JOC The Journal of Organic Chemistry

Article

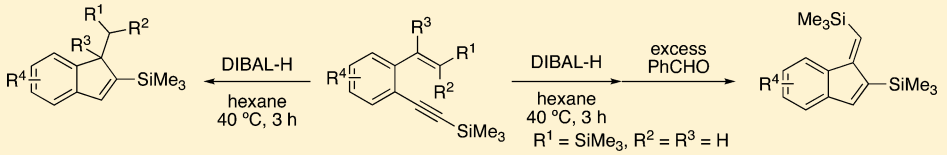
pubs.acs.org/joc

Diisobutylaluminum Hydride Promoted Cyclization of *o*-(Trimethylsilylethynyl)styrenes to Indenes

Hidenori Kinoshita, Nobuyoshi Hirai, and Katsukiyo Miura*

Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-ohkubo, Sakura-ku, Saitama 338-8570, Japan

Supporting Information



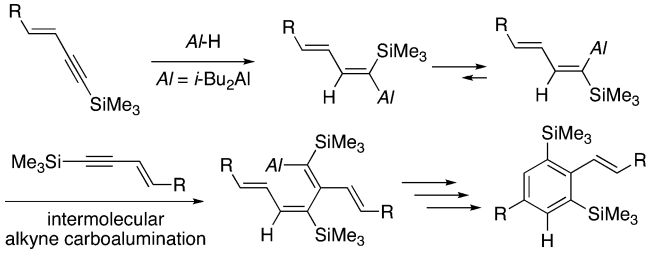
ABSTRACT: The reaction of *o*-(trimethylsilylethynyl)styrenes with diisobutylaluminum hydride (DIBAL-H) provides 2-trimethylsilyl-1*H*-indenes efficiently. The cyclization mechanism involves regioselective hydroalumination of the alkynyl moiety, geometrical isomerization of the alkenylaluminums formed, and intramolecular carboalumination. With substrates bearing a 2-(trimethylsilyl)ethenyl group (R^1 = Me_3Si, R^2 = R^3 = H), bis-silylated benzofulvenes are obtained upon treatment of the reaction mixture with an excess amount of benzaldehyde.

INTRODUCTION

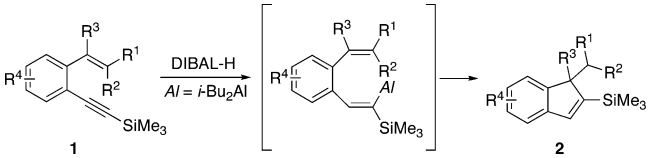
Indenes and benzofulvenes appear frequently as useful substances, such as biologically active compounds[1] and functional molecular materials.[2] Indenes are also precursors to indenyl anions used as ligands in transition-metal complexes.[3] Therefore, efficient syntheses of indenes[4] and benzofulvenes[5] have been studied intensively so far. A main approach to this end is to develop transition-metal-catalyzed C−C bond-forming reactions. We herein report the aluminum-mediated cyclization of *o*-(trimethylsilylethynyl)styrenes to indenes and benzofulvenes.

Alkenylaluminums are valuable for C−C bond formation as reactive alkenyl donors,[6] since they can be easily prepared from alkynes by hydroalumination with aluminum hydrides such as DIBAL-H. However, carboalumination of unpolarized C−C multiple bonds with alkenylaluminums has remained largely unexplored.[7] Recently, we have reported the DIBAL-H-promoted cyclodimerization of 1-silylalk-3-en-1-ynes to tetrasubstituted benzenes.[8] A key step of this transformation is intermolecular alkyne carboalumination of a substrate with the α-silylated dienylaluminum intermediate formed from another substrate molecule by hydroalumination (Scheme 1). With this study we expected that α-silylated alkenylaluminums prepared from alkynylsilanes would be utilized for intramolecular carboalumination of C−C multiple bonds leading to carbocycles. To realize this idea, we attempted the DIBAL-H-promoted cyclization of *o*-(trimethylsilylethynyl)styrenes **1** to indenes **2** (Scheme 2).

Scheme 1. Previous Work



Scheme 2. This Work



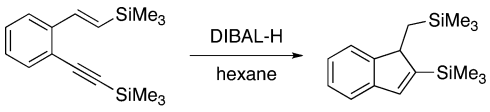
RESULTS AND DISCUSSION

Indene Synthesis. We commenced the optimization of the carboalumination-based indene synthesis by using *o*-(trimethylsilylethynyl)styrene ((*E*)-**1a**) as a probe (Table 1). Treatment of (*E*)-**1a** with 1.5 equiv of DIBAL-H gave the desired indene **2a** in 56% yield along with 35% recovery of (*E*)-**1a** (entry 1). Elongated reaction time improved the yields of **2a** (entries 2 and 3). However, the reaction for 12 h decreased the yield with a complex mixture of unidentified products (entry 4). It is likely that the cyclized product prior to an aqueous workup is not stable and decomposes during the reaction course. Although the reaction rate decreased at a lower temperature, the combined yield of **2a** and recovered (*E*)-**1a** reached 97% due to suppression of the side reactions (entry 5). The best result was obtained when the reaction was carried out at 40 °C for 3 h. Under these conditions, the desired indene **2a** was isolated in 97% yield (entry 6). A decreased amount of DIBAL-H was not effective (entry 7).

Received: June 20, 2014
Published: August 5, 2014

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

Table 1. Optimization of Indene Synthesis[a]



(*E*)-**1a** **2a**

			yield (%)[b]	
entry	time	temp (°C)	(*E*)-**1a**	**2a**
1	5 min	50	35	56
2	10 min	50	8	86
3	30 min	50	0	89
4	12 h	50	0	61
5	30 min	40	22	75
6	3 h	40	0	97 (97)[c]
7[d]	3 h	40	0	92

[a](*E*)-**1a** (0.50 mmol) and DIBAL-H (1.0 M in hexane, 0.75 mmol) were used. [b]Determined by ^{1}H NMR analysis using dibenzyl ether as an internal standard. [c]Isolated yield. [d]With DIBAL-H (0.60 mmol).

With the optimized reaction conditions in hand, we tested the cyclization of various *o*-(trimethylsilylethynyl)styrenes **1** to explore the scope and limitations. The results are shown in Table 2. Styrene (*E*)-**1b**, fluorinated on the benzene ring, was smoothly cyclized to **2b** (entry 1). When *o*-(trimethylsilylethynyl)-stilbenes (*E*)-**1c**–**e** (R^1 = Ph, *p*-F-C_6H_4, *p*-Me-C_6H_4) were subjected to the reaction conditions, the corresponding indenes **2c**–**e** were obtained in excellent yields (entries 2–4). Introduction of these aryl groups as R^1 did not affect the transformation negatively. Stilbene (*E*)-**1f** (R^1 = *p*-MeO-C_6H_4) showed low reactivity, probably due to deactivation of DIBAL-H by coordination of the methoxy group. With an increased amount of DIBAL-H, the desired indene **2f** was formed in good yield (entry 5). Styrene (*E*)-**1g** (R^1 = *n*-Hex) also underwent the cyclization to **2g** (entry 6). 1-Octyl-2-[(*E*)-2-(trimethylsilyl)-ethenyl]benzene (**3**), a doubly reduced product, was also formed in 12% yield. In contrast, the reaction of (*E*)-**1h** (R^1 = *t*-Bu) gave **2h** in only 11% yield with a complex mixture of byproducts (entry 7). Presumably the *tert*-butyl group retards the key carboalumination step (vide infra) by steric hindrance.

We next examined the effect of alkene geometry on the cyclization. The cyclization of *β*-silylated styrene (*Z*)-**1a** proceeded successfully, although it was slightly less efficient than that of (*E*)-**1a** (entry 8). Stilbenes (*Z*)-**1c** and (*Z*)-**1i** also have enough reactivity for the indene formation (entries 9 and 10). Unexpectedly the reaction of *β*-alkylated styrene (*Z*)-**1g** resulted in a trace amount of **2g**, unlike that of (*E*)-**1g** (entry 11 vs 6). In this case, **3** was obtained as the main product in 41% yield along with unidentified byproducts. Both the *Z* geometry and the electron-donating character of a hexyl group possibly decelerate the intramolecular carboalumination step (vide infra).

The parent substrate **1j** was efficiently converted into **2j** under the standard conditions (entry 12). As predicted from the sterically demanding alkene terminus, no desired product was formed from *β*,*β*-dimethylstyrene **1k** (entry 13). To our surprise *α*-methylstyrene **1l** was successfully cyclized to 1,1-dimethylindene **2l** with the formation of the quaternary carbon (entry 14). Similarly *α*,*β*-disubstituted styrene **1m** is usable for the cyclization. Treatment of **1m** with DIBAL-H for 24 h gave spiroindene **2m** in moderate yield (entry 15).

To extend the utility of the present cyclization, we tried the synthesis of six-membered carbocycles from homologated substrates **1n**,**o** (Scheme 3). However, neither of them could be cyclized to the desired products. These reactions just gave inseparable product mixtures formed by C–C double/triple bond reduction and unidentified side reactions.

Mechanistic Aspects. A plausible mechanism for the present cyclization is shown in Scheme 4. First, site-selective and regioselective hydroalumination of an *o*-(trimethylsilylethynyl)-styrene (**1**) with DIBAL-H forms the *α*-silylalkenylaluminum (*Z*)-**4** with a trans configuration between aryl and alumino groups. The intermediate (*Z*)-**4** is reversibly converted into its geometrical isomer (*E*)-**4**.[9] Intramolecular carboalumination of (*E*)-**4** gives the aluminated indene **5**, which undergoes hydrolysis leading to the corresponding indene **2**.

To verify the formation of **5**, the reaction mixture obtained from (*E*)-**1a** and DIBAL-H was treated with MeOD (Scheme 5). As expected, this deuteration provided indene **2a**-*d*, bearing a deuterio(trimethylsilyl)methyl ($CHDSiMe_3$) group at C1, with high diastereoselectivity. On the other hand, the cyclization of (*Z*)-**1a** followed by deuteration exclusively formed the diastereomer of **2a**-*d*: that is, **2a**′-*d*. Judging from the fact that spontaneous carboalumination proceeds in a *syn*-addition mode,[10] the cyclization of (*E*)-**1a** would give *u*-**2a**-*d* via (*E*,*E*)-**4a** and *u*-**5a**. Similarly *l*-**2a**-*d* would be formed from (*Z*)-**1a** via (*Z*,*E*)-**4a** and *l*-**5a**. Therefore, we tentatively assigned **2a**-*d* and **2a**′-*d* to *u* and *l* isomers, respectively. Although the relative configurations of **2a**-*d* and **2a**′-*d* are not clear,[11] the stereospecificity observed would support the presence of concerted intramolecular carboalumination as the key step.

We further conducted a deuteration experiment using (*E*)-**1g** to gain a mechanistic insight into the formation of **3** (Scheme 6). Similar to the case of (*E*)-**1a**, the reaction of (*E*)-**1g** gave deuterated indene **2g**-*d* (>99% D) mainly. The byproduct **3**-*d* was obtained in 14% yield. The ^{1}H and ^{13}C NMR analysis of **3**-*d* revealed that it was doubly deuterated at the silylated and benzylic carbons. The benzylic deuteration is indicative of alkene hydroalumination. The competitive hydroalumination is possibly due to slow cyclization of the corresponding alkenylaluinum intermediate (*E*,*E*)-**4g**.

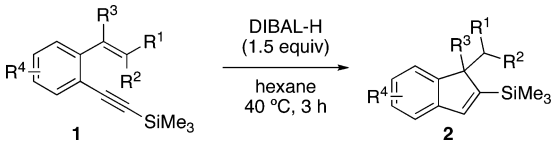
Benzofulvene Synthesis. We turned our attention to the reaction of the aluminated intermediate **5** with carbon electrophiles for further transformation. When PhCHO (2 equiv) as the electrophile was introduced into the reaction mixture from (*E*)-**1a** and DIBAL-H, no expected adduct was observed. Instead, benzofulvene (*E*)-**7a** was obtained as a single stereoisomer in 71% yield (Table 3, entry 1). The structure of (*E*)-**7a** was clearly confirmed by X-ray structure analysis (CCDC 992868).[12] The effect of the amount of the aldehyde was investigated (entries 2–4). Use of a large excess (10 equiv) of PhCHO gave an 89% isolated yield of (*E*)-**7a** (entry 3). Shortening the time for the treatment with PhCHO slightly decreased the yield of (*E*)-**7a** (entries 5 and 6). Use of other carbonyl compounds (paraformaldehyde and acetone) was not effective in the formation of (*E*)-**7a**.

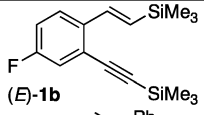
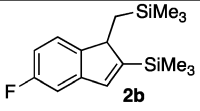
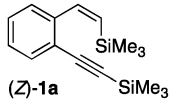
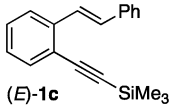
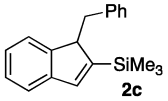
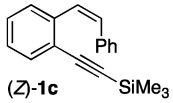
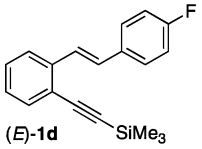
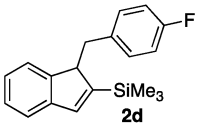
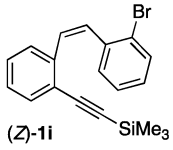
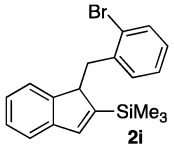
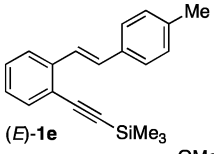
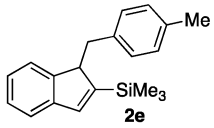
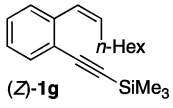
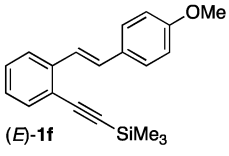
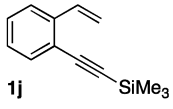
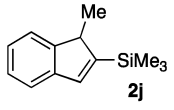
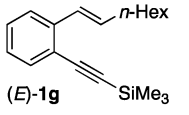
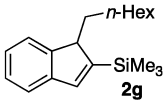
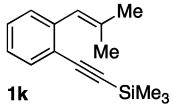
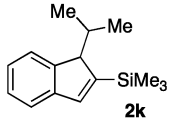
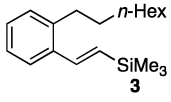
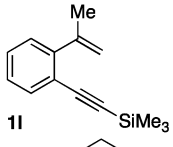
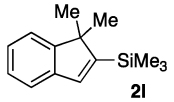
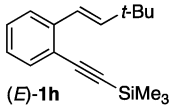
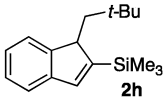
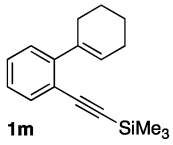
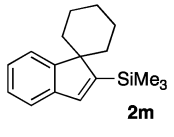
As shown in Scheme 7, the fulvene synthesis from (*Z*)-**1a** resulted in failure. Only a trace amount of (*E*)-**7a** could be detected, and **2a** was the main product (47% yield). The cyclization of (*E*)-**1b** followed by treatment with PhCHO gave (*E*)-**7b** in 77% yield. Unfortunately the yield of (*E*)-**7g** from (*E*)-**1g** was only 23%, and the corresponding benzofulvene was not detected in the reaction of (*E*)-**1c**. Thus, the benzofulvene synthesis is limited to (*E*)-*β*-silylstyrenes **1**.

The formation of (*E*)-**7a** from (*E*)-**1a** can be rationalized by the dehydroalumination of *u*-**5a** with PhCHO via the six-membered cyclic transition state (TS) **A** (Scheme 8). This type

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171–8181

Table 2. Scope and Limitations of Indene Synthesis[a]



entry	substrate **1**	product **2**	yield[b] (%)[b]	entry	substrate **1**	product **2**	yield[b] (%)[b]
1[c]	 (*E*)-**1b**	 **2b**	94	8	 (*Z*)-**1a**	**2a**	82
2	 (*E*)-**1c**	 **2c**	92	9	 (*Z*)-**1c**	**2c**	76
3	 (*E*)-**1d**	 **2d**	95	10	 (*Z*)-**1i**	 **2i**	90
4	 (*E*)-**1e**	 **2e**	93	11	 (*Z*)-**1g**	**2g** **3**	trace 41
5[d]	 (*E*)-**1f**	 **2f**	78	12	 **1j**	 **2j**	85
6	 (*E*)-**1g**	 **2g**	81	13	 **1k**	 **2k**	N.D.[e]
		 **3**	12	14	 **1l**	 **2l**	95
7	 (*E*)-**1h**	 **2h**	11	15	 **1m**	 **2m**	17 (60)[f]

[a]All reactions were conducted with **1** (0.50 mmol) and DIBAL-H (1.0 M in hexane, 0.75 mmol) at 40 °C for 3 h. [b]Isolated yield. [c]An *E*:*Z* mixture of **1b** (*E*:*Z* = 94:6) was used. [d]With DIBAL-H (1.25 mmol). [e]Not detected. [f]The reaction was conducted at 40 °C for 24 h.

of carbonyl reduction with alkylaluminums has been revealed.[13] In TS **A**, the silyl group α to the alumino group may assist the β-hydride elimination by the β-carbocation stabilizing ability (β-silicon effect), which is a possible reason for the efficient conversion of (*E*)-β-silylstyrenes **1** into benzofulvenes (*E*)-**7**. The unsuccessful result with (*Z*)-**1a** is probably because TS **B** in the dehydroalumination step is destabilized by steric hindrance between two trimethylsilyl groups.

CONCLUSION

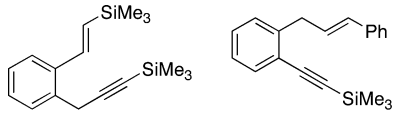
In conclusion, we have succeeded in the efficient synthesis of silylated indenes by the DIBAL-H-promoted cyclization of *o*-(silylethynyl)styrenes. Although the compatibility of this cyclization with polar functional groups is limited, a variety of substrates having a different substituent or substitution pattern can be converted into the corresponding silylated indenes in good to high yields. The application to benzofulvene synthesis has also been demonstrated. The present study shows the utility of silicon-directed hydroalumination of alkynes and subsequent intramolecular carboalumination toward carbocycle synthesis. Further application of this strategy to other carbocyclizations is now under investigation.

EXPERIMENTAL SECTION

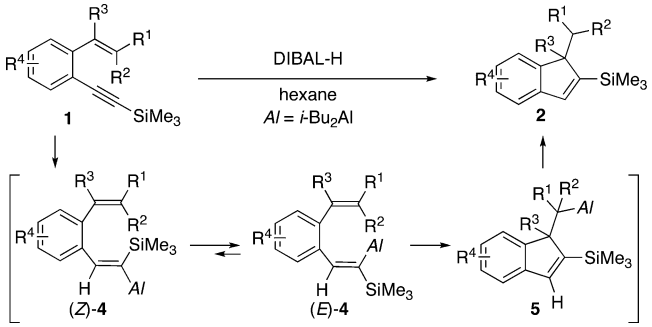
General Experimental Considerations. Unless otherwise noted, all reactions were carried out under an argon atmosphere. All reagents were purchased from common suppliers and used as received. Analytical thin-layer chromatography was performed using 0.25 mm silica gel 60 F_{254} plates. Chromatography was performed using silica gel 60 N (spherical, neutral, 63−210 μm). NMR spectra were recorded on a 300, 400, or 500 MHz NMR spectrometer. The chemical shifts are reported with reference at 7.26 ppm ($CHCl_3$) for the proton and at 77.0 ppm (centered on the signal of $CDCl_3$) for the carbon. Data for ^{1}H NMR are

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

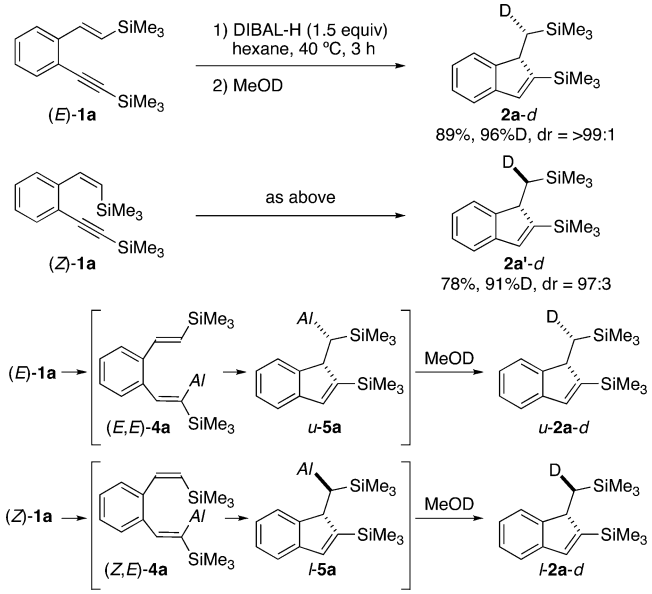
Scheme 3



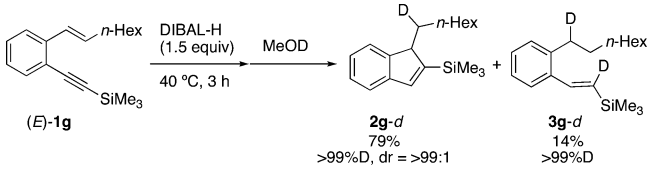
Scheme 4. Plausible Reaction Mechanism



Scheme 5. Cyclization Followed by Deuteration



Scheme 6. Deuteration Experiment with (*E*)-1g



reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constants (*J*, reported as values in hertz (Hz)), and integration. Infrared spectra and high-resolution mass spectra were obtained for all new compounds. The high-resolution mass analysis was conducted by a double-focusing magnetic sector mass spectrometer. Melting points were measured for solid compounds. X-ray single-crystal analysis of (*E*)-**7a** was conducted.

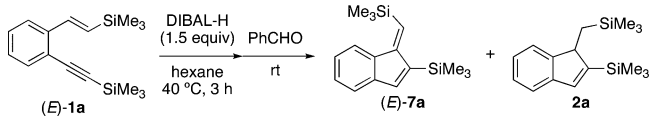
Synthesis of 1-[(*E*)-2-(Trimethylsilyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*E*)-1a). *1-Iodo-2-[2-(trimethylsilyl)ethynyl]benzene (**S1**) [CAS: 137648-47-6].*[14] *n*-BuLi (2.6 M in hexane, 13.9 mL, 36.1 mmol) was added to a solution of 1-bromo-2-[2-(trimethylsilyl)ethynyl]benzene (3.98 g, 15.7 mmol) in THF (70 mL) at −78 °C. After 30 min of stirring, I_2 (9.99 g, 39.3 mmol) was added to the reaction mixture. The mixture was warmed to room temperature over 4 h and quenched with water. The aqueous mixture was treated with saturated aqueous $Na_2S_2O_3$ and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 1-iodo-2-[2-(trimethylsilyl)-ethynyl]benzene (**S1**) as a yellow oil (4.36 g, 14.5 mmol, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 9H), 6.99 (td, J = 7.6, 1.6 Hz, 1H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.47 (dd, J = 7.8, 1.6 Hz, 1H), 7.84 (dd, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 98.8, 101.2, 106.5, 127.7, 129.5, 129.6, 132.7, 138.7.

*1-Iodo-2-[(E)-2-(trimethylsilyl)ethenyl]benzene ((E)-**S2**).* DIBAL-H (1.0 M in hexane, 21.1 mL, 21.1 mmol) was added to a solution of **S1** (3.21 g, 10.7 mmol) in hexane (17 mL) at room temperature. After 48 h of stirring, the reaction mixture was treated with 40% aqueous Rochelle salt for 1 h and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 1-iodo-2-[(*E*)-2-(trimethylsilyl)-ethenyl]benzene ((*E*)-**S2**) as a yellow oil (2.28 g, 9.18 mmol, 86%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 6.36 (d, J = 18.6 Hz, 1H), 6.93 (td, J = 7.7, 1.5 Hz, 1H), 7.04 (d, J = 18.6 Hz, 1H), 7.31 (tt, J = 7.8, 0.6 Hz, 1H), 7.54 (dd, J = 7.8, 1.8 Hz, 1H), 7.83 (dd, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.3, 99.9, 126.5, 128.3, 129.2, 133.5, 139.4, 141.1, 147.2; IR (neat) 3058, 3007, 2954, 2896, 1597, 1578, 1557, 1456, 1432 1247, 1008, 984, 864, 842, 753 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{15}ISi$ [M$^+$] 301.9988, found 301.9992.

*1-[(E)-2-(Trimethylsilyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]-benzene ((E)-**1a**).* A solution of (*E*)-**S2** (1.51 g, 5.00 mmol) in THF (3 mL) and trimethylsilylacetylene (TMSA; 0.85 mL, 6.00 mmol) were added to a mixture of $PdCl_2(PPh_3)_2$ (70.1 mg, 0.10 mmol), CuI (19.5 mg, 0.10 mmol), Et_2NH (6 mL), and THF (3 mL) at room temperature. After 16 h of stirring, the reaction mixture was quenched with water and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave (*E*)-**1a** (1.26 g, 4.62 mmol, 92%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9H), 0.27 (s, 9H), 6.55 (d, J = 19.5 Hz, 1H), 7.17, (td, J = 7.8, 1.0 Hz, 1H), 7.28 (tt, J = 7.8, 0.5 Hz, 1H), 7.44 (dd, J = 7.8, 1.0 Hz, 1H), 7.44 (d, J = 19.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.3, 0.02, 99.3, 103.3, 121.8, 124.5, 127.4, 128.6, 131.6, 132.6, 140.0, 141.6; IR (neat) 3062, 3021, 2956, 2898, 2155, 1950, 1603, 1558, 1470, 1249, 990, 869, 757 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{24}Si_2$ [M$^+$] 272.1417, found 272.1423.

Synthesis of 4-Fluoro-2-iodo-1-[(*E*)-2-(trimethylsilyl)-ethenyl]benzene ((*E*)-1b). *2-Bromo-4-fluoro-1-[2-(trimethylsilyl)-ethynyl]benzene (**S3**).* TMSA (2.57 mL, 18.2 mmol) was added to a mixture of $PdCl_2(PPh_3)_2$ (246 mg, 0.350 mmol), CuI (66.7 mg,

Table 3. Optimization of Benzofulvene Synthesis[a]

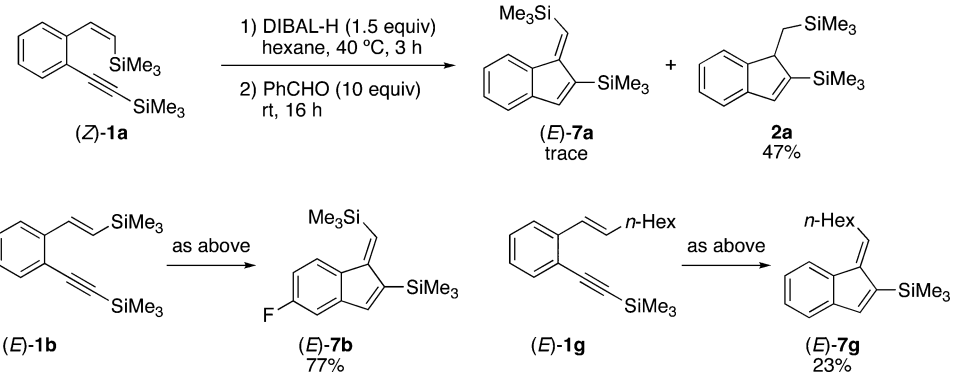


			yield (%)[c]	
entry	amt of PhCHO (equiv)	time (h)[b]	(*E*)-**7a**	**2a**
1	2	16	71	16
2	5	16	80	11
3	10	16	91 (89)[d]	5
4	20	16	90	4
5	10	2	80	11
6	10	5	84	9

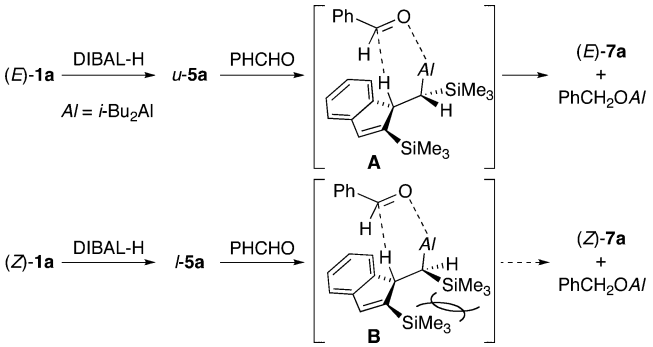
[a]The initial cyclization was carried out with (*E*)-**1a** (0.5 mmol) and DIBAL-H (0.75 mmol) in hexane at 40 °C for 3 h. After it was cooled to room temperature, the reaction mixture was treated with benzaldehyde. [b]The time for the treatment with PhCHO. [c]Determined by ^{1}H NMR analysis using dibenzyl ether as an internal standard. [d]Isolated yield.

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

Scheme 7. Formation of Benzofulvenes 7



Scheme 8. Plausible Mechanism for Benzofulvene Formation



0.350 mmol), 2-bromo-4-fluoro-1-iodobenzene (5.20 g, 17.3 mmol), and Et_2NH (20 mL) at 0 °C. After 16 h of stirring at room temperature, the reaction mixture was quenched with water and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 2-bromo-4-fluoro-1-[2-(trimethylsilyl)ethynyl]benzene (**S3**; 3.52 g, 13.0 mmol, 75%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (s, 9H), 6.97 (td, J = 8.4, 2.4 Hz, 1H), 7.32 (dd, J = 8.2, 2.4 Hz, 1H), 7.47 (dd, J = 8.6, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 99.4, 102.0, 114.5 (d, $^2J_{C-F}$ = 21.0 Hz), 119.9 (d, $^2J_{C-F}$ = 24.0 Hz), 121.7 (d, $^4J_{C-F}$ = 4.0 Hz), 126.4 (d, $^3J_{C-F}$ = 10.0 Hz), 134.6 (d, $^3J_{C-F}$ = 9.0 Hz), 161.8 (d, $^1J_{C-F}$ = 252.0 Hz); IR (neat) 3073, 2960, 2899, 2167, 1595, 1482, 1263, 1252, 1194, 858 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}BrFSi$ [M$^+$] 269.9876, found 269.9877.

*4-Fluoro-2-iodo-1-[2-(trimethylsilyl)ethynyl]benzene (**S4**).* n-BuLi (2.6 M in hexane, 5.23 mL, 13.6 mmol) was added to a solution of **S3** (3.07 g, 11.3 mmol) in THF (50 mL) at −78 °C. After 30 min of stirring at −78 °C, I_2 (4.00 g, 15.8 mmol) was added to the mixture at −78 °C. The resultant mixture was warmed to room temperature over 2 h. After quenching with water, the aqueous mixture was treated with saturated aqueous $Na_2S_2O_3$ and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 4-fluoro-2-iodo-1-[2-(trimethylsilyl)ethynyl]benzene (**S4**; 3.51 g, 11.0 mmol, 97%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 9H), 7.01 (td J = 8.4, 2.7 Hz, 1H), 7.43 (dd, J = 8.7, 5.7 Hz, 1H), 7.56 (dd, J = 8.1, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 98.5, 101.1 (d, $^3J_{C-F}$ = 8.0 Hz), 105.5, 115.3 (d, $^2J_{C-F}$ = 21.0 Hz), 125.9 (d, $^2J_{C-F}$ = 24.0 Hz), 126.1 (d, $^4J_{C-F}$ = 4.0 Hz), 133.6 (d, $^3J_{C-F}$ = 8.0 Hz), 161.3 (d, $^1J_{C-F}$ = 254.0 Hz); IR (neat) 3067, 2959, 2898, 2164, 1589, 1474, 1251, 1194, 845 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}FISi$ [M$^+$] 317.9737, found 317.9732.

*4-Fluoro-2-iodo-1-[2-(trimethylsilyl)ethenyl]benzene (**S5**) (E:Z = 95:5).* DIBAL-H (1.0 M in hexane, 20.8 mL, 20.8 mmol) was added to a solution of **S4** (3.29 g, 10.4 mmol) in hexane (16.6 mL) at room temperature. After 72 h, the mixture was treated with 40% aqueous Rochelle salt at 0 °C and stirred at room temperature for 2 h. Then the aqueous mixture was extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 4-fluoro-2-iodo-1-[2-(trimethylsilyl)ethenyl]benzene (**S5**) as an *EZ* mixture (*E*:*Z* = 95:5, 2.70 g, 8.43 mmol, 81%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) for *E* isomer δ 0.18 (s, 9H), 6.28 (d, J = 18.9 Hz, 1H), 6.98 (d, J = 18.9 Hz, 1H), 7.05 (tdd, J = 8.4, 2.7, 0.6 Hz, 1H), 7.49 (dd, J = 8.9, 6.0 Hz, 1H), 7.55 (dd, J = 8.0, 2.7 Hz, 1H), for *Z* isomer δ −0.05 (s, 9H), 5.89 (d, J = 14.7 Hz, 1H), 7.12 (d, J = 14.7 Hz, 1H), 7.16−7.61 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for *E* isomer δ −1.3, 98.9 (d, $^3J_{C-F}$ = 8.0 Hz), 115.6 (d, $^2J_{C-F}$ = 21.0 Hz), 126.0 (d, $^2J_{C-F}$ = 24.0 Hz), 127.1 (d, $^3J_{C-F}$ = 8.0 Hz), 133.4, 137.5 (d, $^4J_{C-F}$ = 3.0 Hz), 145.9, 161.5 (d, $^1J_{C-F}$ = 251.0 Hz), for *Z* isomer δ −0.07, 98.2 (d, $^3J_{C-F}$ = 8.0 Hz), 114.7 (d, $^2J_{C-F}$ = 21.0 Hz), 125.4 (d, $^2J_{C-F}$ = 24.0 Hz), 129.9 (d, $^3J_{C-F}$ = 8.0 Hz), 134.6, 140.5 (d, $^4J_{C-F}$ = 4.0 Hz), 148.7, 161.2 (d, $^1J_{C-F}$ = 250.0 Hz); IR (neat) 2954, 2897, 1591, 1473, 1248, 1227, 863, 841 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{14}FISi$ [M$^+$] 319.9893, found 319.9897.

*4-Fluoro-1-[2-(trimethylsilyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]-benzene (**1b**) (E:Z = 94:6).* A solution of **S5** (0.91 g, 2.84 mmol) in THF (3 mL) and TMSA (0.51 mL, 3.60 mmol) were added to a mixture of $PdCl_2(PPh_3)_2$ (42.1 mg, 0.06 mmol), CuI (11.4 mg, 0.06 mmol), Et_2NH (6 mL), and THF (3 mL) at 0 °C. After overnight stirring at room temperature, the reaction mixture was quenched with water and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 4-fluoro-1-[2-(trimethylsilyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]-benzene (**1b**; 0.72 g, 2.48 mmol, 87%) as an *E*:*Z* mixture (*E*:*Z* = 94:6) of a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) for *E* isomer δ 0.17 (s, 9H), 0.27 (s, 9H), 6.46 (d, J = 19.2 Hz, 1H), 6.99 (tdd, J = 8.4, 2.7, 0.6 Hz, 1H), 7.13 (dd, J = 9.0, 2.7 Hz, 1H), 7.37 (d, J = 19.2 Hz, 1H), 7.56 (dd, J = 8.7, 5.7 Hz, 1H), for *Z* isomer δ 0.02 (s, 9H), 0.25 (s, 9H), 5.90 (d, J = 15.3 Hz, 1H), 6.95−7.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) for *E* isomer δ −1.3, −0.1, 100.5, 102.0 (d, $^4J_{C-F}$ = 2.0 Hz), 116.2 (d, $^2J_{C-F}$ = 22.0 Hz), 118.7 (d, $^2J_{C-F}$ = 22.0 Hz), 123.3 (d, $^3J_{C-F}$ = 9.0 Hz), 126.3 (d, $^3J_{C-F}$ = 9.0 Hz), 131.3, 136.5 (d, $^4J_{C-F}$ = 3.0 Hz), 140.5, 161.6 (d, $^1J_{C-F}$ =246.0), for *Z* isomer δ −1.6, −0.08, 100.4, 102.4 (d, $^4J_{C-F}$ = 3.0 Hz), 115.1 (d, $^2J_{C-F}$ = 22.0 Hz), 118.6 (d, $^2J_{C-F}$ = 23.0 Hz), 124.0 (d, $^3J_{C-F}$ = 10.0 Hz), 129.7 (d, $^3J_{C-F}$ = 9.0 Hz), 133.9, 138.9 (d, $^4J_{C-F}$ = 3.0 Hz), 144.7, 161.5 (d, $^1J_{C-F}$ =246.0); IR (neat) 3071, 2957, 2898, 2155, 1602, 1473, 1250, 844 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{23}FSi_2$ [M$^+$] 290.1322, found 290.1323.

Synthesis of 1-[(*E*)-2-(Phenyl)ethenyl]-2-[2-(trimethylsilyl)-ethynyl]benzene ((*E*)-1c). *1-Iodo-2-[(E)-2-(phenyl)ethenyl]benzene (**S6**) [CAS: 5025-41-2].*[15] Sodium bis(trimethylsilyl)amide (1.9 M in THF, 4.2 mL, 8.0 mmol) was added dropwise to a solution of diethyl benzylphosphonate (1.83 g, 8.02 mmol) in THF (2 mL) at 0 °C. After 10 min of stirring, a solution of 2-iodobenzaldehyde (1.86 g, 8.02 mmol) in THF (5 mL) was added to the mixture. After 12 h of stirring at room temperature, the reaction mixture was quenched with water and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane/AcOEt 5/1) gave 1-iodo-2-[(*E*)-2-phenylethenyl]-benzene (**S6**) as a colorless oil (1.83 g, 5.98 mmol, 75%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.69 (td, J = 7.5,1.8 Hz, 1H), 6.97 (d, J = 16.2 Hz,

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

1H), 7.24−7.42 (m, 5H), 7.53−7.58 (m, 2H), 7.63 (dd, J = 7.8, 1.5 Hz, 1H), 7.88 (dd, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 100.4, 126.3, 126.8, 128.0, 128.4, 128.7, 128.9, 131.6, 132.4, 136.9, 139.6, 140.3.

*1-[(E)-2-(Phenyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((E)-**1c**).* The Sonogashira coupling of **S6** (1.69 g, 5.52 mmol) and TMSA (0.93 mL, 6.60 mmol) by the method for the synthesis of (*E*)-**1a** gave (*E*)-**1c** (1.43 g, 5.18 mmol, 94%) as a white solid: mp 55.5−57.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.31 (s, 9H), 7.18 (d, J = 16.4 Hz, 1H), 7.19 (td, J = 7.6, 1.2 Hz, 1H), 7.27−7.34 (m, 2H), 7.35−7.40 (m, 2H), 7.49 (dd, J = 7.8, 1.2 Hz, 1H), 7.52−7.56 (m, 2H), 7.68 (d, J = 16.4 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.03, 99.6, 103.6, 122.0, 124.5, 126.7, 126.8, 127.1, 127.8, 128.7, 130.1, 132.8, 137.4, 139.1; IR (Nujol) 3080, 3022, 2151, 1494, 1447, 1250, 965, 868 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}Si$ [M$^+$] 276.1334, found 276.1325.

Synthesis of 1-[(*E*)-2-(4-Fluorophenyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*E*)-1d). Sodium bis(trimethylsilyl)amide (1.9 M in THF, 2.6 mL, 5.0 mmol) was added to a solution of diethyl (4-fluorobenzyl)phosphonate (1.48 g, 6.01 mmol) in THF (15 mL) at 0 °C. After 10 min of stirring, a solution of 2-(trimethylsilylethynyl)benzaldehyde (1.02 g, 5.04 mmol) in THF (8 mL) was added to the mixture. After 16 h of stirring, the reaction mixture was quenched with aqueous NH_4Cl and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane/AcOEt 40/1) gave (*E*)-**1d** as a needle crystal (0.72 g, 2.45 mmol, 49%): mp 52.5−54.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 9H), 7.07 (t, J = 8.7 Hz, 2H), 7.14 (d, J = 16.8 Hz, 1H), 7.19 (td, J = 7.7, 1.2 Hz, 1H), 7.32 (tdd, J = 7.8, 1.4, 0.3 Hz, 1H), 7.46−7.54 (m, 3H), 7.58 (d, J = 16.5 Hz, 1H), 7.65 (dt, J = 8.1, 0.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.03, 99.7, 103.5, 115.7 (d, $^3J_{C-F}$ = 22.5 Hz), 122.0, 124.5, 126.6, 127.1, 128.1, 128.5 (d, $^2J_{C-F}$ = 96.3 Hz), 128.7, 132.9, 133.6 (d, $^4J_{C-F}$ = 5.0 Hz), 138.9, 162.5 (d, $^1J_{C-F}$ = 246.3 Hz); IR (Nujol) 3033, 2154, 1598, 1508, 1233, 969 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{19}FSi$ [M$^+$] 294.1240, found 294.1242.

Synthesis of 1-[(*E*)-2-(4-Methylphenyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*E*)-1e). *1-Iodo-2-[(E)-2-(4-methylphenyl)ethenyl]benzene (**S7**).* This compound was prepared from 2-iodobenzaldehyde (1.86 g, 8.02 mmol) and diethyl 4-methylbenzyl phosphonate (1.94 g, 8.01 mmol) by the method for the synthesis of **S6**. Stilbene **S7** (2.39 g, 7.46 mmol, 93%) was obtained as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 6.92−6.97 (m, 1H), 6.94 (d, J = 16.5 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.24−7.29 (m, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.61 (dd, J = 7.5, 1.5 Hz, 1H), 7.87 (dd, J = 8.0, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 100.4, 126.1, 126.7, 128.3, 128.7, 129.4, 131.4, 131.5, 134.1, 138.0, 139.5, 140.4; IR (neat) 3048, 3023, 2918, 2859, 1629, 1579, 1512, 1460, 1432, 1216, 1009, 959, 802, 746 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{13}I$ [M$^+$] 320.0062, found 320.0054.

*1-[(E)-2-(4-Methylphenyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]-benzene ((E)-**1e**).* The Sonogashira coupling of **S7** (1.28 g, 4.00 mmol) with TMSA (0.68 mL, 4.80 mmol) by the method for the synthesis of (*E*)-**1a** gave (*E*)-**1e** (0.97 g, 3.35 mmol, 84%) as a white solid: mp 54.0−55.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.31 (s, 9H), 2.37 (s, 3H), 7.16 (d, J = 16.5 Hz, 1H), 7.15−7.20 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.31 (td, J = 7.5, 1.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.47 (dd, J = 7.8, 1.0 Hz, 1H), 7.63 (d, J = 16.5 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.05, 21.3, 99.5, 103.6, 121.9, 124.4, 125.8, 126.6, 126.9, 128.7, 129.4, 130.1, 132.8, 134.7, 137.8, 139.3; IR (Nujol) 3060, 3018, 2954, 2154, 1514, 1248, 967, 841 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}Si$ [M$^+$] 290.1491, found 290.1488.

Synthesis of 1-[(*E*)-2-(4-Methoxylphenyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*E*)-1f). Sodium bis(trimethylsilyl)amide (1.9 M in THF, 1.9 mL, 3.6 mmol) was added to a solution of diethyl (4-methoxybenzyl)phosphonate (0.93 g, 3.60 mmol) in THF (9 mL) at 0 °C. After 10 min of stirring, a solution of 2-(trimethylsilylethynyl)benzaldehyde (0.61 g, 3.02 mmol) in THF (5 mL) was added to the mixture. After overnight stirring at room temperature, the reaction mixture was quenched with aqueous NH_4Cl and extracted with AcOEt. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane/AcOEt = 5/1) gave (*E*)-**1f** (0.51 g, 1.66 mmol, 55%) as a white solid: mp 62.0−64.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 9H), 3.84 (s, 3H), 6.91 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 16.2 Hz, 1H), 7.16 (td, J = 7.5, 1.2 Hz, 1H), 7.30 (td, J = 7.7, 0.9 Hz, 1H), 7.45−7.49 (m, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 16.2 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.05, 55.3, 99.4, 103.7, 114.2, 121.7, 124.2, 124.6, 126.7, 127.9, 128.7, 129.7, 130.2, 132.8, 139.4, 159.5; IR (Nujol) 3035, 2145, 1604, 1512, 1445, 1251, 1033, 972, 842 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}OSi$ [M$^+$] 306.1440, found 306.1444.

Synthesis of 1-[(*E*)-Oct-1-enyl]-2-[2-(trimethylsilyl)ethynyl]-benzene ((*E*)-1g). *1-Bromo-2-[(E)-oct-1-enyl]benzene (**S8**).* A solution of (*E*)-1-iodooct-1-ene (3.81 g, 16.0 mmol) in THF (8 mL) was added to a solution of $Pd(PPh_3)_4$ (0.46 g, 0.40 mmol) in THF (17 mL) at room temperature. After 30 min of stirring, a solution of 2-bromophenylboronic acid (1.61 g, 8.00 mmol) in THF (8 mL) and aqueous NaOH (1 M, 16.8 mL, 16.8 mmol) were added to the mixture. The resultant mixture was heated under reflux for 12 h and then cooled to room temperature. The reaction mixture was diluted with water (10 mL) and Et_2O (20 mL) and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 1-bromo-2-[(*E*)-oct-1-enyl]benzene (**S8**; 1.59 g, 5.95 mmol, 74%) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3H), 1.26−1.40 (m, 6H), 1.49 (quint, J = 7.5 Hz, 2H), 2.51 (qd, J = 7.5, 1.0 Hz, 2H), 6.17 (dt, J = 16.0, 7.0 Hz, 1H), 6.70 (d, J = 16.0, 1H), 7.05 (td, J = 8.0, 1.5 Hz, 1H), 7.24 (t, J = 7.3 Hz, 1H), 7.49 (dd, J = 7.8, 1.5 Hz, 1H), 7.52 (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.01, 14.1, 22.6, 28.9, 29.2, 31.7, 33.1, 123.1, 126.8, 127.3, 128.0, 128.6, 132.8, 134.3, 137.7; IR (neat) 3061, 2955, 2925, 2854, 1466, 1435, 1249, 1022, 963 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{19}Br$ [M$^+$] 266.0670, found 266.0676.

*1-Iodo-2-[(E)-oct-1-enyl]benzene (**S9**).* This compound was prepared from **S8** (1.22 g, 4.57 mmol) by the method for the synthesis of **S4** from **S3**. 1-Iodo-2-[(*E*)-oct-1-enyl]benzene (**S9**; 1.17 g, 3.72 mmol, 81%) was obtained as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 3H), 1.27−1.42 (m, 6H), 1.44−1.54 (m, 2H), 2.25 (qd, J = 7.0, 1.2 Hz, 2H), 6.09 (dt, J = 15.6, 7.2 Hz, 1H), 6.55 (d, J = 15.6 HZ, 1H), 6.89 (td J = 7.6, 1.6 Hz, 1H), 7.25−7.30 (m, 1H), 7.44 (dd, J = 7.6, 1.6 Hz, 1H), 7.81 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 28.8, 29.1, 31.7, 32.9, 99.4, 126.3, 128.19, 128.24, 133.5, 134.4, 139.3, 141.0; IR (neat) 3059, 3026, 2955, 2925, 2854, 1461, 1431, 1010, 960, 745 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{19}I$ [M$^+$] 314.0531, found 314.0544.

*1-[(E)-Oct-1-enyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((E)-**1g**).* The Sonogashira coupling of **S9** (961 mg, 3.06 mmol) with TMSA (0.52 mL, 3.67 mmol) by the method for the synthesis of (*E*)-**1a** gave (*E*)-**1g** (715 mg, 2.51 mmol, 82%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 9H), 0.90 (t, J = 6.6 Hz, 3H), 1.26−1.42 (m, 6H), 1.45−1.55 (m, 2H), 2.25 (qd, J = 6.9, 1.5 Hz, 2H), 6.32 (dt, J = 15.6, 6.9 Hz, 1H), 6.86 (d, J = 15.6 Hz, 1H), 7.11 (td, J = 7.5, 1.2 Hz, 1H), 7.24 (td, J = 7.8, 1.2 Hz, 1H), 7.42 (dd, J = 7.6, 1.2 Hz, 1H), 7.49 (dd, J = 7.5, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.01, 14.1, 22.6, 28.9, 29.1, 31.8, 33.2, 98.8, 103.9, 121.0, 124.5, 126.3, 127.7, 128.6, 132.7, 133.2, 139.9; IR (neat) 3087, 3060, 3025, 2957, 2926, 2855, 2154, 1474, 1446, 1250, 966, 867, 842 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{28}Si$ [M$^+$] 284.1960, found 284.1958.

Synthesis of 1-[(*E*)-3,3-Dimethylbut-1-enyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*E*)-1h). *2-Bromo-1-[(E)-3,3-dimethylbut-1-enyl]benzene (**S10**).* This compound was prepared from 2-bromophenylboronic acid (2.01 g, 10.0 mmol) and (*E*)-1-iodo-3,3-dimethylbut-1-ene (4.20 g, 20.0 mmol) by the method for the synthesis of **S8**. 2-Bromo-1-[(*E*)-3,3-dimethylbut-1-enyl]benzene (**S10**; 1.70 g, 7.11 mmol, 71%) was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 9H), 6.18 (d, J = 15.9 Hz, 1H), 6.65 (d. J = 15.9 Hz, 1H), 7.05 (td, J = 7.8, 1.5 Hz, 1H), 7.24 (td, J = 7.7, 1.2 Hz, 1H), 7.47−7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.5, 33.7, 123.5, 123.9, 126.8, 127.3, 128.0, 132.8, 137.8, 144.8; IR (neat) 3056, 2959, 2865, 1465, 1438 1024, 968 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{15}Br$ [M$^+$] 238.0357, found 238.0366.

*1-[(E)-3,3-Dimethylbut-1-enyl]-2-iodobenzene (**S11**).* This compound was prepared from **S10** (1.70 g, 7.11 mmol) by the method

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

for the synthesis of **S4** from **S3**. 1-[(*E*)-3,3-Dimethylbut-1-enyl]-2-iodobenzene (**S11**; 1.81 g, 6.33 mmol, 89%) was obtained as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (s, 9H), 6.10 (d, J = 16.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.89 (td, J = 7.5, 1.5 Hz, 1H), 7.28 (td, J = 7.0, 0.5 Hz, 1H), 7.44 (dd, J = 8.0, 1.5 Hz, 1H), 7.81 (dd, J = 7.8, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.5, 33.7, 99.9, 126.3, 128.2, 128.2, 129.0, 139.3, 141.1, 144.9; IR (neat) 3058, 2958, 2903, 2865, 1461, 1433, 1362, 1011, 966 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{15}I$ [M^+] 286.0218, found 286.0223.

*1-[(E)-3,3-Dimethylbut-1-enyl]-2-[2-(trimethylsilyl)ethynyl]-benzene ((E)-**1h**).* The Sonogashira coupling of **S11** (1.67 g, 5.84 mmol) with TMSA (0.99 mL, 7.01 mmol) by the method of the synthesis of (*E*)-**1a** gave (*E*)-**1h** (1.30 g, 5.07 mmol, 87%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (s, 9H), 1.14 (s, 9H), 6.32 (d, J = 16.5 Hz, 1H), 6.85 (d, J = 16.5 Hz, 1H), 7.12 (td, J = 7.5, 1.5 Hz, 1H), 7.25 (td, J = 7.3, 1.0 Hz, 1H), 7.42 (dd, J = 7.8, 1.0 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.05, 29.5, 33.7, 98.8, 103.8, 121.3, 123.0, 124.4, 126.3, 128.6, 132.5, 140.0, 143.5; IR (neat) 3087, 3060, 3025, 2959, 2902, 2866, 2154, 1644, 1472, 1250, 971, 872, 843 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{24}Si$ [M^+] 256.1647, found 256.1652.

Synthesis of 1-[(*Z*)-2-(Trimethylsilyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*Z*)-1a). DIBAL-H (1.0 M in hexane, 15.5 mL, 15.5 mmol) was added to a solution of 1-iodo-2-(trimethylsilylethynyl)benzene (2.10 g, 7.00 mmol) in Et_2O (21 mL) at room temperature. The reaction was monitored with TLC and GC-MS. After 305 h of stirring, the reaction mixture was quenched with 40% aqueous Rochelle salt and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. The residue was checked with ^{1}H NMR. The formation of 1-iodo-2-[(*Z*)-2-(trimethylsilyl)ethenyl]-benzene was confirmed. Therefore, this compound was used in the next step without further purification. The Sonogashira coupling of 1-iodo-2-((*Z*)-trimethylsilylethenyl)benzene with TMSA (0.99 mL, 7.00 mmol) by the method for the synthesis of (*E*)-**1a** gave 1-[(*Z*)-2-(trimethylsilyl)-ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*Z*)-**1a**) (0.54 g, 1.98 mmol, 28% yield over 2 steps) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.02 (s, 9H), 0.25 (s, 9H), 5.91 (d, J = 15.0, 1H), 7.20 (td, J = 7.5, 1.5 Hz, 1H), 7.25 (td, J = 7.3, 1.5 Hz, 1H), 7.30 (dd, J = 8.0, 1.5 Hz, 1H), 7.44 (dd, J = 7.5, 1.0 Hz, 1H), 7.53 (d, J = 15.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.04, 0.11, 99.1, 103.7, 122.3, 127.2, 127.8, 128.1, 132.2, 133.7, 142.6, 145.2; IR (neat) 3061, 2958, 2898, 2157, 1592, 1472, 1249, 869, 841 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{24}Si_2$ [M^+] 272.1417, found 272.1421.

Synthesis of 1-[(*Z*)-2-Phenylethenyl]-2-[2-(trimethylsilyl)-ethynyl]benzene ((*Z*)-1c). *n*-BuLi (2.6 M in hexane, 0.412 mL, 1.07 mmol) was added to a solution of 1-bromo-2-[(*Z*)-2-phenylethenyl]-benzene (0.25 g, 0.97 mmol) in THF (5 mL) at −78 °C. After 30 min of stirring at −78 °C, I_2 (0.27 g, 1.07 mmol) was added to the mixture. The resultant mixture was warmed to room temperature over 2 h and quenched with water. The aqueous mixture was treated with saturated aqueous $Na_2S_2O_3$ and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. The residue was checked with ^{1}H NMR. The formation of 1-iodo-2-[(*Z*)-(phenyl)ethenyl]benzene was confirmed. Therefore, this compound was used in the next step without further purification. The Sonogashira coupling of 1-iodo-2-[(*Z*)-(phenyl)ethenyl]benzene with TMSA (0.141 mL, 1.00 mmol) by the method for the synthesis of (*E*)-**1a** gave 1-[(*Z*)-2-phenylethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene (0.17 g, 0.61 mmol, 63% yield over two steps) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 9H), 6.67 (d, J = 12.4 Hz, 1H), 6.82 (d, J = 12.4 Hz, 1H), 7.07 (td, J = 7.4, 0.8 Hz, 1H), 7.14 (td, J = 7.6, 1.2 Hz, 1H), 7.16−7.23 (m, 6H), 7.48 (dd, J = 7.6, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.01, 99.1, 103.7, 122.7, 126.9, 127.1, 128.0, 128.1, 128.7, 128.9, 129.0, 131.1, 132.6, 137.0, 129.8; IR (neat) 3081, 3059, 3023, 2959, 2898, 2155, 1474, 1445, 1250, 869, 843, 759 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}Si$ [M^+] 276.1334, found 276.1345.

Synthesis of 1-[(*Z*)-2-(2-Bromophenyl)ethenyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((*Z*)-1i). Sodium bis-(trimethylsilyl)amide (1.9 M in THF, 9.58 mL, 18.2 mmol) was added to a solution of (2-bromobenzyl)triphenylphosphonium bromide (11.2 g, 21.8 mmol) in THF (90 mL) at 0 °C. After 30 min of stirring, a solution of 2-iodobenzaldehyde (4.22 g, 18.2 mmol) in THF (50 mL) was added to the mixture at −78 °C. The mixture was warmed to room temperature overnight and quenched with water. The aqueous mixture was extracted with hexane/AcOEt (1/1). The organic layer was dried over Na_2SO_4 and evaporated. The residue was checked with ^{1}H NMR. The formation of 1-[(*Z*)-2-(bromophenyl)ethenyl]-2-iodobenzene was confirmed. Therefore, this compound was used in the next step without further purification. The Sonogashira coupling of 1-[(*Z*)-2-(bromophenyl)ethenyl]-2-iodobenzene with TMSA (2.57 mL, 18.2 mmol) by the method for the synthesis of (*E*)-**1a** gave (*Z*)-**1i** (5.12 g, 14.4 mmol, 79% yield over two steps) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 6.74 (d, J = 12.0 Hz, 1H), 6.97−7.02 (m, 3H), 7.03−7.07 (m, 2H), 7.07−7.14 (m, 2H), 7.46 (d, J = 7.6 Hz, 1H), 7.57−7.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.04, 99.4, 103.5, 122.9, 124.0, 126.9, 127.0, 127.9, 128.7, 128.9, 130.0, 130.4, 131.0, 132.6, 132.6, 137.6, 138.8; IR (neat) 3061, 3022, 2959, 2898, 2155, 1463, 1434, 1250, 1025, 868, 758 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{19}BrSi$ [M^+] 354.0439, found 354.0444.

Synthesis of 1-(Oct-1-enyl)-2-[(*Z*)-2-(trimethylsilyl)ethynyl]-benzene ((*Z*)-1g). *1-Bromo-2-(oct-1-ynyl)benzene (**S12**) [CAS: 121221-93-0].*[16] The Sonogashira coupling of 1-bromo-2-iodobenzene (5.11 g, 18.1 mmol) with 1-octyne (2.94 mL, 19.9 mmol) by the reported method[16] gave 1-bromo-2-(oct-1-ynyl)benzene (**S12**; 4.33 g, 16.3 mmol, 90%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, J = 7.0 Hz, 3H), 1.30−1.37 (m, 4H), 1.47−1.53 (m, 2H), 1.60−1.67 (m, 2H), 2.46 (t, J = 7.0 Hz, 2H), 7.11 (td, J = 8.0, 1.5 Hz, 1H), 7.22 (td, J = 7.5, 1.0 Hz, 1H), 7.42 (dd, J = 7.8, 1.5 Hz, 1H), 7.55 (dd, J = 8.0, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 19.6, 22.6, 28.5, 28.5, 31.3, 79.4, 95.6, 125.4, 126.1, 126.8, 128.6, 132.2, 133.3.

*1-Bromo-2-[(Z)-oct-1-enyl]benzene (**S13**).* DIBAL-H (1.0 M in hexane, 17.6 mL, 17.6 mol) was added to **S12** (4.25 g, 16.0 mmol) at room temperature. The mixture was stirred at 50 °C for 22 h. The resultant mixture was treated with 40% aqueous Rochelle salt at 0 °C and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 1-bromo-2-[(*Z*)-oct-1-enyl]benzene (**S13**; 1.97 g, 7.37 mmol, 46%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, J = 6.5 Hz, 3H), 1.18−1.32 (m, 6H), 1.41 (quint, J = 7.5 Hz, 2H), 2.17 (qd, J = 7.5, 1.5 Hz, 2H), 5.77 (td, J = 11.5, 7.5 Hz, 1H), 6.44 (d, J = 11.5 Hz, 1H), 7.07−7.12 (m, 1H), 7.24−7.29 (m, 2H), 7.57 (d, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 28.3, 28.9, 29.6, 31.6, 124.0, 126.7, 128.1, 128.3, 130.6, 132.5, 134.1, 137.7; IR (neat) 3065, 3015, 2955, 2925, 2855, 1467, 1432, 1026, 762 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{19}Br$ [M^+] 266.0670, found 266.0665.

*1-Iodo-2-[(Z)-oct-1-enyl]benzene (**S14**).* This compound was prepared from **S13** (1.57 g, 5.88 mmol) by using the same method to synthesize **S4** from **S3**. 1-Iodo-2-[(*Z*)-oct-1-enyl]benzene (**S14**; 1.51 g, 4.81 mmol, 82%) was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 6.8 Hz, 3H), 1.17−1.33 (m, 6H), 1.37−1.45 (m, 2H), 2.17 (qd, J = 7.2 1.6 Hz, 2H), 5.77 (dt, J = 11.2, 7.6 Hz, 1H), 6.44 (d, J = 11.2 Hz, 1H), 7.08−7.12 (m, 1H), 7.24−7.29 (m, 2H), 7.57 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 28.3, 28.9, 29.6, 31.7, 124.0, 126.7, 128.1, 128.3, 130.6, 132.5, 134.1, 137.7; IR (neat) 3065, 3014, 2955, 2925, 2854, 1467, 1432, 1026, 762 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{19}I$ [M^+] 314.0531, found 314.0533.

*1-[(Z)-Oct-1-enyl]-2-[2-(trimethylsilyl)ethynyl]benzene ((Z)-**1g**).* The Sonogashira coupling of **S14** (1.10 g, 3.50 mmol) with TMSA (0.59 mL, 4.20 mmol) by the method for the synthesis of (*E*)-**1a** gave (*Z*)-**1g** (912 mg, 3.21 mmol, 91%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.25 (s, 9H), 0.87 (t, J = 6.5 Hz, 3H), 1.20−1.34 (m, 6H), 1.44 (quint, J = 7.5 Hz, 2H), 2.25 (qd, J = 7.3, 1.5 Hz, 2H), 5.75 (td, J = 11.5, 7.0 Hz, 1H), 6.65 (d, J = 11.5 Hz, 1H), 7.16 (td, J = 7.5 Hz, 1H), 7.27 (td, J = 7.3, 1.0 Hz, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.47 (dd, J = 7.5, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.03, 14.1, 22.6, 28.7, 28.9, 29.8, 31.7, 98.7, 104.0, 122.5, 126.2, 127.2, 127.9, 128.6, 132.5, 134.0, 140.0; IR (neat) 3060, 3013, 2957, 2925, 2855, 2156, 1474, 1445, 1250, 868, 842, 759 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{28}Si$ [M^+] 284.1960, found 284.1968.

Synthesis of 1-Ethenyl-2-[2-(trimethylsilyl)ethynyl]benzene (1j). The Sonogashira coupling of 2-bromostyrene (1.84 g, 10.0 mmol)

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

with TMSA (2.8 mL, 20.0 mmol) by the method for the synthesis of (*E*)-**1a** gave **1j** (0.82 g, 4.09 mmol, 41%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 9H), 5.36 (dd, J = 11.1, 1.2 Hz, 1H), 5.83 (dd, J = 17.7, 1.2 Hz, 1H), 7.19 (td, J = 7.5, 1.5 Hz, 1H), 7.21 (dd, J = 17.7, 11.1 Hz, 1H), 7.29 (td, J = 7.8, 1.5 Hz, 1H), 7.46 (dd, J = 7.7, 1.5 Hz, 1H), 7.57 (dt, J = 7.8, 0.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.01, 99.1, 103.3, 115.5, 121.8, 124.5, 127.3, 128.6, 132.8, 134.8, 139.3; IR (neat) 3087, 3062, 3016, 2959, 2898, 2155, 1474, 1250, 868, 843 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{16}Si$ [M$^+$] 200.1021, found 200.1012.

Synthesis of 1-(2-Methylprop-1-enyl)-2-[2-(trimethylsilyl)-ethynyl]benzene (1k). *n*-BuLi (2.6 M in hexane, 1.73 mL, 4.5 mmol) was added to a solution of isopropyltriphenylphosphonium iodide (1.95 g, 4.50 mmol) in THF (10 mL) at 0 °C. After 30 min of stirring, a solution of 2-(trimethylsilylethynyl)benzaldehyde (0.91 g, 4.50 mmol) in THF (5 mL) was added to the mixture at 0 °C. The resultant mixture was stirred at room temperature overnight, quenched with water, and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 1-(2-methylprop-1-enyl)-2-[2-(trimethylsilyl)-ethynyl]benzene (**1k**; 776 mg, 3.40 mmol, 76%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.25 (s, 9H), 1.81 (d, J = 1.0 Hz, 3H), 1.93 (d, J = 1.0 Hz, 3H), 6.48 (t, J = 1.0 Hz, 1H), 7.10−7.14 (m, 1H), 7.21−7.30 (m, 2H), 7.45 (d, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.03, 19.6, 26.6, 98.3, 104.4, 122.4, 123.9, 125.7, 128.0, 128.9, 132.2, 136.5, 141.1; IR (neat) 3087, 3060, 3021, 2961, 2931, 2909, 2155, 1474, 1444, 1249, 874, 843, 758 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{20}Si$ [M$^+$] 228.1334, found 228.1328.

Synthesis of 1-(1-Methylethenyl)-2-[2-(trimethylsilyl)-ethynyl]benzene (1l). *1-Bromo-2-(1-methylethenyl)benzene (**S15**).* *n*-BuLi (2.6 M in hexane, 3.85 mL, 10 mmol) was added to a solution of methyltriphenylphosphonium bromide (3.58 g, 10.0 mmol) in Et_2O (50 mL) at 0 °C. After 1 h, 2-bromoacetophenone (1.99 g, 10.0 mmol) was added to the mixture at 0 °C. The resultant mixture was stirred at room temperature overnight, quenched with water, and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 1-bromo-2-(1-methylethenyl)benzene (**S15**; 0.84 g, 4.42 mmol, 44%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (dd, J = 1.5, 0.9 Hz, 3H), 4.93−4.95 (m, 1H), 5.21−5.24 (m, 1H), 7.11 (td, J = 7.5, 2.1 Hz, 1H), 7.19 (dd, J = 7.7, 2.1 Hz, 1H), 7.27 (td, J = 7.5, 1.2 Hz, 1H), 7.55 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 116.0, 121.5, 127.2, 128.3, 130.0, 132.7, 144.8, 145.8; IR (neat) 3082, 3053, 2971, 2914, 1641, 1469, 1433, 1025, 903, 759 cm^{-1}; HRMS (EI) calcd for C_9H_9Br [M$^+$] 195.9888, found 195.9884.

*1-Iodo-2-(1-methylethenyl)benzene (**S16**).* This compound was prepared from **S15** (665 mg, 3.37 mmol) by using the same method to synthesize **S4** from **S3**. 1-Iodo-2-(1-methylethenyl)benzene (**S16**; 693 mg, 2.84 mmol, 84%) was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 3H), 4.89 (d, J = 0.4 Hz, 1H), 5.22 (t, J = 1.6 Hz, 1H), 6.94 (td, J = 7.6, 1.6 Hz, 1H), 7.17 (dd, J = 7.6, 1.6 Hz, 1H), 7.30 (td, J = 7.4, 1.2 Hz, 1H), 7.83 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 96.9, 116.0, 128.0, 128.4, 128.5, 139.2, 148.4, 148.8; IR (neat) 3080, 3049, 2967, 2912, 2851, 1641, 1467, 1428, 1011, 903, 759 cm^{-1}; HRMS (EI) calcd for C_9H_9I [M$^+$] 243.9749, found 243.9745.

*1-(1-Methylethenyl)-2-[2-(trimethylsilyl)ethynyl]benzene (**1l**).* The Sonogashira coupling of **S16** (578 mg, 2.37 mmol) with TMSA (0.40 mL, 2.84 mmol) by the method for the synthesis of (*E*)-**1a** gave **1l** (419 mg, 1.95 mmol, 82%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.23 (s, 9H), 2.18 (dd, J = 1.5, 1.0 Hz, 3H), 5.13 (dd, J = 1.5, 1.0 Hz, 1H), 5.20−5.21 (m, 1H), 7.18 (td, J = 7.5, 1.5 Hz, 1H), 7.21 (dd, J = 7.0, 1.5 Hz, 1H), 7.26 (td, J = 7.5, 1.5 Hz, 1H), 7.47 (dt, J = 7.8, 0.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2, 23.1, 97.8, 104.7, 115.7, 120.6, 126.6, 127.8, 128.4, 133.1, 144.8, 146.5; IR (neat) 3084, 3060, 3022, 2960, 2917, 2899, 2157, 1636, 1479, 1438, 1250, 867, 843 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{18}Si$ [M$^+$] 214.1178, found 214.1177.

Synthesis of 1-Cyclohexenyl-2-[2-(trimethylsilyl)ethynyl]-benzene (1m). *1-(2-Bromophenyl)cyclohexanol (**S17**).* This compound was synthesized by the reported method.[17] *n*-BuLi (2.6 M in hexane, 7.2 mL, 19.0 mmol) was added to a solution of 1,2-dibromobenzene (2.37 mL, 20.0 mmol) in THF (60 mL)/Et_2O (60 mL) at −110 °C over 45 min. After 1 h of stirring at this temperature, cyclohexanone (2.0 mL, 19.0 mmol) was added to the mixture at −110 °C. The mixture was stirred at −110 °C for another 1 h and then at room temperature for 12 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane/AcOEt 5/1) gave 1-(2-bromophenyl)cyclohexanol (**S17**; 3.58 g, 14.0 mmol, 70%) as a white solid: mp 45.0−46.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26−1.34 (m, 1H), 1.64−1.88 (m, 5H), 1.97−2.02 (m, 2H), 2.14−2.22 (m, 2H), 2.66 (s, 1H), 7.06−7.11 (m, 1H), 7.27−7.32 (m, 1H), 7.58 (dd, J = 7.8, 1.6 Hz, 1H), 7.64 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 25.3, 35.7, 74.2, 120.8, 127.49, 127.52, 128.4, 135.3, 146.1; IR (neat) 3568, 3433, 3059, 2928, 1701, 1561, 1425, 969, 754 cm^{-1}; HRMS (EI$^+$) calcd for $C_{12}H_{15}BrO$ [M$^+$] 254.0306, found 254.0308.

*1-Bromo-2-(cyclohexenyl)benzene (**S18**).* This compound was synthesized by the reported method.[18] *p*-TsOH·H_2O (126 mg, 1.40 mmol, 10 mol %) was added to a solution of **S17** (3.58 g 14.0 mmol) in toluene under air. The mixture was heated under reflux for 1 h, cooled to room temperature, and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave 1-bromo-2-(cyclohexenyl)-benzene (**S18**; 2.95 g, 12.5 mmol, 89%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66−1.73 (m, 2H), 1.74−1.81 (m, 2H), 2.15−2.21 (m, 2H), 2.25−2.31 (m, 2H), 5.61−5.64 (m, 1H), 7.08 (td, J = 7.4, 2.0 Hz, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.24 (td, J = 7.6, 1.2 Hz, 1H), 7.53 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.8, 25.3, 29.3, 122.6, 127.0, 127.1, 127.9, 130.1, 132.6, 139.2, 145.5; IR (neat) 3050, 2929, 2856, 2834, 1587, 1559, 1466, 1433, 1022, 749 cm^{-1}; HRMS (EI$^+$) calcd for $C_{12}H_{13}Br$ [M$^+$] 236.0201, found 236.0198.

*1-Cyclohexenyl-2-iodobenzene (**S19**).* This compound was prepared from **S18** (2.95 g, 12.5 mmol) by using the same method to synthesize **S4** from **S3**. 1-Cyclohexenyl-2-iodobenzene (; 3.20 g, 11.3 mmol, 90%) was obtained as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66−1.72 (m, 2H), 1.76−1.81 (m, 2H), 2.15−2.25 (m, 4H), 5.55−5.58 (m, 1H), 6.91 (td, J = 7.8, 2.0 Hz, 1H), 7.13 (dd, J = 7.6, 1.6 Hz, 1H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.82 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.9, 25.2, 29.7, 98.7, 127.2, 127.9, 128.0, 128.8, 139.0, 142.0, 149.3; IR (neat) 3046, 2996, 2928, 2855, 2832, 1580, 1554, 1461, 1428, 1014, 751 cm^{-1}; HRMS (EI$^+$) calcd for $C_{12}H_{13}I$ [M$^+$] 284.0062, found 284.0050.

*1-Cyclohexenyl-2-[2-(trimethylsilyl)ethynyl]benzene (**1m**).* The Sonogashira coupling of **S19** (2.84 g, 10.0 mmol) with TMSA (1.70 mL, 12.0 mmol) by the method for the synthesis of (*E*)-**1a** gave **1m** (1.57 g, 6.17 mmol, 62%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 9H), 1.64−1.73 (m, 2H), 1.73−1.81 (m, 2H), 2.18−2.22 (m, 2H), 2.39−2.44 (m, 2H), 5.80−5.83 (m, 1H), 7.12−7.17 (m, 2H), 7.25 (td, J = 7.6, 1.2 Hz, 1H), 7.45 (dd, J = 8.0 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.02, 22.1, 23.1, 25.5, 28.9, 96.9, 104.9, 120.9, 126.1, 127.1, 127.9, 128.4, 132.9, 138.0, 147.6; IR (neat) 3059, 3022, 2930, 2857, 2834, 2156, 1474, 1439, 1249, 867, 843, 757 cm^{-1}; HRMS (EI$^+$) calcd for $C_{17}H_{22}Si$ [M$^+$] 254.1491, found 254.1501.

Synthesis of 1-[(*E*)-2-(Trimethylsilyl)ethenyl]-2-[3-(trimethylsilyl)prop-2-ynyl]benzene (1n). 1-Bromo-2-[(*E*)-(trimethylsilyl)ethenyl]benzene was prepared from 1-bromo-2-(trimethylsilylethynyl)benzene (7.48 g, 29.5 mmol) by the same method for the synthesis of **S2** from **S1**. The residue obtained after the reaction was checked with ^{1}H NMR. The formation of 1-bromo-2-[(*E*)-(trimethylsilyl)ethenyl]benzene was confirmed. Therefore, this compound was used in the next step without further purification. A solution of 1-bromo-2-[(*E*)-(trimethylsilyl)ethenyl]benzene in THF (30 mL) was added to Mg turnings (729 mg, 30.0 mmol) over 1 h. After 2 h of stirring, the reaction mixture was transferred into a solution of 3-bromo-1-(trimethylsilyl)prop-1-yne (4.28 g, 22.4 mmol) in THF (20 mL) via cannula. The mixture was heated under reflux for 12 h. The reaction mixture was cooled to room temperature, quenched with aqueous NH_4Cl, and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave **1n** (3.89 g, 13.6 mmol, 46%

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

yield over two steps) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 18H), 3.68 (s, 2H), 6.40 (d, J = 18.5 Hz, 1H), 7.17 (d, J = 18.5 Hz, 1H), 7.22−7.26 (m, 2H), 7.39−7.42 (m, 1H), 7.51−7.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.2, 0.1, 24.4, 87.1, 104.0, 125.7, 127.1, 128.0, 128.8, 132.5, 133.3, 137.4, 140.6; IR (neat) 3066, 3019, 2956, 2898, 2176, 1604, 1475, 1249, 1018, 986, 843 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{26}Si_2$ [M$^+$] 286.1573, found 286.1574.

Synthesis of (*E*)-1-Cinnamyl-2-[2-(trimethylsilyl)ethynyl]-benzene (1o). A solution of 1-bromo-2-(trimethylsilylethenyl)-benzene (2.04 g, 8.00 mmol) in THF (8 mL) was slowly added to Mg turnings (219 mg, 9.00 mmol) in THF (1 mL) at room temperature over 1 h. The resultant mixture was heated under reflux for 2 h and cooled to room temperature. The reaction mixture was transferred into a solution of (*E*)-(3-bromoprop-1-enyl)benzene (0.90 mL, 6.10 mmol) in THF (8 mL) via syringe. The mixture was heated under reflux for 12 h. The reaction mixture was cooled to room temperature, quenched with aqueous NH_4Cl, and extracted with hexane/AcOEt (30/1). The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane/AcOEt 30/1) gave (*E*)-1-cinnamyl-2-[2-(trimethylsilyl)ethynyl]benzene (**1o**; 719 mg, 2.48 mmol, 41%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (s, 9H), 3.72 (dd, J = 7.0, 1.0 Hz, 1H), 6.37 (dt, J = 15.5, 7.0 Hz, 1H), 6.49 (d, J = 15.5 Hz, 1H), 7.15−7.21 (m, 2H), 7.25−7.30 (m, 4H), 7.35−7.36 (m, 2H), 7.47 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.03, 37.9, 98.5, 103.8, 122.6, 126.0, 126.1, 127.0, 128.3, 128.4, 128.8, 131.2, 132.5, 137.5, 142.5; IR (neat) 3082, 3060, 3027, 2959, 2898, 2155, 1480, 1447, 1250, 844 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}Si$ [M$^+$] 290.1491, found 290.1505.

General Procedure for Indene Synthesis. DIBAL-H (1.0 M in hexane, 0.75 mL, 0.75 mmol) was added to **1** (0.50 mmol) in a 10 mL two-necked flask at room temperature. The mixture was stirred at 40 °C for 3 h and then cooled to room temperature. The reaction mixture was treated with 40% aqueous Rochelle salt (3 mL) for 30 min and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified with silica gel column chromatography (hexane).

*1-(Trimethylsilyl)methyl-2-trimethylsilyl-1H-indene (**2a**).* The reaction of **1a** (136 mg, 0.500 mmol) with DIBAL-H (1.0 M in hexane, 0.75 mL, 0.75 mmol) by the general procedure gave **2a** (133 mg, 0.485 mmol, 97%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.25 (s, 9H), 0.26 (s, 9H), 1.24 (dd, J = 15.0, 6.0 Hz, 1H), 1.47 (dd, J = 15.0, 5.7 Hz, 1H), 3.80 (td, J = 6.0, 1.8 Hz, 1H), 7.03 (d, J = 1.8 Hz, 1H), 7.16 (td, J = 7.5, 1.2 Hz, 1H), 7.24 (td, J = 7.2, 0.6 Hz, 1H), 7.35 (dd, J = 7.2, 1.2 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.24, 0.3, 17.7, 50.8, 120.7, 123.6, 124.5, 126.3, 140.1, 144.6, 151.8, 155.4; IR (neat) 3065, 2953, 2898, 1531, 1459, 1410, 1248, 836 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{26}Si_2$ [M$^+$] 274.1573, found 274.1576.

*5-Fluoro-1-(trimethylsilyl)methyl-2-trimethylsilyl-1H-indene (**2b**).* Yellow oil (138 mg, 0.472 mmol, 94%): ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.26 (s, 9H), 0.25 (s, 9H), 1.23 (dd, J = 15.0, 6.0 Hz, 1H), 1.43 (dd, J = 15.0, 6.0 Hz, 1H), 3.76 (tt, J = 6.0, 1.0 Hz, 1H), 6.85 (ddd, J = 9.0, 8.3, 2.5 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 7.00 (dd, J = 9.0, 2.5 Hz, 1H), 7.30 (dd, J = 8.5, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.3, 0.3, 17.8, 50.3, 107.5 (d, $^2J_{C-F}$ = 22.0 Hz), 111.1 (d, $^2J_{C-F}$ = 23.8 Hz), 124.1 (d, $^3J_{C-F}$ = 8.8 Hz), 139.3 (d, $^4J_{C-F}$ = 3.8 Hz), 146.3 (d, $^3J_{C-F}$ = 7.5 Hz), 147.2 (d, $^4J_{C-F}$ = 1.3 Hz), 158.3, 162.3 (d, $^1J_{C-F}$ = 240.0 Hz); IR (neat) 3069, 3033, 2953, 2898, 1610, 1599, 1535, 1465, 1248, 838 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{25}FSi_2$ [M$^+$] 292.1479, found 292.1479.

*1-Benzyl-2-trimethylsilyl-1H-indene (**2c**).* Colorless oil (128 mg, 0.460 mmol, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.30 (s, 9H), 2.29 (dd, J = 13.8, 11.2 Hz, 1H), 3.59 (dd, J = 13.8, 4.0 Hz, 1H), 3.89 (ddd, J = 10.8, 4.0, 1.6 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 6.94 (td, J = 7.6, 1.2 Hz, 1H), 7.08 (dd, J = 1.6, 0.4 Hz, 1H), 7.17−7.33 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.4, 37.8, 55.3, 120.8, 124.0, 124.5, 126.3, 126.5, 128.2, 129.3, 140.6, 140.7, 144.7, 149.9, 153.4; IR (neat) 3061, 3026, 2953, 2917, 2852, 1603, 1537, 1496, 1454, 1247, 1057, 1052, 1019, 889, 857, 835, 754, 732, 697 cm^{-1}; HRMS (EI$^+$) calcd for $C_{19}H_{22}Si$ [M$^+$] 278.1491, found 278.1494.

*1-(4-Fluorobenzyl)-2-trimethylsilyl-1H-indene (**2d**).* Yellow oil (141 mg, 0.476 mmol, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.29 (s, 9H), 2.32 (dd, J = 14.0, 10.5 Hz, 1H), 3.54 (dd, J = 14.0, 4.5 Hz, 1H), 3.83 (ddd, J = 10.8, 4.5, 1.8 Hz, 1H), 6.59 (d, J = 7.5 Hz, 1H), 6.94−7.02 (m, 3H), 7.07 (dd, J = 1.8, 0.6 Hz, 1H), 7.10−7.14 (m, 2H), 7.20 (td, J = 7.5, 0.6 Hz, 1H), 7.32 (dt, J = 7.5, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.4, 36.9, 55.2, 114.0 (d, $^2J_{C-F}$ = 21.1 Hz), 120.9, 123.9, 124.5, 126.6, 130.6 (d, $^3J_{C-F}$ = 7.5 Hz), 136.0 (d, $^4J_{C-F}$ = 3.0 Hz), 140.9, 144.7, 149.6, 153.0, 161.5 (d, $^1J_{C-F}$ = 243.8 Hz); IR (neat) 3065, 3038, 2929, 2853, 1601, 1510, 1456, 1249, 1225, 1052, 838 cm^{-1}; HRMS (EI$^+$) calcd for $C_{19}H_{21}FSi$ [M$^+$] 296.1397, found 296.1411.

*1-(4-Methylbenzyl)-2-trimethylsilyl-1H-indene (**2e**).* White solid (136 mg, 0.466 mmol, 93%): mp 40.0−43.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.29 (s, 9H), 2.24 (dd, J = 13.5, 11.0 Hz, 1H), 2.36 (s, 3H), 3.54 (dd, J = 13.8, 4.5 Hz, 1H), 3.86 (ddd, J = 11.3, 4.5, 1.5 Hz, 1H), 6.60 (d, J = 7.5 Hz, 1H), 6.94 (td, J = 7.5, 1.5 Hz, 1H), 7.07 (d, J = 1.5 Hz, 1H), 7.08−7.13 (m, 4H), 7.18 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.6, 21.1, 37.3, 55.4, 120.7, 124.1, 124.4, 126.5, 128.9, 129.1, 135.6, 137.4, 140.6, 144.7, 150.0, 153.4; IR (Nujol) 3021, 1249, 1053, 837 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{24}Si$ [M$^+$] 292.1647, found 292.1654.

*1-(4-Methoxybenzyl)-2-trimethylsilyl-1H-indene (**2f**).* White solid (120 mg, 0.389 mmol, 78%): mp 59.5−61.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.29 (s, 9H), 2.24 (dd, J = 14.0, 11.0 Hz, 1H), 3.52 (dd, J = 14.0, 4.5 Hz, 1H), 3.83 (s, 3H), 3.81−3.87 (m, 1H), 6.60 (d, J = 7.5 Hz, 1H) 6.85 (d, J = 8.5 Hz, 2H), 6.95 (td, J = 7.5, 1.0 Hz, 1H), 7.06 (d, J = 1.0 Hz, 1H), 7.11 (d, J = 8.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.4, 36.9, 55.2, 55.6, 113.6, 120.8, 124.1, 124.4, 126.5, 130.2, 132.6, 140.6, 144.7, 150.0, 153.4, 158.1; IR (Nujol) 3056, 3033, 1512, 1248, 834 cm^{-1}; HRMS (EI$^+$) calcd for $C_{20}H_{24}OSi$ [M$^+$] 308.1596, found 308.1588.

*1-Heptyl-2-trimethylsilyl-1H-indene (**2g**).* Colorless oil (116 mg, 0.405 mmol, 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.84 (t, J = 6.8 Hz, 3H), 0.86−0.91 (m, 1H), 0.98−1.09 (m, 1H), 1.17−1.27 (m, 8H), 1.75−1.84 (m, 1H), 2.04−2.14 (m, 1H), 3.65 (t, J = 4.4 Hz, 1H), 7.04 (d, J = 1.6 Hz, 1H), 7.17 (td, J = 7.2, 1.2 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.6, 14.0, 22.6, 24.4, 29.1, 30.0, 30.9, 31.8, 54.1, 120.7, 122.7, 124.7, 126.3, 140.6, 145.1, 150.6, 153.4; IR (neat) 3064, 3020, 2955, 2927, 2855, 1534, 1459, 1248, 1034, 836 cm^{-1}; HRMS (EI$^+$) calcd for $C_{19}H_{30}Si$ [M$^+$] 286.2117, found 286.2118.

*1-Octyl-2-[(E)-2-(trimethylsilyl)ethenyl]benzene (**3**).* Colorless oil (17 mg, 0.058 mmol, 12%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9H), 0.87 (t, J = 10.8 Hz, 3H), 1.23−1.40 (m, 10H), 1.53−1.60 (m, 2H), 2.69 (t, J = 8.0 Hz, 1H), 6.37 (d, J = 19.2 Hz, 1H), 7.10−7.20 (m, 4H), 7.50−7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.2, 14.1, 22.7, 29.3, 29.5, 29.6, 31.3, 31.9, 33.4, 125.5, 126.1, 127.7, 129.6, 131.1, 137.2, 140.2, 141.3; IR (neat) 3064, 3014, 2955, 2926, 2854, 1477, 1467, 1247, 987, 865, 839 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{32}Si$ [M$^+$] 288.2273, found 288.2274.

*1-(2,2-Dimethylpropyl)-2-trimethylsilyl-1H-indene (**2h**).* Colorless oil (14 mg, 0.054 mmol, 11%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9H), 1.05 (s, 9H), 1.55 (dd, J = 14.5, 6.0 Hz, 1H), 2.06 (dd, J = 14.8, 2.5 Hz, 1H), 3.60−3.63 (m, 1H), 7.01 (d, J = 2.0 Hz, 1H), 7.15 (td, J = 7.5, 1.5 Hz, 1H), 7.22 (t, J = 7.0 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1, 30.8, 31.6, 42.8, 51.6, 120.7, 123.8, 124.8, 126.1, 140.4, 144.4, 152.9, 155.2; IR (neat) 3063, 3023, 2952, 2904, 2867, 1535, 1476, 1463, 1364, 1248, 1029, 835 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{26}Si$ [M$^+$] 258.1804, found 258.1809.

*1-(2-Bromobenzyl)-2-trimethylsilyl-1H-indene (**2i**).* Colorless oil (161 mg, 0.451 mmol, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.32 (s, 9H), 2.25 (dd, J = 13.5, 12.0 Hz, 1H), 3.71 (dd, J = 14.0, 5.0 Hz, 1H), 4.13 (dd, J = 11.5, 4.5 Hz, 1H), 6.33 (d, J = 7.5 Hz, 1H), 6.91 (td, J = 7.5, 1.0 Hz, 1H), 6.97 (dd, J = 8.0, 2.0 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 7.14−7.23 (m, 3H), 7.35 (d, J = 7.5 Hz, 1H), 7.63 (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.4, 38.8, 52.8, 120.9, 124.2, 124.5, 124.8, 126.5, 127.0, 128.2, 132.6, 132.9, 139.7, 140.8, 144.7, 149.1, 153.6; IR (neat) 3062, 3021, 2954, 2895, 1567, 1537, 1468, 1442, 1248, 1047, 1025, 855 cm^{-1}; HRMS (EI$^+$) calcd for $C_{19}H_{21}BrSi$ [M$^+$] 356.0596, found 356.0599.

*1-Methyl-2-trimethylsilyl-1H-indene (**2j**).* Colorless oil (86 mg, 0.425 mmol, 85%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 1.36

dx.doi.org/10.1021/jo501383v | J. Org. Chem. 2014, 79, 8171−8181

(d, J = 7.5 Hz, 3H), 3.56 (qd, J = 7.5, 1.5 Hz, 1H), 7.03 (d, J = 1.5 Hz, 1H), 7.16−7.27 (m, 2H), 7.33−7.36 (m, 1H), 7.41 (d, J = 6.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.7, 16.9, 49.1, 120.7, 122.5, 124.9, 126.4, 139.6, 144.2, 152.3, 155.2; IR (neat) 3065, 3018, 2957, 2928, 2896, 2871, 1534, 1459, 1247, 836 cm^{-1}; HRMS (EI$^+$) calcd for $C_{13}H_{18}Si$ [M$^+$] 202.1178, found 202.1189.

*1,1-Dimethyl-2-trimethylsilyl-1H-indene (**2l**).* Colorless oil (103 mg, 0.476 mmol, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 9H), 1.35 (s, 6H), 6.93 (s, 1H), 7.16−7.27 (m, 2H), 7.28−7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.02, 25.5, 54.6, 120.9, 125.3, 126.3, 138.6, 142.5, 157.1, 159.9; IR (neat) 3063, 3018, 2956, 2924, 2898, 2864, 1530, 1467, 1449, 1248, 1000, 837 cm^{-1}; HRMS (EI$^+$) calcd for $C_{14}H_{20}Si$ [M$^+$] 216.1334, found 216.1342.

*2′-Trimethylsilylspiro[cyclohexane-1,1′-indene] (**2m**).* White solid (77 mg, 0.300 mmol, 60%): mp 61.0−62.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 1.24−1.30 (m, 2H), 1.35−1.48 (m, 1H), 1.72−1.79 (m, 2H), 1.91−2.08 (m, 5H), 6.94 (s, 1H), 7.14 (td, J = 7.4, 1.6 Hz, 1H), 7.25 (td, J = 7.4, 0.8 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 22.7, 25.6, 32.8, 58.8, 121.1, 124.3, 124.8, 126.4, 139.1, 143.9, 155.3, 160.8; IR (Nujol) 3086, 3059, 3034, 1938, 1540, 1448, 1247, 838 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{24}Si$ [M$^+$] 256.1647, found 256.1645.

*(1RS,1′SR)-1-[1-Deuterio(trimethylsilyl)methyl]-2-trimethylsilyl-1H-indene (**2a**-d; u-**2a**-d).* The reaction of **1a** (136 mg, 0.500 mmol) with DIBAL-H (1.0 M in hexane, 0.75 mL) was performed at 40 °C for 3 h. The reaction mixture was cooled to room temperature and then treated with MeOD (1 mL) for 3 h. The reaction mixture was quenched with 40% aqueous Rochelle salt (3 mL), stirred for 30 min, and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave **2a**-*d* (123 mg, 0.445 mmol, 89%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.26 (s, 9H), 0.25 (s, 9H), 1.18−1.22 (m, 1H), 3.78 (d, J = 4.5 Hz, 1H), 7.02 (dd, J = 2.0, 0.5 Hz, 1H), 7.15 (td, J = 7.5, 1.0 Hz, 1H), 7.23 (t, J = 7.0 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.5, −0.3, 17.3 (t, J = 17.5 Hz), 50.7, 120.7, 123.5, 124.5, 126.3, 140.1, 144.6, 151.8, 155.4; IR (neat) 3065, 3022, 2953, 2895, 2136, 1937, 1532, 1459, 1407, 1249, 1051, 838 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{25}DSi$ [M$^+$] 275.1636, found 275.1621.

*(1RS,1′RS)-1-[1-Deuterio(trimethylsilyl)methyl]-2-trimethylsilyl-1H-indene (**2a**′-d; l-**2a**-d).* Colorless oil (107 mg, 0.388 mmol, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.24 (s, 9H), 0.27 (s, 9H), 1.46 (d, J = 5.6 Hz, 1H), 3.81 (d, J = 5.6 Hz, 1H), 7.04 (d, J = 1.6 Hz, 1H), 7.17 (td, J = 7.6, 1.2 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.3, 0.3, 17.3 (t, J = 18.0 Hz), 50.7, 120.7, 123.5, 124.5, 126.3, 140.1, 144.6, 151.8, 155.4; IR (neat) 3065, 3021, 2953, 2897, 2868, 2147, 1937, 1531, 1459, 1406, 1248, 1020, 1011, 837 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{25}DSi$ [M$^+$] 275.1636, found 275.1639.

*1-(1-Deuterioheptyl)-2-trimethylsilyl-1H-indene (**2g**-d).* Colorless oil (113 mg, 0.393 mmol, 79%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 9H), 0.84 (t, J = 7.2 Hz, 3H), 0.85−0.91 (m, 1H), 0.99−1.07 (m, 1H), 1.15−1.28 (m, 8H), 1.74−1.81 (m, 1H), 3.65 (dd, J = 5.8, 1.2 Hz, 1H), 7.05 (dd, J = 1.8, 0.8 Hz, 1H), 7.17 (td, J = 7.2, 1.2 Hz, 1H), 7.24 (td, J = 7.4, 0.8 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.64, 14.0, 22.6, 24.3, 29.1, 30.0, 30.5 (d, J = 19.0 Hz), 31.8, 54.0, 120.7, 122.8, 124.7, 126.2, 140.6, 145.1, 150.7, 153.4; IR (neat) 3064, 3023, 2955, 2925, 2853, 2150, 1534, 1460, 1247, 1055, 836 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{29}DSi$ [M$^+$] 287.2180, found 287.2183.

*1-(1-Deuteriooctyl)-2-[(E)-2-deuterio-2-(trimethylsilyl)ethenyl]-benzene (**3g**-d).* Colorless oil (21 mg, 0.0723 mmol, 14%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H), 1.23−1.40 (m, 10H), 1.53−1.59 (m, 2H), 2.67 (t, J = 8.0 Hz, 1H), 7.10−7.14 (m, 1H), 7.15−7.20 (m, 3H), 7.50−7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.2, 14.1, 22.7, 29.3, 29.5, 29.6, 31.2, 31.9, 33.0 (t, J = 19.0 Hz), 125.5, 126.1, 127.7, 129.6, 130.7 (t, J = 20.0 Hz), 137.2, 140.2, 141.3; IR (neat) 3062, 3014, 2955, 2925, 2854, 1475, 1467, 1247, 992, 839 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{30}D_2Si$ [M$^+$] 290.2399, found 290.2396.

General Procedure for Benzofulvene Synthesis. DIBAL-H (1.0 M in hexane, 0.75 mL, 0.75 mmol) was added to **1** (0.50 mmol) in a 10 mL two-necked flask at room temperature. The mixture was heated at 40 °C for 3 h and then cooled to room temperature. Benzaldehyde (0.51 mL, 5 mmol) was added to the resultant mixture. After 16 h of stirring at room temperature, the reaction mixture was treated with 40% aqueous Rochelle salt (3 mL) for 30 min and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified with silica gel column chromatography (hexane).

*(E)-1-(Trimethylsilylmethylene)-2-trimethylsilyl-1H-indene ((E)-**7a**).* The reaction of **1a** (136 mg, 0.500 mmol) with DIBAL-H (1.0 M in hexane, 0.75 mL, 0.75 mmol) and benzaldehyde (0.51 mL, 5.0 mmol) by the general procedure gave (*E*)-**7a** (121 mg, 0.445 mmol, 89% yield) as a yellow crystal: mp 39.5−40.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 9H), 0.36 (s, 9H), 6.51 (d, J = 0.6 Hz, 1H), 7.08 (s, 1H), 7.13−7.24 (m, 3H), 7.66 (dd, J = 7.5, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.1, 0.0, 120.6, 123.1, 125.1, 127.9, 137.0, 138.4, 142.4, 145.0, 145.1, 158.7; IR (Nujol) 3063, 3020, 2954, 2898, 1581, 1518, 1453, 1250, 1091, 857 cm^{-1}; HRMS (EI$^+$) calcd for $C_{16}H_{24}Si_2$ [M$^+$] 272.1417, found 272.1428.

*(E)-5-Fluoro-1-(trimethylsilylmethylene)-2-trimethylsilyl-1H-indene ((E)-**7f**).* Yellow oil (112 mg, 0.386 mmol, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 0.35 (s, 9H), 6.49 (s, 1H), 6.84 (td, J = 8.8, 2.4 Hz, 1H), 6.90 (dd, J = 8.8, 2.4 Hz, 1H), 7.01 (s, 1H), 7.57 (dd, J = 8.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.14, −0.06, 107.7 (d, $^2J_{C-F}$ = 22.0 Hz), 111.4 (d, $^2J_{C-F}$ = 23.0 Hz), 123.9 (d, $^3J_{C-F}$ = 10.0 Hz), 134.2 (d, $^4J_{C-F}$ = 1.0 Hz), 137.1, 141.1 (d, $^4J_{C-F}$ = 2.0 Hz), 147.2 (d, $^3J_{C-F}$ = 8.0 Hz), 147.5, 157.5, 163.1 (d, $^1J_{C-F}$ = 244.0 Hz); IR (neat) 3069, 2955, 2898, 1598, 1520, 1459, 1251, 1133, 1092, 848 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{23}FSi_2$ [M$^+$] 290.1322, found 290.1311.

*(E)-1-Heptylidene-2-trimethylsilyl-1H-indene ((E)-**7g**).* Pale yellow solid (33.0 mg, 0.116 mmol, 23%): mp 42.0−47.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H), 1.31−1.39 (m, 4H), 1.42−1.50 (m, 2H), 1.65 (quint, J = 7.6 Hz, 2H), 2.81 (q, J = 7.6 Hz, 2H), 6.43 (t, J = 7.6 Hz, 1H), 6.99 (s, 1H), 7.18 (td, J = 7.2, 1.6 Hz, 1H), 7.23 (td, J = 7.2, 1.2 Hz, 1H), 7.26−7.31 (m, 1H), 7.73 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.02, 14.0, 22.6, 29.2, 29.6, 30.0, 31.7, 120.7, 124.0, 125.2, 127.2, 137.9, 139.2, 139.6, 143.7, 144.1, 144.7; IR (Nujol) 3065, 1627, 1510, 1247, 839 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{28}Si$ [M$^+$] 284.1960, found 284.1955.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and a CIF file giving NMR spectral data for all new substrates and isolated products and crystallographic data for (*E*)-**7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for K.M.: kmiura@apc.saitama-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) (a) Majetich, G.; Shimkus, J. M. *J. Nat. Prod.* **2010**, *73*, 284. (b) Solomak, T.; Stacko, P.; Veetil, A. T.; Pospisil, T.; Klan, P. *J. Org. Chem.* **2010**, *75*, 7300. (c) Lee, B. H.; Choi, Y. L.; Shin, S.; Heo, J.-N. *J. Org. Chem.* **2011**, *76*, 6611.

(2) Yang, J.; Lakshmikantham, M. V.; Cava, M. P.; Lorcy, D.; Bethelot, J. R. *J. Org. Chem.* **2000**, *65*, 6739.

(3) (a) Möller, A. C.; Heyn, R. H.; Blom, R.; Swang, O.; Görbitz, C. H.; Kopf, J. *Dalton Trans.* **2004**, 1578. (b) Chirik, P. J. *Organometallics* **2010**, *29*, 1500. (c) Gloeckner, A.; Bauer, H.; Maekawa, M.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Sun, Y.; Sitzmann, H.; Tamm, M.; Walter, M. D. *Dalton Trans.* **2012**, *41*, 6614.

(4) For recent examples of indene syntheses, see: (a) Wang, S.; Zhu, Y.; Wang, Y.; Lu, P. *Org. Lett.* **2009**, *11*, 2615. (b) Tobisu, M.; Nakai, H.; Chatani, N. *J. Org. Chem.* **2009**, *74*, 5471. (c) Reddy, B. V. S.; Reddy, B. B.; Rao, K. V. R.; Yadav, J. S. *Tetrahedron Lett.* **2010**, *51*, 5697. (d) Xu, T.; Yang, Q.; Li, D.; Dong, J.; Yu, Z.; Li, Y. *Chem. Eur. J.* **2010**, *16*, 9264. (e) Tran, D. N.; Cramer, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 8181. (f) Tran, D. N.; Cramer, N. *Angew. Chem., Int. Ed.* **2011**, *50*, 11098. (g) Zhou, F.; Han, X.; Lu, X. *J. Org. Chem.* **2011**, *76*, 1491. (h) Sato, T.; Onuma, T.; Nakamura, I.; Terada, M. *Org. Lett.* **2011**, *13*, 4992. (i) Nun, P.; Gaillard, S.; Poater, A.; Cavallo, L.; Nolan, S. P. *Org. Biomol. Chem.* **2011**, *9*, 101. (j) Usanov, D. L.; Yamamoto, H. *Org. Lett.* **2012**, *14*, 414. (k) McGonigal, P. R.; de León, C.; Wang, Y.; Homs, A.; Solorio-Alvarado, C. R.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 13093. (l) Zhao, J.; Clark, D. A. *Org. Lett.* **2012**, *14*, 1668. (m) Eom, D.; Park, S.; Park, Y.; Ryu, T.; Lee, P. H. *Org. Lett.* **2012**, *14*, 5392. (n) Dethe, D. H.; Murhade, G. *Org. Lett.* **2013**, *15*, 429. (o) Mondal, S.; Mohamed, R. K.; Manoharan, M.; Phan, H.; Alabugin, I. V. *Org. Lett.* **2013**, *15*, 5650. (p) Becker, P.; Priebbenow, D. L.; Pirwerdjan, R.; Bolm, C. *Angew. Chem., Int. Ed.* **2014**, *53*, 269.

(5) For recent examples of benzofulvene syntheses, see: (a) Ye, S.; Gao, K.; Zhao, H.; Wang, X.; Wu, J. *Chem. Commun.* **2009**, 5406. (b) Bryan, C. S.; Lautens, M. *Org. Lett.* **2010**, *12*, 2754. (c) Tsuchikama, K.; Kasagawa, M.; Endo, K.; Shibata, T. *Synlett* **2010**, 97. (d) Ye, S.; Yang, X.; Wu, J. *Chem. Commun.* **2010**, *46*, 2950. (e) Kim, K. H.; Kim, S. H.; Park, B. R.; Kim, J. N. *Tetrahedron Lett.* **2010**, *51*, 3368.

(6) (a) Akiyama, K.; Gao, F.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 419. (b) Gao, F.; McGrath, K. P.; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 14315. (c) May, T. J.; Dabrowski, J. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 736. (d) Cottet, P.; Müller, D.; Alexakis, A. *Org. Lett.* **2013**, *15*, 828. (e) Takimoto, M.; Hou, Z. *Chem. Eur. J.* **2013**, *19*, 11439. (f) McGrath, K. P.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 1910.

(7) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2213.

(8) Kinoshita, H.; Ishikawa, T.; Miura, K. *Org. Lett.* **2011**, *13*, 6192.

(9) (a) Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520. (b) Eisch, J. J.; Rhee, S.-G. *J. Am. Chem. Soc.* **1975**, *97*, 4673 and reference 6a..

(10) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Housecroft, C. E., Ed.; Pergamon: Oxford, U.K., 1995; Vol. *1*, p 464.

(11) The relative configurations of **2a**-*d* and **2a**′-*d* could not be determined on the basis of the coupling constants between vicinal protons on the stereogenic centers because the *J* values are so close. However, the formation of benzofulvene (*E*)-**7a** from (*E*)-**1a** suggests the presence of *u*-**5a** as an intermediate (Scheme 8), which provides a good reason for our assignment.

(12) See the Supporting Information for details.

(13) Ashby, E.; Yu, S. H. *J. Org. Chem.* **1970**, *35*, 1034.

(14) Karpov, G. V.; Popik, V. V. *J. Am. Chem. Soc.* **2007**, *129*, 3792.

(15) Roman, D. S.; Takahashi, Y.; Charette, A. B. *Org. Lett.* **2011**, *13*, 3242.

(16) Kashiki, T.; Shinamura, S.; Kohara, M.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwahara, H. *Org. Lett.* **2009**, *11*, 2473.

(17) Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481.

(18) Shinozuka, T.; Shimada, K.; Matsui, S.; Yamane, T.; Ama, M.; Fukuda, T.; Taki, M.; Takeda, Y.; Otsuka, E.; Yamato, M.; Mochizuki, S.; Ohhota, K.; Naito, S. *Bioorg. Med. Chem.* **2006**, *14*, 6789.