# A Facile Preparation of 2-(2-Hydroxyethyl)homoallenylsilanes Using *In Situ* Generated Homoallenylindium Reagent

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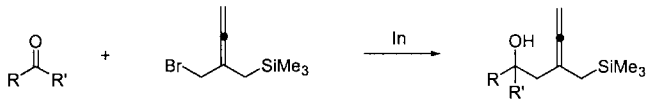
*In situ* generated homoallenylindium reagents derived from the reaction of indium with 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene reacted with a variety of aldehydes in DMF to produce 2-(2-hydroxyethyl)homoallenylsilanes at room temperature in good to excellent yields. 2- or 3-Hydroxybenzaldehyde that contains labile hydrogen was reacted with homoallenylindium reagent to provide the homoallenylsilanes. In the case of 4-formylbenzoic acid, the desired compound was produced in 88% yield. 4-Bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene was prepared from monoacetylation and mesylation of 2-butyn-1,4-diol, addition of trimethylsilylmethyl anion, saponification and mesylation followed by Finkelstein reaction.

**Keywords :** 4-Bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene, Indium, Homoallenylation, 2-(2-Hydroxyethyl)homoallenylsilane.

## Introduction

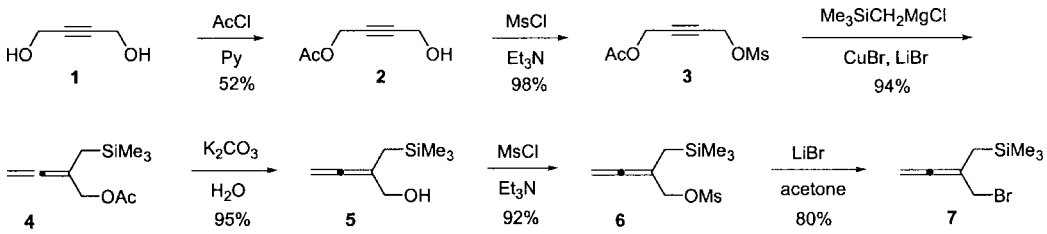
Carbon-carbon bond formation using allyl metal is one of the fundamental processes in organic synthesis.[1] Although allyl metal-mediated allylation of a variety of aldehydes and ketones received much attention, less attention has been paid to homoallenylation of the carbonyl compounds. As part of our continuing effort to synthesize 2-methyl-3-trimethylsilylmethyl dihydrofuran derivatives from homoallenyl alcohols, we needed a versatile method to prepare 2-(2-hydroxyethyl)-homoallenylsilanes. Generally, 2-(2-hydroxyethyl)allylsilanes can be prepared by lithiation followed by silylation of 3-methylhomoallylic alcohols,[2] by ring opening reactions of epoxides with organometallic reagents derived from 2-haloallylsilanes[3] and by indium-mediated allylsilylation of carbonyl compounds.[4] To the best of our knowledge, none of these methods has been applied to the synthesis of 2-(2-hydroxyethyl)homoallenylsilanes. The addition of organometallic reagents derived from the halomethylhomoallenylsilanes on aldehydes or ketones would be used to produce 2-(2-hydroxyethyl)homoallenylsilane. However, we could not effectively prepare the corresponding Grignard reagents from the halomethylhomoallenylsilianes. In addition Grignard reagents must be employed in excess in reactions with electrophiles having any labile hydrogens to obtain the products in good yields. Therefore, we turned our attention to other organometallic reagents to synthesize 2-(2-hydroxyethyl)-homoallenylsilanes. Recently, indium has been employed in numerous organic transformations because they have some prominent advantages with regards to easy handling, high reactivity and selectivity, and low toxicity.[5] Indeed, it has been shown to be effective in allylation of carbonyl compounds[6] and aldimines,[7] in ring expansion reaction,[8] in Prins type cyclization,[9] and in intramolecular carbocyclizations.[10] Our interest in applying indium metal to modern organic synthesis has us to investigate the participation of indium-mediated homoallenylation.[11] In this letter, we report of our results on the indium-mediated homoallenylation of aldehydes and ketones (Scheme 1).[12]




**Scheme 1**

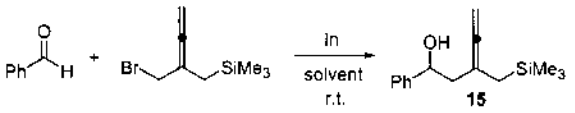
## Results and Discussion

The necessary building block, 4-bromo-3-[(trimethylsilyl)-methyl]-1,2-butadiene (**7**), was prepared from 2-butyn-1,4-diol as follows (Scheme 2). 2-Butyn-1,4-diol reacted with acetyl chloride in the presence pyridine to give monoacetyl compound **2** in 52% yield. Treatment of **2** with methanesulfonyl chloride and triethylamine produced the desired




**Scheme 2**

**Table 1**. Examination of optimum condition of In-mediated homoallenylation of benzaldehyde




| Entry | Solvent | Time (h) | Isolated yield (%) |
|---|---|---|---|
| 1 | $CH_2Cl_2$ | 12 | 0 |
| 2 | THF | 12 | 11 |
| 3 | $H_2O$ | 4 | 88 |
| 4 | DMF | 1 | 92 |

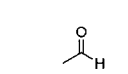
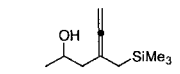
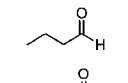
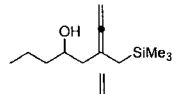
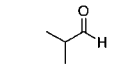
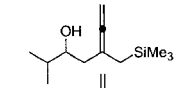
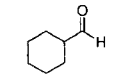
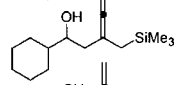
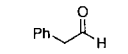
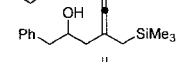
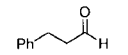
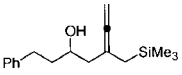
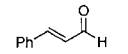
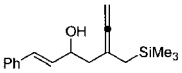
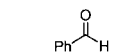
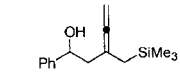
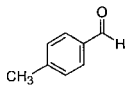
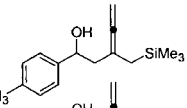
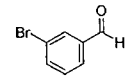
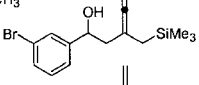
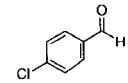
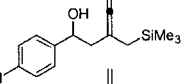
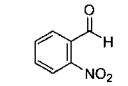
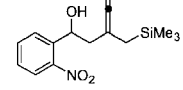
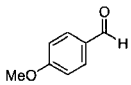
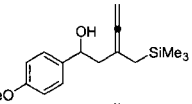
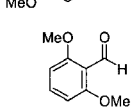
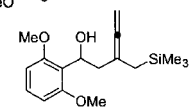
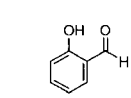
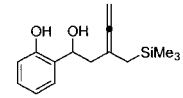
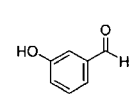
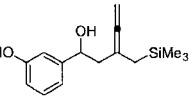
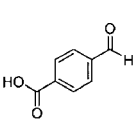
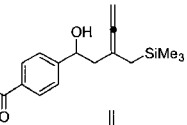
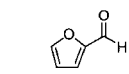
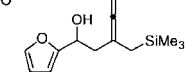
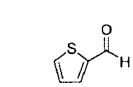
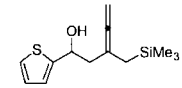
compound **3**. **3** reacted with (trimethylsilyl)methylmagnesium chloride in the presence of copper bromide and lithium bromide to give homoallenylsilane **4**. Saponification of **4** and mesylation followed by Finkelstein reaction with lithium bromide afforded 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene (**7**) in good yield.

To find optimum conditions for indium-mediated homoallenylation, initially benzaldehyde reacted with **7** in the presence of indium in various solvents. The results are summarized in Table 1. Of the solvents tested $H_2O$, THF, $CH_2Cl_2$ and DMF, the best results were obtained in DMF. The indium-mediated reaction of benzaldehyde with homoallenyl bromide **7** in DMF afforded the homoallenylated product **15** in 92% yield (entry 4). The same reaction in other solvents, however, gave lower yields as well as longer reaction time.

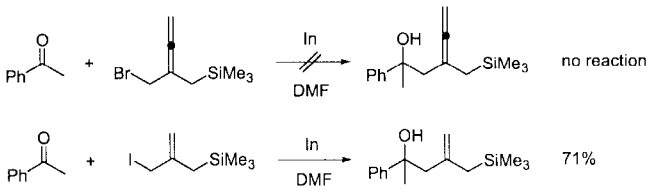
Table 2 summarizes the experimental results and illustrates the efficiency and scope of the present method. As can be seen in Table 2, various aliphatic aldehydes (entries 1-7) gave the desired compounds in good yields. Cinnamaldehyde was treated with homoallenyl bromide to produce the desired compound in 47% yield. For the aromatic aldehydes, the presence of various substituents, such as methyl (entry 9), bromo (entry 10), chloro (entry 11), nitro (entry 12), monomethoxy (entry 13), or dimethoxy (entry 14) on the aromatic ring showed little effects on either the reaction rate or yields. It should be mentioned that 2- or 3-hydroxybenzaldehyde (entries 15 and 16) that contains an acidic hydrogen reacted with homoallenylindium reagent to provide the desired compounds **22** and **23** in 89% and 86% yields, respectively. Even if, 4-formylbenzoic acid reacted with **7** to give the desired compound in 88% yield (entry 17). In the case of 2-furaldehyde and 2-thiophenecarboxaldehyde, the corresponding homoallenylsilanes were obtained in good yields (entry 18 and 19). The present method reached a limit with ketones. Acetophenone did not reacted with 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene under the identical conditions. However, indium reagent derived from 3-iodo-2-(trimethylsilylmethyl)propene reacted with acetophenone to give 1-methyl-3-[(trimethylsilyl)methyl]-1-phenyl-4-buten-1-ol in 71% yield (Scheme 3).[4]

In summary, *in situ* generated homoallenylindium reagents derived from the reaction of indium with 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene reacted with a variety of aldehydes in DMF to produce 2-(2-hydroxyethyl)homo-

**Table 2**. Indium-mediated homoallenylation of aldehydes

| Entry | Starting materials | Products | | Isolated yield (%)[a] |
|---|---|---|---|---|
| 1 |  |  | **8** | 88 |
| 2 |  |  | **9** | 89 |
| 3 |  |  | **10** | 87 |
| 4 |  |  | **11** | 54 |
| 5 |  |  | **12** | 67 |
| 6 |  |  | **13** | 61 |
| 7 |  |  | **14** | 47 |
| 8 |  |  | **15** | 92 |
| 9 |  |  | **16** | 73 |
| 10 |  |  | **17** | 89 |
| 11 |  |  | **18** | 93 |
| 12 |  |  | **19** | 90 |
| 13 |  |  | **20** | 80 |
| 14 |  |  | **21** | 83 |
| 15 |  |  | **22** | 89 |
| 16 |  |  | **23** | 86 |
| 17 |  |  | **24** | 88 |
| 18 |  |  | **25** | 83 |
| 19 |  |  | **26** | 69 |

[a]All reactions were carried out with indium reagent derived from an equimolar mixture of indium and homoallenylsilane in DMF at room temperature.




**Scheme 3**

allenylsilanes at room temperature in good yields. 2- or 3-Hydroxybenzaldehyde that contains an acidic hydrogen reacted with homoallenylindium reagent to provide the homoallenylsilanes. In the case of 4-formylbenzoic acid, the desired compound was produced in 88% yield. 4-Bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene was prepared from monoacetylation and mesylation of 2-butyn-1,4-diol, addition of trimethylsilylmethyl anion, saponification and mesylation followed by Finkelstein reaction. Because synthetic methods for the preparation of 2-(2-hydroxyethyl)allylsilanes were reported mainly in the previous works, the present method complements the existing synthetic methods.

## Experimental Section

The $^1$H NMR and $^{13}$C NMR spectra were recorded on Brucker IFS 48 (400 MHz) spectrometer. Proton chemical shifts ($\delta$) were reported in ppm downfield from tetramethylsilane (TMS), and $^{13}$C resonances were recorded using the 77.0 ppm $CDCl_3$ resonance peak of the solvent as internal reference. Fourier transform infrared (FTIR) spectra were recorded on a JASCO IR 100 spectrophotometer. Mass spectra were obtained on a Autospec, M363 series. Column chromatography was performed on silica gel (Merck, 230-400 mesh). The gas chromatograms were obtained on HP 5890.

**Typical procedure for indium-mediated homoallenylation reaction: 3-[(Trimethylsilyl)methyl]-1-phenyl-3,4-pentadien-1-ol (15)**. To a solution of indium [indium powder (99.99%) purchased from Aldrich Chem Co.; 58 mg, 0.5 mmol) in DMF (0.6 mL) was added 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene (110 mg, 0.5 mmol) in DMF (0.6 mL). After the reaction mixture was stirred for 30 min at room temperature, benzaldehyde (37 mg, 0.35 mmol) was added. After 40 min at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ether (3 × 25 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL) and dried with $MgSO_4$, filtered and concentracted *in vacuo*. The residue was purified by silica gel chromatography (hexane : EtOAc = 20 : 1) leading to 3-[(trimethylsilyl)methyl]-1-phenyl-3,4-pentadien-1-ol (80 mg, 92%).

**4-Acetoxy-2-butyn-1-ol (2)**: To solution of acetyl chloride (4.475 g, 57 mmol) in $CH_2Cl_2$ (10 mL) was added mixture of 2-butyn-1,4-diol (**1**) (4.910 g, 57 mmol) and pyridine (6.249 g, 79 mmol) in $CH_2Cl_2$ (50 mL) at 0 °C. The mixture was stirred for 30 min at r.t., the reaction mixture was quenched with 10% HCl solution. The aqueous layer was extracted with $CH_2Cl_2$ (3 × 25 mL), and the combined organic layer were washed with water (30 mL), dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel chromatography (EtOAc/Hexane = 1/2) leading to (3.829 g, 52%) as an oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.71 (t, $J$ = 1.81 Hz, 2H), 4.31 (t, $J$ = 1.77 Hz, 2H), 2.10 (s, 3H), 1.81 (s, 1H); IR (film) 3350, 2900, 1750, 1250 cm$^{-1}$.

**1-Acetoxy-4-methanesulfonyloxy-2-butyne (3)**: To solution of methanesulfonyl chloride (641 mg, 5.6 mmol) in $CH_2Cl_2$ (5 mL) was added mixture of 4-acetoxy-2-butyn-1-ol (**2**) (600 mg, 4.86 mmol) and $Et_3N$ (617 mg, 5.6 mmol) at 0 °C. After stirred for 30 min at r.t., the $CH_2Cl_2$ layer was diluted with $CH_2Cl_2$ (25 mL), washed twice with water, dried with $MgSO_4$, and concentrated to give **3** (942 mg, 98%) as an oil which was pure enough for the next step: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.89 (t, $J$ = 1.82 Hz, 2H), 4.72 (t, $J$ = 1.58 Hz, 2H), 3.13 (s, 3H), 2.11 (s, 3H).

**4-Acetoxy-3-[(trimethylsilyl)methyl]-1,2-butadiene (4)**: LiBr (1737 mg, 20 mmol) and CuBr (2869 mg, 20 mmol) were stirred in THF (40 mL) at r.t. for 15 min. To this solution was added $TMSCH_2MgCl$ (20 mL of a 1.0 M solution in $Et_2O$). After stirring at -78 °C for 15 min, HMPA (10 mL) was added followed immediately by the crude **3** prepared above (3.755 g, 18.2 mmol) at -78 °C. Then, the solution was gradually warmed to r.t. and stirred additional 30 min. The mixture was quenced with $NH_4Cl$ solution and extracted with hexane. Combined hexane extracts were washed with water twice, dried, and concentrated to give a crude oil. Purification on silica gel (EtOAc/Hexane = 1/3) gave **4** (3.390 g, 94%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.70 (m, 2H), 4.41 (t, $J$ = 2.63 Hz, 2H), 2.01 (s, 3H), 1.27 (t, $J$ = 2.63 Hz, 3H), 0.00 (s, 9H).

**2-[(Trimethylsilyl)methyl]-2,3-butadien-1-ol (5)**: To a solution of $K_2CO_3$ (2.211 g, 16 mmol) in water (2 mL) was added **4** (3.161 g, 16 mmol) in MeOH (20 mL). The solution was stirred at r.t. for 30 min. After the bulk of the solvent was removed on a rotary evaporator at r.t., the white suspension was diluted with brine and extracted with $Et_2O$ (3 × 25 mL). The combined extracts were dried with $MgSO_4$ and concentrated to afford **5** (2.356 g, 95%) which was sufficiently pure: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.82 (m, $J$ = 2.72 Hz, 2H), 3.90 (t, $J$ = 1.20 Hz, 2H), 1.60 (s, 1H), 1.26 (t, $J$ = 2.58 Hz, 2H), 0.00 (s, 9H).

**4-Methanesulfonyloxy-3-[(trimethylsilyl)methyl]-1,2-butadiene (6)**: To solution of methanesulfonyl chloride (304 mg, 3.0 mmol) in $CH_2Cl_2$ (1 mL) was added mixture of **5** (310 mg, 2.0 mmol) and $Et_3N$ (304 mg, 3.0 mmol) in $CH_2Cl_2$ (5 mL) at 0 °C. The mixture was stirred at r.t. for 30 min. The mixture was diluted with $CH_2Cl_2$, washed twice with water, dried with $MgSO_4$ and concentrated to give a crude oil (431 mg, 92%), which was sufficiently pure for the next step: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.77 (m, $J$ = 2.20 Hz, 2H), 4.56 (t, $J$ = 2.01 Hz, 2H), 2.95 (s, 3H), 1.33 (t, $J$ = 2.63 Hz, 2H), 0.00 (s, 9H).

**4-Bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene (7)**: To LiBr (3.800 g, 44 mmol) were stirred in acetone (20 mL)

at 0 °C. This solution was added **6** (2.600 g, 11 mmol), the mixture was stirred for 30 min at r.t. and work up in a usual way. Purification on silica gel (hexane) gave **7** (1.900 g, 80%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.68 (m, 2H), 3.91 (t, $J$ = 1.60 Hz, 2H), 1.42 (t, $J$ = 2.73 Hz, 2H), 0.00 (s, 9H).

**4-[(Trimethylsilyl)methyl]-4,5-hexadien-2-ol (8)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.73 (m, 2H), 3.98-3.95 (m, 1H), 2.07 (m, 3H), 1.35 (d, $J$ = 1.83 Hz, 2H), 1.23 (d, $J$ = 6.10 Hz, 3H), 0.07 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 117.11, 69.83, 66.04, 38.60, 27.43, 21.52, 1.36, -1.17; IR (film) 3380, 3020, 2960, 2280, 1700, 1620, 1410, 1370, 1250 cm$^{-1}$; MS (CI) calcd for $C_{10}H_{20}OSi$ $[M+H]^-$ 185, found 185.

**6-[(Trimethylsilyl)methyl]-6,7-octadien-4-ol (9)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.72 (s, 2H), 3.77-3.76 (m, 1H), 2.06-2.00 (m, 3H), 1.51-1.30 (m, 6H), 0.97-0.08 (m, 3H), 0.06 (d, $J$ = 2.13 Hz, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 206.20, 98.26, 75.68, 69.40, 42.85, 39.02, 21.69, 18.98, 14.20, -1.06; IR (film) 3600, 3430, 3020, 2910, 2820, 2280, 1715, 1620, 1450, 1240 cm$^{-1}$.

**2-Methyl-5-[(trimethylsilyl)methyl]-5,6-heptadien-3-ol (10)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.72 (m, 2H), 3.53 (m, 1H), 2.17-1.99 (m, 3H), 1.77-1.67 (m, 1H), 1.37-1.32 (m, 2H), 0.92 (dd, $J$ = 2.44, 2.13 Hz, 6H), 0.06 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 117.35, 79.17, 66.51, 33.13, 32.91, 27.53, 18.84, 18.17, -1.16; IR (film) 3400, 3030, 2960, 2290, 1720, 1410, 1250 cm$^{-1}$.

**1-Cyclohexyl-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (11)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.79-4.40 (m, 2H), 3.97 (s, 1H), 0.97-2.1 (m, 15H), 0.04 (d, $J$ = 2.44 Hz, 9H); IR (film) 3400, 3010, 2950, 2290, 2100, 1630, 1400, 1245 cm$^{-1}$.

**4-[(Trimethylsilyl)methyl]-1-phenyl-4,5-hexadien-2-ol (12)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.32-7.23 (m, 5H), 4.74 (m, 2H), 4.01-3.98 (m, 1H), 2.82 (m, 2H), 2.12 (m, 3H), 1.43-1.30 (m, 2H), 0.03 (d, $J$ = 0.92 Hz, 9H); MS (CI) calcd for $C_{16}H_{24}OSi$ $[M+H]^+$ 261, found 261.

**5-[(Trimethylsilyl)methyl]-1-phenyl-5,6-heptadien-3-ol (13)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.35-7.17 (m, 5H), 4.74 (t, $J$ = 2.29 Hz, 2H), 3.82 (m, 1H), 2.78 (m, 2H), 2.13-2.07 (m, 3H), 1.92-1.76 (m, 2H), 1.34 (q, $J$ = 2.74 Hz, 2H), 0.07 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 128.60, 128.56, 128.51, 128.44, 125.96, 125.84, 117.37, 72.94, 66.11, 37.63, 36.98, 31.87, 27.51; IR (film) 3400, 3020, 2960, 1710, 1410, 1370, 1240 cm$^{-1}$; MS (CI) calcd for $C_{17}H_{26}OSi$ $[M+H]^+$ 275, found 275.

**5-[(Trimethylsilyl)methyl]-1-phenyl-1,5,6-heptatrien-3-ol (14)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.62-7.33 (m, 5H), 6.81-6.62 (m, 1H), 6.27 (dd, $J$ = 6.41, 6.10 Hz, 1H), 4.79-4.73 (m, 2H), 4.49 (d, $J$ = 6.41 Hz, 1H), 2.55 (m, 3H), 1.39 (q, $J$ = 4.06 Hz, 2H), 0.08 (s, 9H).

**3-[(Trimethylsilyl)methyl]-1-(*p*-methylphenyl)-3,4-pentadien-1-ol (16)**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.21 (d, $J$ = 8.03 Hz, 2H), 7.10 (d, $J$ = 7.96 Hz, 2H), 4.75 (q, $J$ = 4.33 Hz, 1H), 4.69 (t, $J$ = 2.63 Hz, 2H), 2.32-2.20 (m, 6H), 1.35-1.25 (m, 2H), 0.00 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 207.71, 142.04, 138.16, 130.13, 126.91, 99.13, 76.95, 72.99, 46.13, 22.62, 22.23, 0.00; IR (film) 3360, 2920, 1940, 1500, 1410, 1230 cm$^{-1}$; MS (CI) calcd for $C_{16}H_{24}OSi$ $[M+H]^+$ 261, found 261.

**1-(*m*-Bromophenyl)-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (17)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.57-7.18 (m, 4H), 4.84-4.75 (m, 3H), 2.48 (s, 1H), 2.34-2.27 (m, 2H), 1.37 (q, $J$ = 2.84 Hz, 2H), 0.07 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 206.65, 146.29, 130.59, 130.07, 129.14, 124.62, 122.61, 97.83, 76.34, 71.46, 45.14, 21.57, -1.04; IR (film) 3390, 2920, 1700, 1230 cm$^{-1}$; MS (CI) calcd for $C_{15}H_{21}BrOSi$ $[M+H]^-$ 326, found 326.

**1-(*p*-Chlorophenyl)-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (18)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.25 (s, 4H), 4.75-4.68 (m, 3H), 2.44 (d, $J$ = 2.13 Hz, 1H), 2.25-2.21 (m, 2H), 1.29 (q, $J$ = 2.64 Hz, 2H), 0.00 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 206.63, 142.46, 133.12, 128.60, 127.40, 97.87, 76.28, 71.45, 45.11, 21.55, -1.03; IR (film) 3900, 3390, 3020, 2980, 2280, 1690, 1590, 1410, 1240 cm$^{-1}$.

**3-[(Trimethylsilyl)methyl]-1-(*o*-nitrophenyl)-3,4-pentadien-1-ol (19)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.89-7.80 (m, 2H), 7.62-7.54 (m, 1H), 7.40-7.31 (m, 1H), 5.32 (dd, $J$ = 2.44, 2.44 Hz, 1H), 4.70 (m, 2H), 2.51-2.11 (m, 2H), 1.34 (t, $J$ = 2.44 Hz, 2H), 0.00 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 206.39, 147.77, 139.39, 133.72, 128.29, 128.18, 124.47, 97.86, 76.15, 67.36, 44.44, 20.80, -1.12.

**1-(*p*-Methoxyphenyl)-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (20)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.34-7.28 (m, 2H), 6.92-6.88 (m, 2H), 4.84-4.73 (m, 3H), 3.82 (s, 3H), 2.38-2.28 (m, 3H), 1.37 (q, $J$ = 2.59 Hz, 2H), 0.06 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 136.19, 132.13, 127.34, 127.21, 114.42, 113.84, 75.90, 71.76, 55.35, 45.00, 21.59, -1.06; IR (film) 3920, 3400, 3010, 2950, 2280, 1660, 1580, 1490, 1400, 1230 cm$^{-1}$; MS (CI) calcd for $C_{16}H_{24}O_2Si$ $[M+H]^-$ 247, found 247.

**1-(2′,6′-Dimethoxyphenyl)-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (21)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.18 (t, $J$ = 8.24 Hz, 1H), 6.56 (d, $J$ = 8.54 Hz, 2H), 5.36-5.29 (m, 1H), 4.57-4.49 (m, 2H), 3.84 (s, 6H), 2.62-2.51 (m, 1H), 2.38-2.28 (m, 1H), 1.62 (s, 1H), 1.40 (s, 2H), 0.05 (s, 9H); IR (film) 3910, 3390, 3020, 2960, 2280, 1410, 1250 cm$^{-1}$.

**1-(*o*-Hydroxyphenyl)-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (22)**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.12 (s, 1H), 7.12-7.08 (m, 1H), 6.90 (dd, $J$ = 1.58, 1.59 Hz, 1H), 6.82-6.74 (m, 2H), 4.94 (dd, $J$ = 2.77, 2.78 Hz, 1H), 4.76-4.74 (m, 2H), 3.07 (s, 1H), 2.53-2.45 (m, 1H), 2.28-2.22 (m, 1H), 1.36-1.25 (m, 2H), 0.00 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 207.03, 156.83, 130.03, 128.14, 127.41, 120.90, 118.45, 99.05, 77.79, 75.07, 44.16, 22.72, 0.00; IR (film) 3340, 2920, 1940, 1570, 1470, 1440, 1400, 1220 cm$^{-1}$.

**1-(*m*-Hydroxyphenyl)-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (23)**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.13 (t, $J$ = 7.82 Hz, 1H), 6.68-6.82 (m, 2H), 6.71-6.68 (m, 1H), 6.31 (s, 1H), 4.77 (q, $J$ = 4.34 Hz, 1H), 4.70 (s, 2H), 2.81 (s, 1H), 2.31-2.25 (m, 2H), 1.34-1.28 (m, 2H), 0.00 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 207.69, 157.07, 146.32, 130.76, 119.31, 116.00, 115.85, 98.93, 77.22, 73.31, 45.75, 22.58.

**1-(*p*-Carboxyphenyl)-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (24)**: $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 8.11 (d, $J$ =

7.93 Hz, 2H), 7.50 (d, $J$ = 8.24 Hz, 2H), 4.94 (s, 1H), 4.79 (t, $J$ = 2.44 Hz, 2H), 2.34 (t, $J$ = 3.19 Hz, 2H), 1.37 (d, $J$ = 2.44 Hz, 2H), 0.07 (s, 9H); IR (film) 3380, 1630, 1410, 1360, 1250 $cm^{-1}$.

**1-Furyl-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (25)**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.31 (t, $J$ = 0.85 Hz, 1H), 6.28-6.19 (m, 2H), 4.80 (t, $J$ = 6.59 Hz, 1H), 4.65 (m, 2H), 2.41 (m, 2H), 2.30 (s, 1H), 1.35-1.27 (m, 2H), 0.00 (s, 9H).

**1-Thienyl-3-[(trimethylsilyl)methyl]-3,4-pentadien-1-ol (26)**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.18 (t, $J$ = 5.65 Hz, 1H), 6.93-6.89 (m, 2H), 5.04 (q, $J$ = 4.31 Hz, 1H), 4.72-4.65 (m, 2H), 2.45-2.37 (m, 3H), 1.36-1.26 (m, 2H), 0.00 (s, 9H).

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