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

Registry No. (±)-(*E*)-**1a**, 57549-92-5; (±)-(*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; (±)-**7b**, 139609-00-0; **8a**, 139609-01-1; (±)-**8b** (isomer 1), 139609-02-2; (±)-**8b** (isomer 2), 139684-74-5; **9a**, 139609-03-3; (±)-**9b** (isomer 1), 139609-04-4; (±)-**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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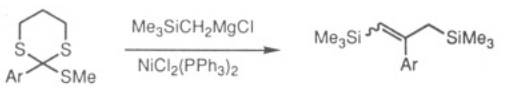
Whereas allylsilanes and vinylsilanes can be considered as allyl anion and vinyl anion synthons,[1] 1,3-bis(trimethylsilyl)propene (**1**) which contains both functionalities could couple with an electrophile E_1 to give either **2a** or **2b**. Further reaction of the latter species with a second electrophile 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 vinylsilanes[6] 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-(bistrimethylsilyl)propenes **7** from the corresponding orthothioesters **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**.

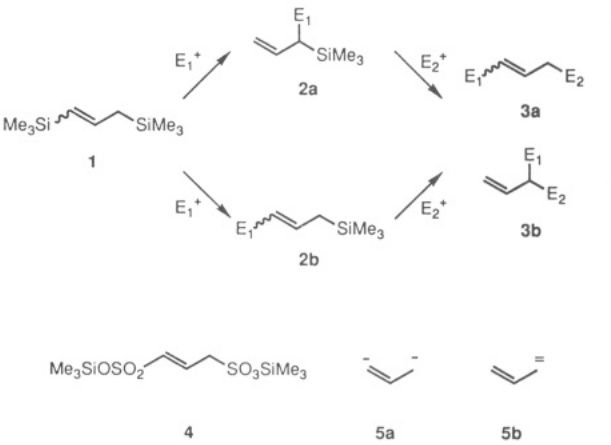


(1)

6

7 **a** Ar = Ph
b Ar = 1-Naphthyl
c Ar = 2-Naphthyl
d Ar = 4-MeC_6H_4

Scheme I



Results and Discussion

When a mixture of *E*- and *Z*-isomers of 2-aryl-1,3-bis(trimethylsilyl)propenes **7**[8] was treated with 2 equiv of *N*-bromosuccinimide (NBS) in CH_2Cl_2 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.

8 **9** **10**

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 CH_2Cl_2 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]

11 **a** R = Ph, R' = CH_2Br
b R = CH_2Br, R' = Ph

12 **a** E = MeCH(OEt)-
b E = $Me(CH_2)_4CO$-
c E = PhCH(OH)-

The $TiCl_4$-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, **7** 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

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(2) The Lewis acid-catalyzed regioselective α-attack of allylsilanes with carbon electrophiles has been extremely rare. An ester group at the γ-position is required to promote such a reaction, and a first silyl group migration from carbon to oxygen has been suggested. Cf. Chan, T.-H.; Kang, G. J. *Tetrahedron Lett.* **1982**, *23*, 3011.
(3) Trost, B. M.; Brandi, A. *J. Org. Chem.* **1984**, *49*, 4811.
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(5) Fleming, I.; Langley, J. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1421.
(6) Corriu, R.; Escudie, N.; Guerin, C. *J. Organomet. Chem.* **1984**, *264*, 207.
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(9) Hosomi, A.; Ando, M.; Sakurai, H. *Chem. Lett.* **1984**, *25*, 1385.

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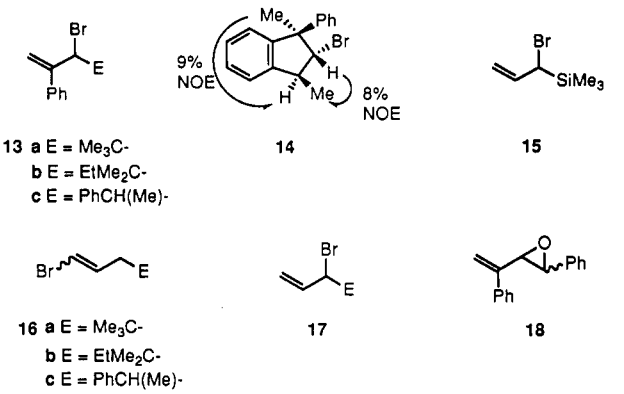
Table I. Reaction of 7 and 9 with Electrophiles

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	$Me(CH_2)_4COCl$	D	12b (65)
12	9a	Me_3CCl	E	13a (68)
13	9a	$EtMe_2CCl$	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: $TiCl_4/CH_2Cl_2$, −78 °C, 0.5 h. D: $TiCl_4/CH_2Cl_2$, −60 °C, 0.5 h. E: $TiCl_4/CH_2Cl_2$, −78 °C, 2 h.

first with 1 equiv of NBS in CH_2Cl_2 at −78 °C and then with $TiCl_4$ (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 $TiCl_4$ 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). Apparently, 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 $TiCl_4$. These results suggest that 1,3-disilylpropenes **7** also serve as a 3,3-propene dianion synthon **5b**.[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, **15**[9] was allowed to react with *tert*-butyl chloride, *tert*-amyl chloride, and (α-bromoethyl)benzene at −78 °C in the presence of $TiCl_4$ 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.

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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 CH_2Cl_2 (5 mL) under N_2 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 $Na_2S_2O_3$ (10 mL), and diluted with CH_2Cl_2 (10 mL). The organic layer was washed with water (10 mL × 3) and dried ($MgSO_4$). 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 CH_2Cl_2 (5 mL) gave **8a** (97 mg, 70%): ^1H NMR ($CDCl_3$) δ 4.48 (s, 2 H), 6.61 (s, 1 H), 7.25–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) 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 $C_9H_8Br_2$ 275.8970, found 275.8982.

Reaction of **9a** (21 mg, 0.08 mmol) and NBS (14 mg, 0.08 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (5 mL) gave **8b** (53 mg, 74%): ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{13}H_{10}Br_2$ 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 CH_2Cl_2 (5 mL) gave **8c** (245 mg, 75%): ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{13}H_{10}Br_2$ 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 CH_2Cl_2 (5 mL) gave **8d** (88 mg, 61%): ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{10}H_{10}Br_2$ 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 CH_2Cl_2 (5 mL) gave **9a** (60 mg, 74%): ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{12}H_{17}BrSi$ 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 CH_2Cl_2 (5 mL) gave **9b** (71 mg, 56%): ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{16}H_{19}BrSi$ 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 CH_2Cl_2 (5 mL) gave **9c** (230 mg, 72%): ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 °C or -78 °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 °C or -78 °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 °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 °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 °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 °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 °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 °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 °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-pentane (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 °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, O*H* 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.

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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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