from Prof. A. Mouriño (Santiago de Compostela, Spain) are gratefully acknowledged.

Registry No. ($\pm$)-(*E*)-1a, 57549-92-5; ($\pm$)-(*Z*)-1a, 57549-93-6; (*E*)-16, 23726-91-2; (*Z*)-16, 23726-92-3; 2a, 127-41-3; 2b, 79-77-6; 5a, 52610-46-5; (*E*)-5b, 124099-60-1; (*Z*)-5b, 139608-99-4; 6, 42741-51-5; 7a, 37079-64-4; ($\pm$)-7b, 139609-00-0; 8a, 139609-01-1; ($\pm$)-8b (isomer 1), 139609-02-2; ($\pm$)-8b (isomer 2), 139684-74-5; 9a, 139609-03-3; ($\pm$)-9b (isomer 1), 139609-04-4; ($\pm$)-9b (isomer 2), 139686-52-5.

Supplementary Material Available: NMR spectra of 8b and 9b (6 pages). Ordering information is given on any current masthead page.

1,3-Bis(trimethylsilyl)propene as 1,3- and 3,3-Propene Dianion Synthons. Reactions of 2-Aryl-1,3-bis(trimethylsilyl)propenes with Electrophiles

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Received January 2, 1992

Whereas allylsilanes and vinylsilanes can be considered as allyl anion and vinyl anion synthons,¹ 1,3-bis(trimethylsilyl)propene (1) which contains both functionalities could couple with an electrophile E_1 to give either 2a or 2b. Further reaction of the latter species with a second electrophile E_2 could afford 1,3-substitution product 3a or the isomeric 3,3-substitution product 3b (Scheme I).² Given this versatility it is surprising that the chemistry of 1 has not been explored more extensively. The reactions of 1 or its derivatives with carbonyl compounds under different conditions leading to the corresponding dienes,³ substituted allylsilanes^{4,5} and vinylsilanes⁶ have been reported. The formation of 4 by treatment of 1 with trimethylsilyl chlorosulfonate appears to be the only known example of using 1 as a 1,3-propene dianion synthon 5a.⁷ Recently, we reported a facile synthesis of 2-aryl-1,3-bis(trimethylsilyl)propenes 7 from the corresponding orthoesters 6 (eq 1).⁸ The availability of these compounds prompted our exploration of using 7 as 1,3- and 3,3-propene dianion synthons 5a and 5b.

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Results and Discussion

When a mixture of *E*- and *Z*-isomers of 2-aryl-1,3-bis(trimethylsilyl)propenes 7⁸ was treated with 2 equiv of *N*-bromosuccinimide (NBS) in CH₂Cl₂ at -78 °C, (*Z*)-2-aryl-1,3-dibromopropenes 8 were obtained in satisfactory yields (Table I, entries 1-4). The stereochemical assignments of 8 are based on NOE experiments. The formation of 8 is stereoselective regardless of the stereochemistry of the starting materials 7. Thus, the reaction of (*E*)-7a with NBS under the same conditions afforded 8a in 71% yield.

Treatment of 7 with 1 equiv of NBS under the same conditions afforded the monobromo products 9 in satisfactory yields (Table I, entries 5-8). These results indicated that the first reaction of 7 proceeds via the typical allylsilane reaction pattern. The bromonium ion intermediate 10 is postulated. Hence, the carbon-silicon bond at C-3 in 10 is apparently more labile giving the α -bromoallylsilane 9 selectively.

The reaction of α -haloallylsilanes with electrophiles has been briefly investigated.⁹ Exposure of 9a to NBS in CH₂Cl₂ at -78 °C yielded 8a (entry 9). The interaction of the carbon-silicon bond with the empty p-lobe in intermediate 11a leading to the double-bond formation may account for the stereoselectivity of this reaction. Presumably, the conformer 11a is more stable than 11b.⁹

The TiCl₄-mediated reactions of 9a with 1,1-diethoxyethane afforded 12a (entry 10). Similarly, treatment of 9a with hexanoyl chloride at -60 °C yielded 12b (entry 11). These observations indicated that 1,3-silylpropenes 7 behave in the manner of two overlapped and transposed allyl silanes. In other words, 7a can be considered as a 1,3-propene dianion synthon 5a. In fact, it is possible to carry out the two reactions in one pot, by allowing 7a to react

(9) Hosomi, A.; Ando, M.; Sakurai, H. *Chem. Lett.* 1984, 25, 1385.

Table I. Reaction of 7 and 9 with Electrophiles

entry	substr	electrophile	condns ^a	product (% yield)
1	7a	NBS	A	8a (70)
2	7b	NBS	A	8b (74)
3	7c	NBS	A	8c (75)
4	7d	NBS	A	8d (61)
5	7a	NBS	B	9a (74)
6	7b	NBS	B	9b (56)
7	7c	NBS	B	9c (72)
8	7d	NBS	B	9d (62)
9	9a	NBS	B	8a (79)
10	9a	MeCH(OEt) ₂	C	12a (90)
11	9a	Me(CH ₂) ₄ COCl	D	12b (65)
12	9a	Me ₃ CCl	E	13a (68)
13	9a	EtMe ₂ CCl	E	13b (57)
14	9a	PhCH(Me)Br	C	14 (65)

^a A: 2 equiv of NBS, -78 °C, 2 h. B: 1 equiv of NBS, -78 °C, 2 h. C: TiCl₄/CH₂Cl₂, -78 °C, 0.5 h. D: TiCl₄/CH₂Cl₂, -60 °C, 0.5 h. E: TiCl₄/CH₂Cl₂, -78 °C, 2 h.

first with 1 equiv of NBS in CH₂Cl₂ at -78 °C and then with TiCl₄ (1.1 equiv) and 1,1-diethoxyethane. The ether 12a was obtained in 50% yield. Similarly, 12b was isolated in 41% yield.

Treatment of 9a with *tert*-alkyl chlorides in the presence of TiCl₄ at -78 °C afforded ipso-substituted products (entries 12 and 13). The reaction of 9a with (α -bromoethyl)benzene afforded 14 in 65% yield (entry 14). Ap-

parently, the intermediate 13c may further undergo intramolecular Friedel-Crafts reaction under the reaction conditions. The yields and the selectivity of the reactions did not change with the order of the addition of the electrophile and TiCl₄. These results suggest that 1,3-disilylpropenes 7 also serve as a 3,3-propene dianion synthon.² The ipso substitution reaction is somewhat interesting, but the origin of such selectivity is unclear. Presumably, the aryl group in 9a may have some kind of the directive effect. Indeed, 15⁹ was allowed to react with *tert*-butyl chloride, *tert*-amyl chloride, and (α -bromoethyl)benzene at -78 °C in the presence of TiCl₄ to give 16a (*E/Z* = 48/52), 16b (*E/Z* = 46/54), and 16c (*E/Z* = 43/57) in 42, 48, and 63% yields, respectively. No trace amount of 17 was obtained at all.

Fluoride ion-mediated reactions of 9 with electrophiles do not show the same regioselectivity. For example, treatment of 9a with benzaldehyde in the presence of CsF (1.1 equiv) and HMPA (1.1 equiv)¹⁰ in refluxing THF afforded 12c and epoxides 18 (*E/Z* = 1:1) in 25% and 53% yield, respectively.

In summary, we have established the first systematic examples of using 1,3-disilylpropene as 1,3- or 3,3-propene

dianion synthons. Sequential replacement of the silyl groups by different electrophiles can readily be achieved.

Experimental Section

General Procedure for the Bromination of 2-Aryl-1,3-bis(trimethylsilyl)propene with NBS. To a solution of 7^{8a} (1.00 mmol) in CH₂Cl₂ (5 mL) under N₂ at -78 °C was added NBS (1.00 or 2.00 mmol), and the mixture was stirred at -78 °C for 2 h, quenched with 10% aqueous Na₂S₂O₃ (10 mL), and diluted with CH₂Cl₂ (10 mL). The organic layer was washed with water (10 mL $\times$ 3) and dried (MgSO₄). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (hexane) to afford the desired product. Compounds 8a-8d and 9a-9d were prepared according to the general procedure above.

(*Z*)-1,3-Dibromo-2-phenyl-1-propene (8a). Reaction of 7a (*E/Z* = 34/66, 131 mg, 0.50 mmol) and NBS (179 mg, 1.00 mmol) in CH₂Cl₂ (5 mL) gave 8a (97 mg, 70%): ¹H NMR (CDCl₃) δ 4.48 (s, 2 H), 6.61 (s, 1 H), 7.25-7.50 (m, 5 H); ¹³C NMR (CDCl₃) δ 30.5, 110.5, 126.3, 128.7, 128.8, 137.8, 141.9; MS *m/z* (rel intensity) 278 (35), 276 (65), 274 (35), 195 (65), 165 (100); HRMS calcd for C₉H₈Br₂ 275.8970, found 275.8982.

Reaction of 9a (21 mg, 0.08 mmol) and NBS (14 mg, 0.08 mmol) in CH₂Cl₂ (5 mL) also gave 8a (17 mg, 79%).

(*Z*)-1,3-Dibromo-2-(1-naphthyl)-1-propene (8b). Reaction of 7b (*E/Z* = 25/75, 70 mg, 0.22 mmol) and NBS (79 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) gave 8b (53 mg, 74%): ¹H NMR (CDCl₃) δ 4.52 (s, 2 H), 6.50 (s, 1 H), 7.45-7.55 (m, 4 H), 7.70-7.91 (m, 3 H); ¹³C NMR (CDCl₃) δ 32.7, 112.0, 124.7, 125.2, 126.1, 126.6, 127.1, 128.5, 129.0, 131.2, 133.7, 135.7, 141.2; MS *m/z* (rel intensity) 328 (11), 326 (22), 324 (11), 245 (41), 165 (100); HRMS calcd for C₁₃H₁₀Br₂ 325.9126, found 325.9121. Anal. Calcd: C, 47.89; H, 3.09. Found: C, 47.74; H, 3.09.

(*Z*)-1,3-Dibromo-2-(2-naphthyl)-1-propene (8c). Reaction of 7c (*E/Z* = 50/50, 312 mg, 1.00 mmol) and NBS (358 mg, 2.00 mmol) in CH₂Cl₂ (5 mL) gave 8c (245 mg, 75%): ¹H NMR (CDCl₃) δ 4.58 (s, 2 H), 6.79 (s, 1 H), 7.32-7.60 (m, 3 H), 7.62-7.95 (m, 4 H); ¹³C NMR (CDCl₃) δ 30.5, 110.9, 123.8, 125.7, 126.6, 126.7, 127.6, 128.3, 128.5, 133.1, 133.2, 134.9, 141.8; MS *m/z* (rel intensity) 328 (26), 326 (48), 324 (26), 245 (17), 16 (100); HRMS calcd for C₁₃H₁₀Br₂ 325.9126, found 325.9135. Anal. Calcd: C, 47.89; H, 3.09. Found: C, 47.42; H, 3.06.

(*Z*)-1,3-Dibromo-2-(4-methylphenyl)-1-propene (8d). Reaction of 7d (*E/Z* = 34/66, 138 mg, 0.50 mmol) and NBS (179 mg, 1.00 mmol) in CH₂Cl₂ (5 mL) gave 8d (88 mg, 61%): ¹H NMR (CDCl₃) δ 2.35 (s, 3 H), 4.47 (s, 2 H), 6.61 (s, 1 H), 7.12-7.38 (AB quartet, *J* = 8 Hz, 4 H); ¹³C NMR (CDCl₃) δ 21.1, 30.7, 109.7, 126.2, 129.5, 134.8, 138.7, 141.7; MS *m/z* (rel intensity) 292 (44), 290 (88), 288 (44), 209 (38), 130 (100); HRMS calcd for C₁₀H₁₀Br₂ 289.9126, found 289.9134. Anal. Calcd: C, 41.42; H, 3.47. Found: C, 41.64; H, 3.66.

3-Bromo-3-(trimethylsilyl)-2-phenyl-1-propene (9a). Reaction of 7a (80 mg, 0.30 mmol) and NBS (54 mg, 0.30 mmol) in CH₂Cl₂ (5 mL) gave 9a (60 mg, 74%): ¹H NMR (CDCl₃) δ 0.05 (s, 9 H), 4.38 (s, 1 H), 5.38 (s, 1 H), 5.49 (s, 1 H), 7.24-7.48 (m, 5 H); ¹³C NMR (CDCl₃) δ -2.4, 43.1, 116.8, 126.9, 127.9, 128.3, 141.5, 148.1; MS *m/z* (rel intensity) 270 (76), 268 (70), 255 (30), 189 (40), 73 (100); HRMS calcd for C₁₂H₁₇BrSi 268.0283, found 268.0282. Anal. Calcd: C, 53.53; H, 6.38. Found: C, 53.90; H, 6.68.

3-Bromo-3-(trimethylsilyl)-2-(1-naphthyl)-1-propene (9b). Reaction of 7b (126 mg, 0.40 mmol) and NBS (72 mg, 0.40 mmol) in CH₂Cl₂ (5 mL) gave 9b (71 mg, 56%): ¹H NMR (CDCl₃) δ 0.10 (s, 9 H), 4.23 (s, 1 H), 5.47 (s, 1 H), 5.82 (s, 1 H), 7.28-7.60 (m, 4 H), 7.68-7.91 (m, 2 H), 8.17 (br d, *J* = 9 Hz, 1 H); ¹³C NMR (CDCl₃) δ -2.1, 44.9, 119.9, 125.1, 125.8, 125.9, 126.1, 126.3, 128.2, 128.5, 131.0, 133.7, 140.2, 147.8; MS *m/z* (rel intensity) 320 (6), 318 (5), 239 (100), 165 (41), 73 (38); HRMS calcd for C₁₆H₁₉BrSi 318.0440, found 318.0427. Anal. Calcd: C, 60.16; H, 6.00. Found: C, 60.27; H, 6.52.

3-Bromo-3-(trimethylsilyl)-2-(2-naphthyl)-1-propene (9c). Reaction of 7c (312 mg, 1.00 mmol) and NBS (179 mg, 1.00 mmol) in CH₂Cl₂ (5 mL) gave 9c (230 mg, 72%): ¹H NMR (CDCl₃) δ 0.04 (s, 9 H), 4.45 (s, 1 H), 5.56 (s, 2 H), 7.35-7.60 (m, 3 H), 7.72-7.95 (m, 4 H); ¹³C NMR (CDCl₃) δ -2.3, 42.9, 117.4, 125.2, 125.5, 126.1, 126.3, 127.6, 128.0, 128.1, 132.9, 133.1, 138.7, 148.0;

MS m/z (rel intensity) 320 (82), 318 (78), 166 (100), 73 (38); HRMS calcd for $C_{16}H_{19}BrSi$ 318.0440, found 318.0432. Anal. Calcd: C, 60.16; H, 6.00. Found: C, 60.47; H, 5.96.

3-Bromo-3-(trimethylsilyl)-2-(4-methylphenyl)-1-propene (9d). Reaction of **7d** (276 mg, 1.0 mmol) and NBS (179 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) gave **9d** (175 mg, 62%): 1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 2.33 (s, 3 H), 4.31 (s, 1 H), 5.38 (s, 1 H), 5.42 (s, 1 H), 7.11 (d, J = 8 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -2.3, 21.1, 43.1, 116.1, 126.7, 129.0, 137.7, 138.6, 147.9; MS m/z (rel intensity) 284 (63), 282 (59), 269 (17), 267 (17), 202 (100), 130 (63), 73 (78); HRMS calcd for $C_{13}H_{19}BrSi$ 282.0434, found 282.0430.

General Procedure for the $TiCl_4$ -Mediated Reaction of **9a with Electrophile.** To a cold ($-60^\circ C$ or $-78^\circ C$) solution of the electrophile (1.10 mmol) and $TiCl_4$ (1.10 mmol) in CH_2Cl_2 (5 mL) was added dropwise a solution of **9a** (1.10 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at $-60^\circ C$ or $-78^\circ C$ for 0.5–2 h, quenched with water, and diluted with CH_2Cl_2 (10 mL). The organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated to give the residue which was chromatographed on silica gel to afford the desired product. Compounds **12a**, **12b**, **13a**, **13b**, **14**, and **16a–c** were prepared by this procedure.

(Z)-1-Bromo-4-ethoxy-2-phenyl-1-pentene (12a). A solution of **9a** (269 mg, 1.00 mmol), 1,1-diethoxyethane (130 mg, 1.10 mmol), and $TiCl_4$ (209 mg, 1.10 mmol) in CH_2Cl_2 (5 mL) was stirred at $-78^\circ C$ for 0.5 h. After workup, the crude product was chromatographed on silica gel (hexane/ CH_2Cl_2 = 1/1) to afford **12a** (242 mg, 90%): 1H NMR ($CDCl_3$) δ 1.10 (t, J = 7 Hz, 3 H), 1.12 (d, J = 7 Hz, 3 H), 2.82 (dd, J = 7, 14 Hz, 1 H), 2.99 (dd, J = 6, 14 Hz, 1 H), 3.35–3.55 (m, 3 H), 6.41 (s, 1 H), 7.24–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.4, 19.8, 40.0, 63.8, 73.5, 106.7, 126.6, 127.7, 128.4, 140.5, 143.9; MS m/z (rel intensity) 270 (8), 268 (7), 189 (65), 73 (100); HRMS calcd for $C_{13}H_{17}BrO$ 268.0463, found 268.0411.

(Z)-1-Bromo-2-phenylnon-1-en-4-one (12b). A solution of **9a** (269 mg, 1.00 mmol), hexanoyl chloride (148 mg, 1.10 mmol), and $TiCl_4$ (209 mg, 1.10 mmol) in CH_2Cl_2 (5 mL) was stirred at $-60^\circ C$ for 0.5 h. After workup, the crude product was chromatographed on silica gel (hexane/ CH_2Cl_2 = 1/4) to yield **12b** (192 mg, 65%): 1H NMR ($CDCl_3$) δ 0.85 (t, J = 6 Hz, 3 H), 1.26 (m, 4 H), 1.59 (m, 2 H), 2.45 (t, J = 7 Hz, 2 H), 3.78 (s, 2 H), 6.65 (s, 1 H), 7.24–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.3, 23.3, 31.2, 42.2, 47.9, 108.8, 126.2, 128.1, 128.7, 139.5, 139.8, 206.4; MS m/z (rel intensity) 296 (4), 294 (4), 215 (100), 99 (13); HRMS calcd for $C_{15}H_{19}BrO$ 294.0620, found 294.0616.

3-Bromo-4,4-dimethyl-2-phenyl-1-pentene (13a). A solution of **9a** (100 mg, 0.37 mmol), *tert*-butyl chloride (38 mg, 0.41 mmol), and $TiCl_4$ (78 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) was stirred at $-78^\circ C$ for 2 h. After workup, the crude product was chromatographed on silica gel (hexane) to afford **13a** (64 mg, 68%): 1H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 4.88 (s, 1 H), 5.45 (s, 1 H), 5.61 (s, 1 H), 7.23–7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.8, 37.4, 67.6, 120.7, 127.1, 127.6, 128.3, 142.4, 149.0; MS m/z (rel intensity) 254 (15), 252 (13), 198 (71), 196 (65), 173 (43), 57 (100); HRMS calcd for $C_{13}H_{17}Br$ 252.0514, found 252.0517.

3-Bromo-4,4-dimethyl-2-phenyl-1-hexene (13b). A solution of **9a** (100 mg, 0.37 mmol), *tert*-amyl chloride (44 mg, 0.41 mmol), and $TiCl_4$ (78 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) was stirred at $-78^\circ C$ for 2 h. After workup, the crude product was chromatographed on silica gel (hexane) to give **13b** (57 mg, 57%): 1H NMR ($CDCl_3$) δ 0.74 (t, 3 H, J = 7 Hz), 0.85 (s, 3 H), 0.97 (s, 3 H), 1.20–1.50 (m, 2 H), 4.93 (s, 1 H), 5.44 (s, 1 H), 5.61 (s, 1 H), 7.25–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 8.3, 23.6, 24.7, 33.2, 39.9, 66.0, 121.2, 127.1, 127.5, 128.3, 130.9, 148.9; MS m/z (rel intensity) 268 (16), 266 (10), 198 (100), 196 (98), 71 (55); HRMS calcd for $C_{14}H_{19}Br$ 266.0671, found 266.0662.

2-Bromo-1,3-dimethyl-1-phenylindan (14). A solution of **9a** (135 mg, 0.50 mmol), 1-bromo-1-phenylethane (102 mg, 0.55 mmol), and $TiCl_4$ (105 mg, 0.55 mmol) in CH_2Cl_2 (5 mL) was stirred at $-78^\circ C$ for 0.5 h. After workup, the crude product was chromatographed on silica gel (hexane) to yield **14** (98 mg, 65%): 1H NMR ($CDCl_3$) δ 1.48 (d, J = 6 Hz, 3 H), 1.64 (s, 3 H), 3.39 (dq, J = 6, 10 Hz, 1 H), 4.08 (d, J = 10 Hz, 1 H), 6.88 (d, J = 7 Hz, 1 H), 7.15–7.35 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 16.0, 22.7, 45.6, 54.1, 71.6, 122.8, 124.4, 126.8, 127.3, 127.4, 127.5, 128.2, 143.4, 145.3,

149.1; MS m/e (rel intensity) 302 (62), 300 (68), 287 (90), 285 (100), 221 (45); HRMS calcd for $C_{17}H_{17}Br$ 300.0514, found 300.0523.

1-Bromo-4,4-dimethyl-1-pentene (16a). A solution of **15** (386 mg, 2.00 mmol), *tert*-butyl chloride (204 mg, 2.20 mmol), and $TiCl_4$ (418 mg, 2.20 mmol) in CH_2Cl_2 (5 mL) was stirred at $-78^\circ C$ for 2 h. After workup, the crude product was chromatographed on silica gel (pentane) to give **16a** (149 mg, 42%, E/Z = 48/52).¹¹ Attempts to separate these isomers were unsuccessful. (*E*)-**16a**: 1H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 1.89 (d, J = 6 Hz, 2 H), 5.96 (d, J = 14 Hz, 1 H), 6.14 (dt, J = 6, 14 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.1, 30.9, 47.1, 105.2, 132.3. (*Z*)-**16a**: 1H NMR ($CDCl_3$) δ 0.92 (s, 9 H), 2.09 (d, J = 6 Hz, 2 H), 6.13 (d, J = 6 Hz, 1 H), 6.22 (dt, J = 10, 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.3, 31.3, 43.4, 108.9, 135.6.

1-Bromo-4,4-dimethyl-1-hexene (16b). A solution of **15** (386 mg, 2.00 mmol), *tert*-amyl chloride (238 mg, 2.20 mmol), and $TiCl_4$ (418 mg, 2.20 mmol) in CH_2Cl_2 (5 mL) was stirred at $-78^\circ C$ for 2 h. After workup, the crude product was chromatographed on silica gel (pentane) to give **16b** (181 mg, 48%, E/Z = 46/54). Attempts to separate these isomers were unsuccessful. (*E*)-**16b**: 1H NMR ($CDCl_3$) δ 0.81 (t, J = 6 Hz, 3 H), 0.87 (s, 6 H), 1.24 (q, J = 6 Hz, 2 H), 2.09 (d, J = 8 Hz, 2 H), 5.96 (d, J = 14 Hz, 1 H), 6.15 (dt, J = 8, 14 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.3, 26.3, 33.3, 34.0, 44.8, 105.1, 132.1. (*Z*)-**16b**: 1H NMR ($CDCl_3$) δ 0.82 (t, J = 6 Hz, 3 H), 0.84 (s, 6 H), 1.19 (q, J = 6 Hz, 2 H), 1.89 (d, J = 7 Hz, 2 H), 6.10 (dt, J = 7, 10 Hz, 1 H), 6.20 (d, J = 10 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.4, 26.5, 33.7, 34.3, 41.2, 108.8, 135.4.

1-Bromo-4-phenyl-1-pentene (16c). A solution of **15** (386 mg, 2.00 mmol), 1-bromo-1-phenylethane (374 mg, 2.20 mmol), and $TiCl_4$ (418 mg, 2.20 mmol) in CH_2Cl_2 (5 mL) was stirred at $-78^\circ C$ for 0.5 h. After workup, the crude product was chromatographed on silica gel (hexane) to give **16c** (284 mg, 63%, E/Z = 43/57). (*E*)-**16c**: 1H NMR ($CDCl_3$) δ 1.24 (d, J = 7 Hz, 3 H), 2.25–2.35 (m, 2 H), 2.78 (sextet, J = 7 Hz, 1 H), 5.85–6.10 (m, 2 H), 7.24–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.3, 39.4, 41.5, 105.3, 126.2, 126.9, 128.4, 136.3, 146.0; HRMS calcd for $C_{11}H_{13}Br$ 224.0201, found 222.0211. (*Z*)-**16c**: 1H NMR ($CDCl_3$) δ 1.28 (d, J = 7 Hz, 3 H), 2.40–2.62 (m, 2 H), 2.86 (sextet, J = 7 Hz, 1 H), 5.97 (apparent q, 1 H, J = 7 Hz), 6.13 (d, 1 H, J = 7 Hz), 7.24–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 38.1, 40.0, 108.6, 126.2, 126.9, 128.4, 133.3, 146.3; HRMS calcd for $C_{11}H_{13}Br$ 224.0201, found 222.0214.

Reaction of **9a with Benzaldehyde and CsF .** To a slurry of benzaldehyde (53 mg, 0.50 mmol), HMPA (150 mg, 0.55 mmol), and CsF (84 mg, 0.55 mmol) in THF (10 mL) was added dropwise **9a** (135 mg, 0.50 mmol), and the mixture was allowed to reflux for 16 h, quenched with water (20 mL), and extracted with CH_2Cl_2 . The organic layer was dried ($MgSO_4$) and evaporated to give a pale yellow residue which was chromatographed on silica gel using hexane/ CH_2Cl_2 (1/1) as the eluent to give **18** (58 mg, 53%, E/Z = 1/1). The column was then eluted with CH_2Cl_2 to give **12c** (38 mg, 25%). **12c**: 1H NMR ($CDCl_3$) δ 1.85 (d, J = 4 Hz, OH group), 3.04 (dd, J = 5, 14 Hz, 1 H), 3.25 (dd, J = 8, 14 Hz, 1 H), 4.81 (m, 1 H), 6.45 (s, 1 H), 7.24–7.36 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 42.9, 72.5, 107.6, 125.8, 126.8, 127.7, 128.1, 128.4, 128.7, 140.0, 143.1, 143.6; HRMS calcd for $C_{16}H_{15}BrO$ 302.0307, found 302.0282. (*Z*)-**18**: 1H NMR ($CDCl_3$) δ 3.67 (d, J = 2 Hz, 1 H), 3.71 (d, J = 2 Hz, 1 H), 5.45 (s, 1 H), 5.50 (s, 1 H), 7.21–7.44 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 61.5, 62.5, 112.1, 125.6, 126.1, 128.1, 128.4, 128.5, 128.6, 137.0, 137.8, 144.0; HRMS calcd for $C_{16}H_{14}O$ 222.1045, found 222.1049. (*E*)-**18**: 1H NMR ($CDCl_3$) δ 4.07 (d, 1 H, J = 4 Hz), 4.40 (d, 1 H, J = 4 Hz), 5.33 (s, 1 H), 5.48 (s, 1 H), 7.19–7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 59.7, 60.2, 114.3, 125.9, 126.9, 127.7, 127.9, 128.4, 134.2, 137.8, 139.5; HRMS calcd for $C_{16}H_{14}O$ 222.1045, found 222.1049.

Acknowledgment. This work is supported by the National Science Council of the Republic of China.

Supplementary Material Available: ^{13}C NMR spectra of **8a**, **9d**, **12a–c**, **13a**, **13b**, **14**, (*E*)- and (*Z*)-**16c**, (*E*)- and (*Z*)-**18**, and a mixture of (*E*)- and (*Z*)-**16a** and **16b** (13 pages). Ordering information is given on any current masthead page.

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