane to give **11a** (63 mg, 90%): ¹H NMR δ 0.34 (s, 27H), 5.70 (d, *J* = 51.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H); ¹³C NMR δ 1.89 (TMS), 121.55 (C2), 126.98 (d, *J* = 2.2 Hz, ph), 128.78 (ph), 128.87 (ph), 134.96 (d, *J* = 3.0 Hz, ph), 171.34 (d, *J* = 318.9 Hz, C1); ¹⁹F NMR δ -81.22 (d, ³*J*_{F-H(trans)} = 51.4 Hz); GC-MS (*t*_R 20.39 min) *m/z* 414 (3.5, M⁺, ⁷⁴Ge), 412 (2.0, M⁺, ⁷²Ge), 410 (1.5, M⁺, ⁷⁰Ge). Anal. Calcd for C₁₇H₃₃FGes₃ (413.31): C, 49.40; H, 8.05. Found: C, 49.04; H, 8.31.

(E)-1-Fluoro-2-phenyl-1-(tributylgermyl)ethene (12a). Treatment of **5a** (*E/Z*, 32:1; 30 mg, 0.11 mmol) with Bu₃GeH (0.059 mL, 56 mg, 0.23 mmol) and AIBN (18 mg, 0.11 mmol) by procedure C (7 h) gave **12a** (38 mg, 91%): ¹H NMR δ 0.91-0.99 (m, 6H), 0.93 (t, *J* = 7.0 Hz, 9H), 1.34-1.50 (m, 12H), 5.72 (d, *J* = 53.2 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H); ¹³C NMR δ 12.69 (CH₂), 14.18 (CH₃), 26.65 (CH₂), 27.57 (CH₂), 119.95 (d, *J* = 3.7 Hz, C2), 127.51 (d, *J* = 2.1 Hz, ph), 128.83 (ph), 129.21 (d, *J* = 7.5 Hz, ph), 134.11 (d, *J* = 3.7 Hz, ph), 171.73 (d, *J* = 212.8 Hz, C1); ¹⁹F NMR δ -102.04 (d, ³*J*_{F-H(trans)} = 52.7 Hz). Anal. Calcd for C₂₀H₃₃FGes (365.08): C, 65.80; H, 9.11. Found: C, 65.57; H, 9.43.

(E)-1-Fluoro-4-phenyl-1-(tributylgermyl)-1-butene (12b). Treatment of **5b(E)** (22 mg, 0.08 mmol) with Bu₃GeH (0.039 mL, 37 mg, 0.15 mmol) and AIBN (12 mg, 0.07 mmol) by procedure C (7 h) gave **12b** (20 mg, 66%): ¹H NMR δ 0.83-0.93 (m, 15H), 1.30-1.41 (m, 12H), 2.49 (dq, *J* = 1.3, 7.3 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H), 4.87 (dt, *J* = 50.6, 7.3 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H); ¹³C NMR δ 12.56 (CH₂), 14.15 (CH₃), 25.67 (C3), 26.75 (CH₂), 27.53 (CH₂), 36.13 (C4), 120.38 (d, *J* = 1.3 Hz, C2), 126.23 (ph), 128.65 (ph), 128.87 (ph), 142.19 (ph), 168.59 (d, *J* = 298.9 Hz, C1); ¹⁹F NMR δ -111.46 (d, ³*J*_{F-H(trans)} = 48.9 Hz). Anal. Calcd for C₂₂H₃₇FGes•0.25H₂O (397.64): C, 66.45; H, 9.51. Found: C, 66.46; H, 9.71.

(E)-1-Fluoro-2-phenyl-1-(triphenylgermyl)ethene (13a). Treatment of **5a** (*E/Z*, 32:1; 25 mg, 0.10 mmol) with Ph₃GeH (58 mg, 0.19 mmol) and AIBN (16 mg, 0.10 mmol) by procedure C gave **13a** (39 mg, 98%): ¹H NMR δ 5.99 (d, *J* = 51.6 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.45-7.51 (m, 9H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.65-7.70 (m, 6H); ¹³C NMR δ 123.27 (d, *J* = 4.0 Hz, C2), 128.18 (ph), 128.90 (ph), 128.98 (phGe), 129.59 (d, *J* = 7.4 Hz, ph), 130.13 (phGe), 133.61 (ph) 134.42 (d, *J* = 1.8 Hz, phGe), 135.61 (phGe), 167.45 (d, *J* = 310.3 Hz, C1); ¹⁹F NMR δ -104.45 (d, ³*J*_{F-H(trans)} =

52.7 Hz). Anal. Calcd for $C_{26}H_{21}FGe$ (426.05): C, 73.47; H, 4.98. Found: C, 73.71; H, 5.35.

(*E/Z*)-1-Fluoro-4-phenyl-1-(triphenylgermyl)-1-butene (13b). Treatment of **5b** (*E/Z*, 2.5:1; 50 mg, 0.17 mmol) with Ph_3GeH (105 mg, 0.34 mmol) and AIBN (10 mg, 0.06 mmol) by procedure C gave **13b** (58 mg, 76%; *E/Z*, 99:1): mp 58-60 °C 1H NMR δ 2.61 (q, $J = 7.4$ Hz, 2H), 2.74 (t, $J = 7.4$ Hz, 2H), 5.15 (dt, $J = 48.7, 7.3$ Hz, 1H), 7.18-7.54 (m, 20H); ^{13}C NMR δ 25.67 (d, $J = 10.0$ Hz, C3), 36.13 (C4), 124.36 (C2), 126.33 (ph), 128.73 (ph), 128.80 (phGe), 128.93 (ph), 129.90 (phGe), 134.66 (phGe), 135.49 (phGe), 141.87 (ph), 164.96 (d, $J = 297.2$ Hz, C1); ^{19}F NMR δ -103.98 (d, $^3J_{F-H(cis)} = 33.9$ Hz, 0.01F, *Z*), -112.54 (d, $^3J_{F-H(trans)} = 48.9$ Hz, 0.99F, *E*). Anal. Calcd for $C_{28}H_{25}FGe$ (453.11): C, 74.22; H, 5.56. Found: C, 74.14; H, 5.80.

(*E/Z*)-1-Fluoro-1-(triphenylgermyl)-1-octene (13c). Treatment of **5c** (*E/Z*, 6.7:1; 24 mg, 0.09 mmol) with Ph_3GeH (54 mg, 0.18 mmol) and AIBN (5 mg, 0.03 mmol) by procedure C gave **13c** (*E/Z*, 49:1; 35 mg, 90%): mp 78-80 °C. Compound **13c**(*E*) had: 1H NMR δ 0.91 (t, $J = 6.9$ Hz, 3H), 1.30-1.41 (m, 8H), 2.28 (q, $J = 7.2$ Hz, 2H), 5.13 (dt, $J = 49.2, 7.5$ Hz, 1H), 7.40-5.59 (m, 15H); ^{13}C NMR δ 14.52 (C8), 24.32 (d, $J = 10.0$ Hz, C3), 23.05, 29.34, 29.58, 31.98 (C 4/5/6/7), 125.59 (C2), 128.81 (ph), 129.89 (ph), 134.84 (d, $J = 1.6$ Hz, ph), 135.51 (ph), 164.27 (d, $J = 295.3$ Hz, C1); ^{19}F NMR δ -105.59 (d, $^3J_{F-H(cis)} = 37.6$ Hz, 0.02F, *Z*), -113.87 (d, $^3J_{F-H(trans)} = 48.9$ Hz, 0.98F, *E*). Anal. Calcd for $C_{26}H_{29}FGe$ (433.12): C, 72.10; H, 6.75. Found: C, 72.20; H, 7.13.

[Cyclohexylidene(fluoro)methyl]triphenylgermane (13e). Treatment of **5e** (51 mg, 0.2 mmol) with Ph_3GeH (123 mg, 0.4 mmol) and AIBN (44 mg, 0.25 mmol) by procedure C gave **13e** (73 mg, 87%): mp 56-58 °C; IR (neat) 2930, 1644, 1433, 1037 cm^{-1} ; 1H NMR δ 1.32 (br s, 2H), 1.55 (br s, 2H), 1.62 (br s, 2H), 1.90 (br s, 2H), 2.46 (br s, 2H), 7.33-7.68 (m, 15H); ^{13}C NMR δ 26.36 (d, $J = 13.5$ Hz), 26.79, 27.58, 27.78 (d, $J = 2.6$ Hz), 29.89 (d, $J = 8.3$ Hz), 128.71, 129.67, 135.42, 135.83 (d, $J = 2.9$ Hz), 136.08 (d, $J = 3.1$ Hz), 154.31 (d, $J = 284.2$ Hz); ^{19}F NMR δ -117.07 (s). Anal. Calcd for $C_{25}H_{25}FGe$ (417.07): C, 71.99; H, 6.04. Found: C, 72.21; H, 6.37.

(*E*)-6-Chloro-1-fluoro-2-methyl-1-(triphenylgermyl)-1-hexene (13f). Treatment of **5f**(*E*) (25 mg, 0.086 mmol) with Ph_3GeH (52.7 mg, 0.17 mmol) by procedure C gave **13f**(*E*) (38 mg, 98%): 1H NMR δ 1.45 (d, $J = 3.7$ Hz, 3H), 1.67 (quint, $J = 7.6$ Hz, 2H), 1.86 (quint, $J = 7.6$ Hz, 2H), 2.34 (td, $J = 7.5, 3.5$ Hz, 2H), 3.61 (t, $J = 6.6$ Hz, 2H), 7.35-7.47 (m, 9H), 7.50-7.65 (m, 6H); ^{13}C NMR δ 17.21 (d, $J = 8.5$ Hz, CH_3), 24.98 (C4), 29.35 (d, $J = 12.4$ Hz, C3), 32.53 (C5), 45.35 (C6), 128.78 (ph), 129.74 (ph), 135.40 (ph), 135.52 (d, $J = 3.0$ Hz, C2), 135.95 (ph), 157.69 (d, $J = 270.6$ Hz, C1); ^{19}F NMR δ -110.75 (sextet, $J = 3.8$ Hz). HRMS (FAB, m/z): calcd for $C_{25}H_{26}ClFGeLi$ (MLi^+), 461.1079; found 461.1071. Anal. Calcd for $C_{25}H_{26}ClFGe$ (454.09): C, 66.21; H, 5.78. Found: C, 453.81; H, 5.99.

(E)-1-Fluoro-2-phenyl-1-[tri(2-furyl)germyl]ethene (14a). Treatment of **5a** (*E/Z*, 32:1; 20 mg, 0.08 mmol) with tri(2-furyl)germane²⁷ (42 mg, 0.15 mmol) and AIBN (5 mg, 0.03 mmol) by procedure C gave **14a** (28 mg, 94%): ¹H NMR δ 6.10 (d, *J* = 50.4 Hz, 1H), 6.56 (dd, *J* = 3.3, 1.7 Hz, 3H), 6.99 (d, *J* = 3.3 Hz, 3H), 7.27-7.61 (m, 5H), 7.83 (d, *J* = 1.5 Hz, 3H); ¹³C NMR δ 110.51 (Ar), 122.93 (Ar), 123.36 (d, *J* = 4.4 Hz, C2), 128.51 (d, *J* = 2.4 Hz, ph), 128.89 (ph), 129.73 (d, *J* = 7.3 Hz, ph), 133.15 (d, *J* = 1.4 Hz, ph), 148.52 (Ar), 150.16 (Ar), 162.40 (d, *J* = 308.9 Hz, C1); ¹⁹F NMR δ -108.23 (d, ³*J*_{F-H(trans)} = 48.9 Hz); GC-MS (*t*_R 15.91 min) *m/z* 396 (5, M⁺, ⁷⁴Ge), 394 (4, M⁺, ⁷²Ge), 392 (3, M⁺, ⁷⁰Ge). Anal. Calcd for C₂₀H₁₅FGeO₃ (394.94): C, 60.82; H, 3.83. Found: C, 60.47; H, 3.58.

(E)-1-Fluoro-4-phenyl-1-[tri(2-furyl)germyl]-1-butene (14b). Treatment of **5b(E)** (20 mg, 0.07 mmol) with tri(2-furyl)germane²⁷ (38 mg, 0.14 mmol) and AIBN (5 mg, 0.03 mmol) by procedure C gave **14b** (16 mg, 55%): ¹H NMR δ 2.58 ('q', *J* = 7.0 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 5.34 (dt, *J* = 47.6, 7.4 Hz, 1H), 6.51-7.79 (m, 14H); ¹³C NMR δ 26.29 (d, *J* = 8.8 Hz, C3), 35.65 (C4), 110.40 (Ar), 122.47 (Ar), 124.71 (C2), 126.37 (ph), 128.74 (ph), 128.88 (ph), 141.74 (ph), 148.34 (Ar), 150.47 (Ar), 160.47 (d, *J* = 297.2 Hz, C1); ¹⁹F NMR δ -115.47 (d, ³*J*_{F-H(trans)} = 48.9 Hz); GC-MS (*t*_R 16.44 min) *m/z* 424 (5, M⁺, ⁷⁴Ge), 422 (4, M⁺, ⁷²Ge), 420 (3, M⁺, ⁷⁰Ge). Anal. Calcd for C₂₂H₁₉FGeO₃ (422.99): C, 62.46; H, 4.53. Found: C, 62.25; H, 4.83.

(E)-2-Phenyl-1-[tris(trimethylsilyl)germyl]ethene (15a). Treatment of **8a(E)** (45 mg, 0.18 mmol) with (TMS)₃GeH (0.058 mL, 54 mg, 0.18 mmol) and AIBN (5 mg, 0.03 mmol) by procedure C gave **15a** (24 mg, 34%; crude ¹H NMR showed 80% product): IR (neat) 2952, 1598, 1397, 1246 cm⁻¹; ¹H NMR δ 0.30 (s, 27H), 6.72 (d, *J* = 18.5 Hz, 1H), 6.86 (d, *J* = 18.5 Hz, 1H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H); ¹³C NMR δ 1.96 (TMS), 126.17 (ph), 126.39 (ph), 127.42 (C1), 128.86 (ph), 139.56 (ph), 143.97 (C2). GC-MS (*t*_R 19.99 min) *m/z* 396 (3.5, M⁺, ⁷⁴Ge), 394 (2.0, M⁺, ⁷²Ge), 392 (1.5, M⁺, ⁷⁰Ge). Anal. Calcd for C₁₇H₃₄GeSi₃ (395.32): C, 51.65; H, 8.67. Found: C, 51.38; H, 8.89.

(E)-2-Phenyl-1-(tributylgermyl)ethene (16a). Treatment of **8a(E)** (30 mg, 0.12 mmol) with Bu₃GeH (0.063 mL, 60 mg, 0.24 mmol) and AIBN (25 mg, 0.15 mmol) by procedure C gave **16a**^{5c} (22 mg, 52%; ¹H NMR of the crude reaction mixture showed almost quantitative conversion to **16a**): ¹H NMR δ 0.88-0.95 (m, 6H), 0.93 (t, *J* = 6.9 Hz, 9H), 1.37-1.43 (m, 12H), 6.66 (d, *J* = 19.0 Hz, 1H), 6.84 (d, *J* = 19.0 Hz, 1H), 7.27 (t, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H); ¹³C NMR δ 13.35 (CH₃), 14.22 (CH₂), 26.94 (CH₂), 27.84 (CH₂), 126.56 (ph), 127.97 (C1), 128.90 (ph), 129.41 (ph), 138.89 (ph), 143.28 (C2).

(E)-2-Phenyl-1-(triphenylgermyl)ethene (17a). Treatment of **8a(E)** (29 mg, 0.12 mmol) with Ph₃GeH (72 mg, 0.24 mmol) and AIBN (20 mg, 0.12 mmol) by procedure C gave **17a**²⁸ (24 mg, 50%;

TLC and ^1H NMR of the crude product showed quantitative conversion to **17a**: ^1H NMR δ 7.01 (d, J = 18.7 Hz, 1H), 7.08 (d, J = 18.7 Hz, 1H), 7.28-7.40 (m, 3H), 7.41-7.45 (m, 9H), 7.51 (d, J = 7.2 Hz, 2 H), 7.59-7.61 (m, 6H).

(E)-1-(Triphenylgermyl)-1-octene (17c). Treatment of **8c(E)** (30 mg, 0.12 mmol) with Ph_3GeH (72 mg, 0.24 mmol) and AIBN (5 mg, 0.03 mmol) by procedure C gave **17c^{5b}** (35 mg, 70%): ^1H NMR δ 0.90-1.40 (m, 11H), 2.26 (q, J = 6.7 Hz, 2H), 6.15-6.19 (m, 2H), 7.35-7.60 (m, 15H).

[(Cyclohexylidene)methyl]triphenylgermane (17e). Treatment of **8e** (52 mg, 0.22 mmol) with Ph_3GeH (135 mg, 0.44 mmol) and AIBN (48 mg, 0.28 mmol) by procedure C gave **17e** (84 mg, 96%): mp 80-82 °C; ^1H NMR δ 1.40 (br s, 2H), 1.56 (br s, 2H), 1.67 (br s, 2H), 2.13 (t, J = 6.1 Hz, 2H), 2.40 (t, J = 6.1 Hz, 2H), 7.30 -7.60 (m, 15H); ^{13}C NMR δ 26.47, 28.18, 29.20, 36.20, 40.53, 115.25 (CH), 128.52, 129.10, 135.24, 138.60, 161.74 (C). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{Ge}$ (399.08): C, 74.24; H, 6.57. Found: C, 74.17; H, 6.91.

(E)-4-Phenyl-1-[tri(2-furyl)germyl]-1-butene (18b). Treatment of **8b(E)** (20 mg, 0.07 mmol) with tri(2-furyl)germane²⁷ (40 mg, 0.15 mmol) and AIBN (5 mg, 0.03 mmol) by procedure C gave **18b** (15 mg, 50%): IR (neat) 2927, 1617, 1453, 1205, 1004 cm^{-1} ; ^1H NMR δ 2.58 (q, J = 7.2 Hz, 2H), 2.81 (t, J = 7.4 Hz, 2H), 6.09 (dd, J = 18.2, 1.3 Hz, 1H), 6.41 (dt, J = 18.2, 6.2 Hz, 1H), 6.53 (dd, J = 3.2, 1.7 Hz, 3H), 6.93 (d, J = 3.1 Hz, 3H), 7.20-7.79 (m, 8H); ^{13}C NMR δ 35.19 (C4), 38.55 (C3), 110.39 (Ar), 120.98 (C1), 122.48 (Ar), 126.3 (ph), 128.75 (ph), 128.92 (ph), 141.93 (ph), 148.27 (Ar), 151.24 (Ar), 153.26 (C2); GC-MS (t_R 16.46 min) m/z 406 (6, M^+ , ^{74}Ge), 404 (4.5, M^+ , ^{72}Ge), 402 (19, M^+ , ^{70}Ge), 107 (100). Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{GeO}_3$ (405.00): C, 65.24; H, 4.98. Found: C, 64.89; H, 5.32.

(E)-1,2-Diphenylethene (19a). Procedure D. Solution of NaOH (8 mg, 0.2 mmol) and H_2O_2 (30% solution, 30 μL , 0.30 mmol) in deionized H_2O (0.5ml) was added to a stirred solution of **10a** (27 mg, 0.077 mmol) in THF (2 mL) at ambient temperature. After 1 h, iodobenzene (13 μL , 24 mg, 0.12 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (5 mg, 0.004 mmol) were added and the resulting brownish mixture was heated at 60 °C (oil bath) for 5 h. The volatiles were evaporated and the residue was partitioned ($\text{H}_2\text{O}/\text{CHCl}_3$). The organic layer was dried (MgSO_4), evaporated and column chromatographed (hexane) to give **19a** (11 mg, 75%) with data identical to commercial sample.

Treatment of **15a** (*E*; 20 mg, 0.05 mmol) with iodobenzene (9 μL , 16 mg, 0.078 mmol) by procedure D (40 °C, 15 h) gave **19a** (*E*; 4.5 mg, 50%).

Treatment of **15a** (*E*; 25 mg, 0.06 mmol) with bromobenzene (11 μL , 16 mg, 0.10 mmol) by procedure D (40 °C, 10 h) gave **19a** (*E*; 10 mg, 88%).

Treatment of **15a** (*E*; 25 mg, 0.06 mmol) with chlorobenzene (10 μL , 11 mg, 0.10 mmol) by procedure D (40 °C, 12 h) gave **19a** (*E*, 4 mg, 37%): GC-MS (t_R 16.6 min) m/z 180 (100, M^+). The (*E,E*)-

1,4-diphenyl-1,3-butadiene (5 mg, 41%) was also isolated from the reaction mixture with data identical to commercial sample: GC-MS (t_R 20.2 min) m/z 206 (100, M^+).

(Z)-1,2-Diphenylethene (19a). Treatment of **10a** [Z; 40 mg, 0.11 mmol; prepared (90%) by hydrosilylation of phenylacetylene with $(TMS)_3SiH/AIBN^{12a}$] with bromobenzene (17 μ L, 26 mg, 0.16 mmol) by procedure D (40 °C, 12 h) gave **19a** (Z, 11 mg, 55%) with data identical to commercial sample.

Treatment of **15a** [Z; 45 mg, 0.11 mmol; prepared (95%) by hydrogermylation of phenylacetylene

with $(\text{TMS})_3\text{GeH}^{18}$] with iodobenzene (19 μL , 35 mg, 0.17 mmol) by procedure D (40 °C, 15 h) gave **19a** (*E/Z*, 25/75; 12 mg, 60%): GC-MS (t_R 13.9 min, *Z*; 16.6 min, *E*) m/z 180 (100, M^+).

(*E*)-1,4-Diphenyl-1-butene (19b). Treatment of **10b** (*E*; 20 mg, 0.053 mmol) with iodobenzene (9 μL , 16 mg, 0.078 mmol) by procedure D gave **19b** (*E*; 7 mg, 56%) with data as reported.²⁹

(*Z*)-1-Fluoro-1,2-diphenylethene (20a). Treatment of **11a** (*E*; 20 mg, 0.048 mmol) with iodobenzene (8 μL , 15 mg, 0.074 mmol) by procedure D (40 °C, 15 h) gave **20a** (6 mg, 63%) with data as reported.³⁰ The crude ^{19}F NMR showed peaks at δ - 114.64 (d, J = 39.5 Hz, 0.80F; **20a**) and -122.66 (dd, J = 44.8, 82.1 Hz, 0.13F; *Z*- β -fluorostyrene³¹).

Subjection of **9a** (*E*; 20 mg, 0.054 mmol) to procedure D [iodobenzene (9 μL , 17 mg, 0.083 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (3.5 mg, 0.003 mmol) were immediately added (1-3 min) after addition of $\text{NaOH}/\text{H}_2\text{O}_2$ to **9a** followed by stirring of the resulting mixture for 9 h at ambient temperature] gave different quantities of **20a** (10-50%) depends on run. The *Z*- β -fluorostyrene³¹ was also isolated from the reaction mixture (30-70%).

Attempted silyldesulfonylation of 5f with TTMSS. Treatment of **5f** (*E/Z*, 1:99; 29 mg, 0.1 mmol) with TTMSS (0.10 mL, 82 mg, 0.33 mmol) and AIBN (25 mg, 0.15 mmol; adding over 4 h period using precision syringe pump) by procedure B (5 h) gave mixture of products. Column chromatography (EtOAc/hexane, 1:4) gave recovered **5f** (10 mg, 35%) and 1-[fluoro(phenylsulfonyl)methyl]-1-methylcyclopentane (8 mg, 31%): ^1H NMR δ 1.33 (s, 3H), 1.55-1.65 (m, 4H), 1.66-1.78 (m, 4H), 4.90 (d, J = 46.4 Hz, 1H), 7.61 (t, J = 7.7 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.98 (d, J = 7.9 Hz, 2H); ^{13}C NMR δ 21.92 (d, J = 4.0 Hz, CH_3), 24.47 (CH_2), 24.79 (CH_2), 46.35 (C1), 109.87 (d, J = 222.0 Hz, CHF), 129.58 (ph), 129.73 (ph), 134.60 (ph), 138.43 (ph); ^{19}F NMR δ -176.52 (d, J = 45.2 Hz); HRMS (FAB, m/z): calcd for $\text{C}_{13}\text{H}_{17}\text{FO}_2\text{SLi}$ (MLi^+), 263.1093; found 263.1082.

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