Application of Vinyl Tris(trimethylsilyl)germanes in Pd-catalyzed Couplings

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SUPPORTING INFORMATION

CONTENTS

1. Experimental procedures and characterization data for compounds:
 - **2a** and **2b** (Germyledesulfonylation protocol, Procedure A): Page S2
 - **4a**, **4c**, **4d**, **4e**, and **4f** (Hydrogermylation protocol, Procedure B): Pages S2-S4
 - **5a(E)**, and **5b(E)** (Coupling protocol under aqueous conditions, Method A): Pages S4-S6
 - **5a(E/Z)**, **5c(E/Z)**, **5d(E/Z)**, **5e(E/Z)**, **5f(E/Z)**, **6c(E/Z)**, and **6f(E/Z)** (Coupling protocol under anhydrous conditions, Method B): Pages S5-S8
2. ¹H NMR spectra for compounds:
 - **5a(E)**: Page S10
 - **5a(E/Z)**: Page S11
 - **5c(E/Z)**: Page S12
 - **5d(E/Z)**: Page S13
 - **5e(E/Z)**: Page S14

General Procedures

^1H (Me_4Si) NMR spectra at 400 MHz, ^{13}C (Me_4Si) at 100.6 MHz and ^{19}F (CCl_3F) at 376.4 MHz were determined with solutions in CDCl_3 . Mass spectra (MS) were obtained by electron ionization (EI) technique. Reagent grade chemicals were used and solvents were dried by reflux over and distillation from CaH_2 (except THF//Na/benzophenone) under an argon atmosphere. TLC was performed on Merck kieselgel 60-F₂₅₄ and products were detected with 254 nm light or by development of color with I_2 . Merck kieselgel 60 (230-400 mesh) was used for column chromatography. 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 $\times$ 0.25 mm $\times$ 25 μm)]. Vinyl sulfones **1a** and **1b** were prepared as reported.⁴ Acetylenes **3a** and **3c-f** were commercially available.

(*E*)-2-Phenyl-1-[tris(trimethylsilyl)germyl]ethene (2a). Procedure A. Argon was bubbled through a solution of **1a**(*E*) (450 mg, 1.84 mmol) in anhydrous benzene or toluene (25 mL) for 15 min. $(\text{Me}_3\text{Si})_3\text{GeH}$ (0.97 mL, 902 mg, 3 mmol) and AIBN (308 mg, 1.84 mmol) were added, and degassing of oxygen was continued for another 10 min and then the solution was heated at 80 °C (oil-bath) for 6 h. The volatiles were evaporated, and the oily residue was column chromatographed (hexane) to give **2a**⁴ (590 mg, 81%): 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); ^{13}C NMR δ 2.0, 126.2, 126.4, 127.4 (C1), 128.9, 139.6, 144.0 (C2). GC-MS (t_R 19.99 min) m/z 396 (3.5, M^+ , ^{74}Ge), 394 (2.0, M^+ , ^{72}Ge), 392 (1.5, M^+ , ^{70}Ge). Anal. Calcd for $\text{C}_{17}\text{H}_{34}\text{GeSi}_3$ (395.32): C, 51.65; H, 8.67. Found: C, 51.38; H, 8.89.

(*E*)-4-Phenyl-1-[tris(trimethylsilyl)germyl]-1-butene (2b). Treatment of **1b**(*E*) (223 mg, 0.82 mmol) with $(\text{Me}_3\text{Si})_3\text{GeH}$ (0.265 mL, 246 mg, 0.82 mmol) and AIBN (137 mg, 0.82 mmol) by procedure A gave **2b** (177 mg, 51%) as an oil: ^1H NMR δ 0.20 (s, 27H), 2.44 ("q", J = 7.1 Hz, 2H), 2.71 (t, J = 7.6 Hz, 2H), 5.73 (d, J = 17.8 Hz, 1H), 5.90 (dt, J = 17.8, 6.3 Hz, 1H) 7.16-7.30 (m, 5H); ^{13}C NMR δ 1.8 (TMS), 36.3 (C4), 39.4 (C3), 124.0 (C1), 126.0 (Ar), 128.6 (Ar), 128.9 (Ar), 142.5 (Ar), 145.7 (C2); MS m/z 424 (10, M^+), 220 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{GeSi}_3$ (424.15): C, 53.90; H, 9.05. Found: C, 53.52; H, 9.29.

(Z)-2-Phenyl-1-[tris(trimethylsilyl)germyl]ethene (4a). **Procedure B.** (Me₃Si)₃GeH (0.323 mL, 300 mg, 1 mmol) was added in one portion via a syringe to a stirred solution of **3a** (0.112 mL, 104 mg, 1 mmol) in dry benzene (3 mL) at ambient temperature under nitrogen atmosphere. After 3 h, the solvent was evaporated in vacuo and the oily residue was purified by flash chromatography on silica gel (hexane) to give **4a**^{8b} (388 mg, 98%): ¹H NMR δ 0.25 (s, 27H), 6.12 (d, *J* = 13.6 Hz, 1H), 7.15-7.35 (m, 5H), 7.41 (d, *J* = 13.6 Hz, 1H).

(Z)-2-(4-Methoxyphenyl)-1-[tris(trimethylsilyl)germyl]ethene (4c). Treatment of **3c** (0.134 mL, 136 mg, 1 mmol) with (Me₃Si)₃GeH (0.323 mL, 300 mg, 1 mmol) and AIBN (16 mg, 0.10 mmol) by procedure B (3 h; 82 °C, oil bath) gave **4c** (358 mg, 84%) as a colorless oil: ¹H NMR δ 0.22 (s, 27H), 3.84 (s, 3H), 6.04 (d, *J* = 13.5 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 13.5 Hz, 1H); ¹³C NMR δ 2.2, 55.7, 114.0, 125.2, 129.5, 133.9, 143.6, 159.2; MS *m/z* 426 (15, M⁺), 220 (100). Anal. Calcd for C₁₈H₃₆GeOSi₃ (426.13): C, 50.83; H, 8.53. Found: C, 50.49; H, 8.61.

(Z)-2-(2-Trifluoromethylphenyl)-1-[tris(trimethylsilyl)germyl]ethene (4d). Treatment of **3d** (0.144 mL, 175 mg, 1 mmol) with (Me₃Si)₃GeH (0.323 mL, 300 mg, 1 mmol) and AIBN (16 mg, 0.10 mmol) by procedure B (3h; 82 °C, oil bath) gave **4d** (371 mg, 80%) as a colorless oil: ¹H NMR δ 0.16 (s, 27H), 6.30 (d, *J* = 13.7 Hz, 1H), 7.34-7.67 (m, 5H); ¹³C NMR δ 2.0, 124.7 (q, *J* = 274.0 Hz), 126.1 (q, *J* = 5.6 Hz), 127.3, 128.5 (q, *J* = 29.6 Hz), 130.4, 131.3, 132.3, 140.6, 140.8; ¹⁹F NMR δ -60.83 (s); MS *m/z* 464 (20, M⁺), 220 (100). Anal. Calcd for C₁₈H₃₃F₃GeSi₃ (464.11): C, 46.66; H, 7.18. Found: C, 47.04; H, 7.44.

(Z)-2-(4-Trifluoromethylphenyl)-1-[tris(trimethylsilyl)germyl]ethene (4e). Treatment of **3e** (0.173 mL, 175 mg, 1 mmol) with (TMS)₃GeH (0.323 mL, 300 mg, 1 mmol) and AIBN (16 mg, 0.10 mmol) by procedure B (3 h; 82 °C, oil bath) gave **4e** (394 mg, 85%) as a colorless oil: ¹H NMR δ 0.16 (s, 27H), 6.32 (d, *J* = 13.7 Hz, 1H), 7.44 (d, *J* = 13.7 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H); ¹³C NMR δ 2.2, 124.7 (q, *J* = 271.9 Hz), 125.5 (q, *J* = 3.7 Hz), 128.5, 129.3 (q, *J* = 32.4 Hz), 131.5, 142.8, 144.6; ¹⁹F NMR δ -62.84 (s); MS *m/z* 464 (2, M⁺), 220 (100). Anal. Calcd for C₁₈H₃₃F₃GeSi₃ (464.11): C, 46.66; H, 7.18. Found: C, 46.31; H, 7.27.

(Z)-1-[Tris(trimethylsilyl)germyl]octene. (4f). Treatment of **3f** (0.152 mL, 114 mg, 1 mmol) with $(\text{Me}_3\text{Si})_3\text{GeH}$ (0.323 mL, 300 mg, 1 mmol) and AIBN (16 mg, 0.10 mmol) by procedure B (3 h, 82 °C, oil bath) gave **4f**^{8b} (384 mg, 95%): ^1H NMR: δ 0.21 (s, 27H), 0.88-0.91 (m, 3H), 1.25-1.43 (m, 8H), 2.05 ("q", $J = 7.4$ Hz, 2H), 5.67 (dt, $J = 12.0, 1.4$ Hz, 1H), 6.33 (dt, $J = 12.0, 6.8$ Hz, 1H).

(E)-1,2-Diphenylethene (5a). Method A. A solution of NaOH (12 mg, 0.3 mmol) and H_2O_2 (30% solution, 20 μL , 0.20 mmol) in deionized H_2O (0.4 mL) was added to a stirred solution of **2a** (25 mg, 0.063 mmol) in THF (3 mL) at ambient temperature. After 15 minutes, iodobenzene (11 μL , 20 mg, 0.095 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 0.006 mmol) were added and the resulting brownish mixture was heated at 45°C (oil bath) for 10 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 purified by column chromatography (hexane) to give **5a** (5.7 mg, 50%) with data identical to a commercial sample.

Treatment of **2a** (25 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.10 mmol) by Method A gave **5a** (10 mg, 88%).

Treatment of **2a** (25 mg, 0.063 mmol) with chlorobenzene (10 μL , 11 mg, 0.10 mmol) by Method A gave **5a** (4 mg, 37%): GC-MS (t_R 16.6 min) m/z 180 (100, M^+). The (*E,E*)-1,4-diphenyl-1,3-butadiene (3 mg, 23%) was also isolated with data identical to a commercial sample and as reported:¹⁶ GC-MS (t_R 20.2 min) m/z 206 (100, M^+).

Treatment of **2a** (25 mg, 0.063 mmol) with phenyl trifluoromethanesulfonate (16 μL , 22 mg, 0.095 mmol) by Method A gave **5a** (1.7 mg, 15%). The (*E,E*)-1,4-diphenyl-1,3-butadiene¹⁶ (4.4 mg, 34%) was also isolated.

Method B. KH (12 mg, 0.3 mmol) and *t*-BuOOH (5.0-6.0 M solution, 37.8 μL , 0.19 mmol) were added to a stirred solution of **2a** (25 mg, 0.063 mmol) in THF (3 mL) at ambient temperature. After 15 min, iodobenzene (11 μL , 20 mg, 0.095 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 0.006 mmol) were added and the resulting brownish mixture was heated at 45°C (oil bath) for 10 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 purified by column chromatography (hexane) to give **5a** (9.1 mg, 80%) with data identical to a commercial sample.

Treatment of **2a** (25 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.10 mmol)

by Method B gave **5a** (5.7 mg, 50%).

Treatment of **2a** (25 mg, 0.063 mmol) with chlorobenzene (10 μ L, 11 mg, 0.10 mmol) by Method B gave **5a** (1.1 mg, 10%). The (*E,Z*)-1,4-diphenyl-1,3-butadiene¹⁷ [0.5 mg, 4%]: GC-MS (t_R 18.7 min) m/z 206 (100, M^+) and the (*E,E*)-1,4-diphenyl-1,3-butadiene¹⁶ (3.3 mg, 25%) were also isolated.

Treatment of **2a** (25 mg, 0.063 mmol) with phenyl trifluoromethanesulfonate (16 μ L, 22 mg, 0.095 mmol) by Method B gave **5a** (2.3 mg, 20%). The (*E,Z*)- (1.6 mg, 12%) and (*E,E*)-1,4-diphenyl-1,3-butadiene (3.0 mg, 24%) were also isolated.

(*E,Z*)-1,2-Diphenylethene (5a). Treatment of **4a** (45 mg, 0.11 mmol) with iodobenzene (19 μ L, 35 mg, 0.17 mmol) by Method A gave **5a** (*E/Z*, 33/67; 12 mg, 60%) with data identical to commercial sample. GC-MS (t_R 13.9 min, *Z*; t_R 16.6 min, *E*) m/z 180 (100, M^+).

Treatment of **4a** (25 mg, 0.063 mmol) with bromobenzene (11 μ L, 16 mg, 0.095 mmol) by Method A gave **5a** (*E/Z*, 1:1; 6 mg, 53%). Diphenyl (0.6 mg, 4%; e.g. 8% consumption of iodobenzene) was also isolated: GC-MS (t_R 11.3 min), m/z 154 (100, M^+).

Treatment of **4a** (25 mg, 0.063 mmol) with chlorobenzene (10 μ L, 11 mg, 0.095 mmol) by Method A gave **5a** (*E/Z*, 2:1; 5 mg, 44%). The isomers of 1,4-diphenyl-1,3-butadiene (1.0 mg, 8%) were also isolated.

Treatment of **4a** (25 mg, 0.063 mmol) with phenyl trifluoromethanesulfonate (16 μ L, 22 mg, 0.095 mmol) by Method A gave **5a** (3.8 mg, 33%; *E/Z*, 99:1). The *E/E* and *E/Z* isomers of 1,4-diphenyl-1,3-butadiene (4.0 mg, 31%) were also isolated.

Treatment of **4a** (22.6 mg, 0.057 mmol) with iodobenzene (9.9 μ L, 18 mg, 0.09 mmol) by Method B gave **5a** (*E/Z*, 3/97; 8.5 mg, 83%).

Treatment of **4a** (22.6 mg, 0.057 mmol) with bromobenzene (9.9 μ L, 14.4 mg, 0.09 mmol) by Method B gave **5a** (*E/Z*, 8/92; 8 mg, 78%).

(*E*)-1,4-Diphenyl-1-butene (5b). Treatment of **2b** (30 mg, 0.071 mmol) with iodobenzene (12 μ L, 22.5 mg, 0.11 mmol) by Method A gave **5b** (7.5 mg, 51%) with data as reported.¹⁸ ¹H NMR δ 2.53 ("q", J = 7.8 Hz, 2H), 2.79 (t, J = 7.8 Hz, 2H), 6.26 (dt, J = 15.8, 6.7 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 7.18-7.34 (m, 10H); ¹³C NMR δ 34.9, 35.8, 125.9, 126.0, 126.9, 128.3, 128.5 (2 $\times$), 129.9, 130.3, 137.7, 141.7; GC-MS (t_R 16.3 min), m/z 208

(100, M^+). Anal. Calcd for $C_{16}H_{16}$ (208.30): C, 92.26; H, 7.74. Found: 91.89; H, 7.39.

Diphenyl (0.5 mg, 3%; e.g. 6% consumption of iodobenzene) was also isolated: GC-MS (t_R 11.3 min), m/z 154 (100, M^+).

Treatment of **2b** (14 mg, 0.033 mmol) with bromobenzene (5 μ L, 8 mg, 0.05 mmol) by Method A gave **5b** (3.4 mg, 73%).

Treatment of **2b** (18 mg, 0.042 mmol) with iodobenzene (7.4 μ L, 13 mg, 0.064 mmol) by Method B gave **5b** (7 mg, 80%).

(E,Z)-1-(4-Methoxyphenyl)-2-phenylethene (5c). Treatment of **4c** (53.6 mg, 0.126 mmol) with iodobenzene (22 μ L, 40 mg, 0.19 mmol) by Method A gave **5c** (*E/Z*, 13:87; 24 mg, 90%) with data as reported.¹⁶ **5c(E)**: 1H NMR δ 3.84 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 16.4 Hz, 1H), 7.07 (d, J = 16.4 Hz, 1H), 7.23-7.50 (m, 7H); ^{13}C NMR δ 55.3, 114.1, 126.2, 126.6, 127.2, 127.7, 128.2, 128.6, 130.1, 137.6, 159.2; MS m/z 210 (100, M^+). **5c(Z)**: 1H NMR δ 3.81 (s, 3H), 6.53 (d, J = 12.4 Hz, 1H), 6.57 (d, J = 12.4 Hz, 1H), 6.78 (d, J = 8.7 Hz, 2H), 7.20-7.31 (m, 7H); ^{13}C NMR δ 55.6, 114.0, 127.3, 128.6, 129.2, 129.2, 130.1, 130.2, 130.6, 138.0, 159.1; MS m/z 210 (100, M^+).

Diphenyl (1.5 mg, 5%; e.g. 10% consumption of iodobenzene) was also isolated: GC-MS [t_R 11.3 min, m/z 154 (100, M^+); t_R 17.4 min and t_R 19.9 min for **5c(Z)** and **5c(E)**, respectively, m/z 210 (100, M^+)].

Treatment of **4c** (26.8 mg, 0.063 mmol) with bromobenzene (11 μ L, 16 mg, 0.095 mmol) by Method A gave **5c** (*E/Z*, 64:36; 6.6 mg, 50%).

Treatment of **4c** (53.6 mg, 0.126 mmol) with iodobenzene (22 μ L, 40 mg, 0.19 mmol) by Method B gave **5c** (*E/Z*, 3:97; 25.4 mg, 96%).

Treatment of **4c** (26.8 mg, 0.063 mmol) with bromobenzene (11 μ L, 16 mg, 0.095 mmol) by Method B gave **5c** (*E/Z*, 2:98; 1.3 mg, 10%). The mixture of isomers of 1,4-di-(4-methoxyphenyl)-1,3-butadiene¹⁹ (5 mg, 30%): GC-MS (t_R 24.9 min, t_R 25.1 min and t_R 26.5 min) m/z 266 (100, M^+) were also isolated.

(E,Z)-1-(2-Trifluoromethylphenyl)-2-phenylethene (5d). Treatment of **4d** (29.2 mg, 0.063 mmol) with iodobenzene (11 μ L, 20 mg, 0.095 mmol) by Method A gave **5d**²⁰ (*E/Z*, 21:79; 6.4 mg, 41%). **5d(E)**: 1H NMR δ 7.07-7.82 (m, 11 H); ^{19}F NMR δ -59.79 (s). **5d(Z)**: 1H NMR δ 6.75 (d, J = 12.2 Hz, 1H), 6.85 (d, J = 12.2 Hz, 1H), 7.07-7.73 (m, 7H); ^{13}C NMR

δ 124.7 (q, $J = 273.7$ Hz), 126.3 (q, $J = 5.3$ Hz), 127.3, 127.5, 127.7, 128.5, 128.8 (q, $J = 29.0$ Hz), 129.6, 131.7, 131.9, 132.6, 136.6, 137.1 (d, $J = 2.3$ Hz); ^{19}F NMR δ -61.56 (s); MS m/z 248 (100, M^+).

Treatment of **4d** (29.2 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.095 mmol) by Method A gave **5d** (*E/Z*, 76:24; 4.7 mg, 30%).

Treatment of **4d** (29.2 mg, 0.063 mmol) with iodobenzene (11 μL , 20 mg, 0.095 mmol) by Method B gave **5d** (*E/Z*, 1:99; 12 mg, 77%).

Treatment of **4d** (29.2 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.095 mmol) by Method B gave **5d** (*E/Z*, 3:97; 2.3 mg, 15%). The by-products tentatively assigned as isomers of 1,4-di-(2-trifluoromethylphenyl)-1,3-butadiene (4.3 mg, 20%) were also isolated: GC-MS (t_{R} 17.2 min, t_{R} 17.5 min and t_{R} 19.1 min) m/z 342 (100, M^+).

(*E,Z*)-1-(4-Trifluoromethylphenyl)-2-phenylethene (5e). Treatment of **4e** (29.2 mg, 0.063 mmol) with iodobenzene (11 μL , 20 mg, 0.095 mmol) by Method A gave **5e** (*E/Z*, 55:45; 12.5 mg, 80%). **5e(E)**:^{21a} ^1H NMR δ 7.14 (d, $J = 16.3$ Hz, 1H), 7.22 (d, $J = 16.3$ Hz, 1H), 7.31-7.63 (m, 9H); ^{19}F NMR δ -62.90 (s); MS m/z 248 (100, M^+). **5e(Z)**:^{21b} ^1H NMR δ 6.62 (d, $J = 12.3$ Hz, 1H), 6.75 (d, $J = 12.3$ Hz, 1H), 7.23-7.50 (m, 9H); ^{19}F NMR δ -62.98 (s); MS m/z 248 (100, M^+).

Treatment of **4e** (29.2 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.095 mmol) by Method A gave **5e** (*E/Z*, 99:1; 10.6 mg, 68%).

Treatment of **4e** (29.2 mg, 0.063 mmol) with chlorobenzene (10 μL , 11 mg, 0.095 mmol) by Method A gave **5e** (*E/Z*, 56:44; 2.3 mg, 15%). The isomers of 1,4-di-(4-trifluoromethylphenyl)-1,3-butadiene²² (6.3 mg, 29%): GC-MS (t_{R} 13.5 min, t_{R} 18.3 min and t_{R} 18.4 min) m/z 342 (100, M^+) were also isolated.

Treatment of **4e** (29.2 mg, 0.063 mmol) with iodobenzene (11 μL , 20 mg, 0.095 mmol) by Method B gave **5e** (*E/Z*, 5:95; 11 mg, 71%).

Treatment of **4e** (29.2 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.095 mmol) by Method B gave **5e** (*E/Z*, 1:99; 9 mg, 58%).

(*E,Z*)-1-Phenyl-1-octene (5f). Treatment of **4f** (25.5 mg, 0.063 mmol) with iodobenzene (11 μL , 20 mg, 0.095 mmol) by Method A gave **5f** (*E/Z*, 45:55; 4.3 mg, 36%) with data as reported. **5f(E)**:¹⁶ ^1H NMR δ 0.91 (t, $J = 6.0$ Hz, 3H), 1.32–1.53 (m, 8H), 2.22 (q, $J = 6.0$ Hz,

2H), 6.24 (dt, $J = 15.0, 6.0$ Hz, 1H), 6.39 (d, $J = 15.0$ Hz, 1H), 7.17-7.37 (m, 5H); ^{13}C NMR δ 14.2, 22.7, 29.0, 29.4, 31.9, 33.2, 126.0, 126.8, 128.5, 129.7, 131.4, 138.1. **5f**(Z): ^{23}H NMR δ 0.91 (t, $J = 6.0$ Hz, 3H), 1.32–1.53 (m, 8H), 2.35 (q, $J = 7.4$ Hz, 2H), 5.69 (dt, $J = 11.7, 7.2$ Hz, 1H), 6.42 (d, $J = 11.7$ Hz, 1H), 7.18-7.35 (m, 5H); MS m/z 188 (100, M^+). Anal. Calcd for $\text{C}_{14}\text{H}_{20}$ (188.31): C, 89.29; H, 10.71. Found: C, 88.93; H, 10.42.

Treatment of **4f** (25.5 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.095 mmol) by Method A gave **5f** (E/Z , 33:67; 7.6 mg, 64%).

Treatment of **4f** (25.5 mg, 0.063 mmol) with iodobenzene (11 μL , 20 mg, 0.095 mmol) by Method B gave **5f** (E/Z , 25:75; 7.0 mg, 60%).

Treatment of **4f** (25.5 mg, 0.063 mmol) with bromobenzene (11 μL , 16 mg, 0.095 mmol) by Method B gave **5f** (E/Z , 20:80; 7.0 mg, 60%).

(E,E,E,Z)-1-(4-Methoxyphenyl)-4-phenyl-1,3-butadiene (6c). Treatment of **4c** (30.0 mg, 0.071 mmol) with β -bromostyrene (14 μL , 20 mg, 0.11 mmol) by Method A gave **6c** (1*E*,3*E*/3*E*,1*Z*, 27:73; 11 mg, 66%) with data as reported.^{19a,24} GC-MS (t_R 21.6 min; Z/E ; t_R 23.1 min; E/E) m/z 236 (100, M^+). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}$ (236.31): C, 86.40; H, 6.82. Found: C, 86.09; H, 6.49.

The isomers of 1,4-diphenyl-1,3-butadiene (3.0 mg, 13% based on β -bromostyrene) and the isomers of 1,4-di-(4-methoxyphenyl)-1,3-butadiene (0.5 mg, 3%) were also isolated.

Treatment of **4c** (30.0 mg, 0.071 mmol) with β -bromostyrene (14 μL , 20 mg, 0.11 mmol) by Method B gave **6c** (1*E*,3*E*/3*E*,1*Z*, 18:82; 8.7 mg, 52%). The isomers of 1,4-diphenyl-1,3-butadiene (2.0 mg, 9% based on β -bromostyrene) and the isomers of 1,4-di-(4-methoxyphenyl)-1,3-butadiene (0.4 mg, 2%) were also isolated.

(E,E,E,Z)-1-phenyl)-1,3-decadiene (6f). Treatment of **4f** (25.5 mg, 0.063 mmol) with β -bromostyrene (13 μL , 18 mg, 0.095 mmol; $E/Z \sim 88:12$) by Method A gave **6f** (1*E*,3*E*/1*E*,3*Z*, 34:66; 9 mg, 67%) as a colorless liquid with data as reported:²⁵ GC-MS (t_R 16.7 and 17.9 min) m/z 214 (22, M^+), 129 (100%). Anal. Calcd for $\text{C}_{16}\text{H}_{22}$ (214.35): C, 89.65; H, 10.35. Found: C, 89.35; H, 10.02.

The third isomer of **6f** ($\sim 10\%$) was also detected in crude reaction mixture: GC-MS (t_R 17.3 min) m/z 214 (M^+).

The isomers of 1,4-diphenyl-1,3-butadiene^{16,17} ($E,E/E,Z$, $\sim 1:1$; 4.0 mg total, 20% based on β -bromostyrene) were also isolated: GC-MS (t_R 18.7 and 20.2 min) m/z 206 (100, M^+).

References.

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S10

5a (*E*)

¹H NMR
400 MHz (Bruker)
CDCl₃

S11

5a (E/Z, 33/67)

¹H NMR
400 MHz (Bruker)
CDCl₃

S12

^1H NMR
400 MHz (Bruker)
 CDCl_3

5c (E/Z, 3/97, ratio based on GC-MS)

S13

¹H NMR
400 MHz (Bruker)
CDCl₃

5d (*E/Z*, 1/99, ratio based on GC-MS)

S14

¹H NMR
400 MHz (Bruker)
CDCl₃

5e (E/Z, 1/99, ratio based on GC-MS)