DOI: 10.1002/ejoc.201101634

Effects of Silyl Substituents on the Palladium-Catalyzed Asymmetric Synthesis of Axially Chiral (Allenylmethyl)silanes and Their S_E2' Chirality Transfer Reactions

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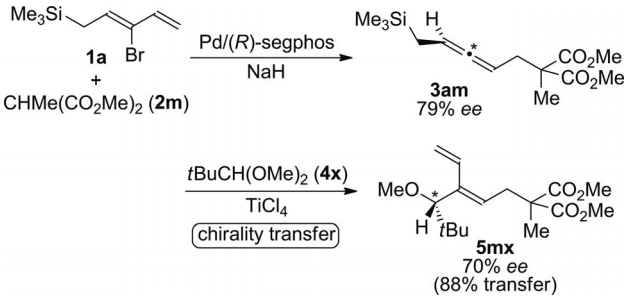
Keywords: Allenes / Chirality / Electrophilic substitution / Palladium

A series of axially chiral 4-substituted-1-silyl-2,3-butadienes [(allenylmethyl)silanes] were synthesized from 3-bromo-5-silylpenta-1,3-dienes by a Pd-catalyzed asymmetric reaction with a soft nucleophile. The optically active (allenylmethyl)-silanes react with an acetal in the presence of $TiCl_4$ to give the enantiomerically enriched 1,3-diene derivatives through an S_E2' pathway. Effects of the silyl groups on the enantioselectivity of the asymmetric allene synthesis and the subsequent S_E2' chirality transfer reaction were studied. It was found that as the steric bulk of the silyl groups in the 3-bromo-5-silylpenta-1,3-dienes was increased from -$SiMe_3$ to -Si*i*Pr_3, the enantioselectivity of the two enantioselective processes also improved.

Introduction

Allenes are important and useful compounds in synthetic organic chemistry.[1,2] Introduction of proper substituents at the appropriate positions of an allenic skeleton induces unique axial chirality in the allenic molecule.[3] Optically active forms of such axially chiral allenes have been utilized as chiral synthons that are capable of transferring their axial chirality onto newly formed stereogenic centers in the products.[4–8] The majority of successful examples of such axis-to-center chirality transfer reactions are categorized into either intramolecular cyclization reactions[4] and/or transformation of allenylmetal species into the corresponding propargyl derivatives.[5] Indeed, examples of transferring the allenic axial chirality onto a stereogenic carbon atom which is derived from the incoming intermolecular reactant have been extremely rare.[6–8]

Recently, we developed a Pd-catalyzed reaction for the preparation of various multisubstituted allenes,[9a–9h] and the use of an appropriate chiral Pd catalyst enables axially chiral allenes of high enantiopurity to be furnished.[7,9i–9l] The reaction was applied to the asymmetric synthesis of axially chiral (allenylmethyl)silanes **3** (Scheme 1), and the obtained enantiomerically enriched **3** were applied in the S_E2' reaction to produce diene derivatives **5** containing a stereogenic carbon atom.[7] The second step of this sequence was a rare example of the intermolecular axis-to-center chirality transfer reaction.[6–8] Although the reaction sequence provides convenient access to optically active (allenylmethyl)silanes **3** and dienyl derivatives **5**, the enantioselectivity of both steps shows rooms for further improvement. To solve this problem, we were interested in modifying the silyl groups in **1** and **3**. We envision that the enantioselectivity of both steps could be improved with bulkier silyl groups. Here we report the substituent effects of the silyl substituents on the two enantioselective reactions, the Pd-catalyzed asymmetric synthesis of (allenylmethyl)silanes[10] and S_E2' chirality transfer reactions.[11]



Scheme 1. Pd-catalyzed asymmetric synthesis of axially chiral (allenylmethyl)silane **3am** and axis-to-center chirality transfer in **5mx**.[7]

Results and Discussion

Preparation of 3-Bromo-5-silylpenta-1,3-dienes

Preparation of 3-bromo-5-trimethylsilylpenta-1,3-diene (**1a**) was reported by Parrain and Santelli in 2000.[12] The starting compound of their method was 1,4-bis(trimethylsilyl)-2-butene (**6a**), which can be easily obtained by the Ti-

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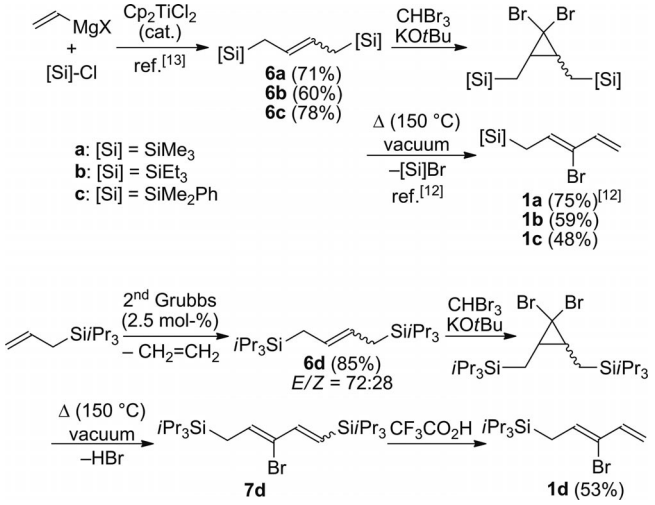
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101634.

catalyzed coupling of vinyl Grignard reagent and chlorotrimethylsilane as reported by Terao and Kambe.[13] The whole sequence is applicable to the preparation of the triethylsilyl and dimethylphenylsilyl analogues, and compounds **1b** and **1c** were prepared in 59 and 48% yield, respectively (Scheme 2, top).



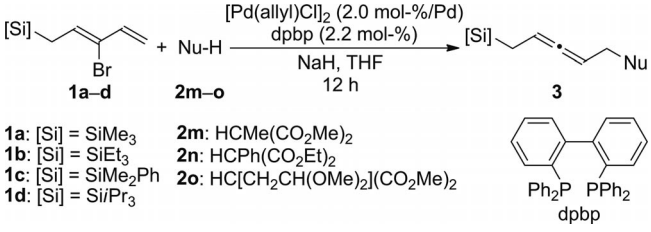
Scheme 2. Preparation of 3-bromo-5-silylpenta-1,3-dienes **1a**–**d**.

For the preparation of triisopropylsilyl derivative **1d**, some modifications of the synthetic scheme are required. The Ti-catalyzed reaction is not applicable to reactions with bulky chlorosilanes, and the reaction of vinylmagnesium chloride with iPr$_3$SiCl failed to give (*E*/*Z*)-1,4-bis(triisopropylsilyl)-2-butene (**6d**). It was found, however, that **6d** could be easily obtained in 85% yield by metathesis homodimerization of commercially available allyltriisopropylsilane in the presence of the second generation Grubbs catalyst[14] in refluxing dichloromethane. Thermolysis of *gem*-dibromocyclopropane, which was prepared from **6d**, afforded an *E*/*Z* mixture of 3-bromo-1,5-bis(triisopropylsilyl)-penta-1,3-diene (**7d**) through elimination of HBr, and desired debromosilylation product **1d** was not obtained. The TIPS group on the sp^2 carbon atom in **7d** was selectively removed by acidic treatment (1% CF_3CO_2H in CH_2Cl_2), and **1d** was obtained in 53% overall yield from **6d** (Scheme 2, bottom). All bromosilyldienes **1a**–**d** were easily purified by standard silica gel chromatography and obtained as the (*Z*)-isomers exclusively.

Palladium-Catalyzed Reactions of 3-Bromo-5-silylpenta-1,3-dienes with Nucleophiles

All 3-bromo-5-silylpenta-1,3-dienes **1a**–**d** obtained as in Scheme 2 are excellent precursors to (allenylmethyl)silane derivatives (Table 1). A series of 4-substituted-1-silyl-2,3-butadienes **3** were synthesized from **1** and appropriate pronucleophile **2** in the presence of NaH (1.0 equiv. with respect to **2**) and a Pd catalyst (2 mol-%), which was generated in situ from [PdCl(π-allyl)]$_2$ and dpbp,[15] in THF.[7] With various malonate-based pronucleophiles **2m**–**o**, the reaction proceeded cleanly, and the isolated yields of the corresponding (allenylmethyl)silanes **3** were excellent and ranged from 81 to 96%. The steric characteristics of the silyl substituents in **1** show no or negligible effects on the chemical yields of **3**. Even with the sterically most demanding silyl group, -SiiPr$_3$, in **1d**, the Pd-catalyzed reaction afforded the desired (allenylmethyl)silanes in good yields (Table 1, Entries 4, 8, 11). All the allenic products are stable and can be purified by standard silica gel chromatography.

Table 1. Palladium-catalyzed synthesis of (allenylmethyl)silanes **3**.[a]



Entry	Bromodiene **1**	Nu-H **2**	Temp [°C]	Yield of **3** [%][b]
1	**1a**	**2m**	23	91 (**3am**)
2	**1b**	**2m**	23	94 (**3bm**)
3	**1c**	**2m**	23	88 (**3cm**)
4	**1d**	**2m**	23	92 (**3dm**)
5	**1a**	**2n**	23	87 (**3an**)
6	**1b**	**2n**	23	89 (**3bn**)
7	**1c**	**2n**	23	83 (**3cn**)
8	**1d**	**2n**	23	96 (**3dn**)
9	**1a**	**2o**	40	84 (**3ao**)
10	**1b**	**2o**	40	92 (**3bo**)
11	**1d**	**2o**	40	81 (**3do**)

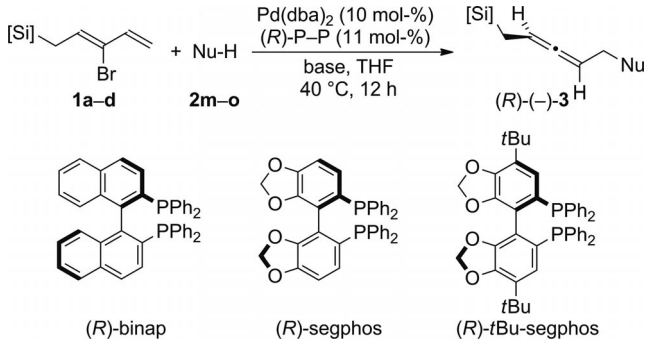
[a] The reaction was carried out with **1** (0.50 mmol) and **2** (0.55 mmol) in THF in the presence of NaH and a Pd catalyst (2 mol-%) generated from [PdCl(π-allyl)]$_2$ and dpbp. [b] Isolated yield after silica gel chromatography.

Substituent Effects on Pd-Catalyzed Asymmetric Synthesis of (Allenylmethyl)silanes 3

The asymmetric synthesis of axially chiral (allenylmethyl)silanes **3** was examined under reaction conditions identical to those reported for the reaction between **1a** and **2m**.[7] That is, with a palladium catalyst (10 mol-%) generated from Pd(dba)$_2$ and an appropriate chiral phosphane ligand in THF at 40 °C. Products (*R*)-**3** were obtained in good enantioselectivity (up to 90% *ee*, Table 2).

Among various chiral phosphane ligands examined, (*R*)-segphos[16] showed the best performance in terms of enantioselectivity. The reaction of **1a** with **2m** with the use of the Pd/(*R*)-segphos species afforded (*R*)-**3am** in 75% yield with 79% *ee* (Table 2, Entry 1). The use of (*R*)-binap and (*R*)-*t*Bu-segphos[17] decreased the enantioselectivity of the same reaction to 43 and 74% *ee*, respectively (Table 2, Entries 2 and 3). Interestingly, a clear correlation was observed between the enantioselectivity of the Pd-catalyzed reaction and the steric bulk of the silyl groups in **1**. The enantioselectivity in **3bm**, **3cm**, and **3dm**, which were obtained by using Pd/(*R*)-segphos-catalyzed reactions with **2m**/NaH as a nucleophile, was 80, 80, and 87% *ee*, respec-

Table 2. Palladium-catalyzed asymmetric synthesis of (allenylmethyl)silanes **3**.[a]



Entry	1	2	Base	P-P	Yield of **3** [%][b]	*ee* of **3** [%][c,d]
1	**1a**	**2m**	NaH	segphos	75 (**3am**)	79 (*R*)
2	**1a**	**2m**	NaH	binap	79 (**3am**)	43 (*R*)
3	**1a**	**2m**	NaH	*t*Bu-segphos	74 (**3am**)	74 (*R*)
4	**1b**	**2m**	NaH	segphos	75 (**3bm**)	80 (*R*)
5	**1c**	**2m**	NaH	segphos	83 (**3cm**)	80 (*R*)
6	**1d**	**2m**	NaH	segphos	85 (**3dm**)	87 (*R*)
7	**1a**	**2n**	CsO*t*Bu	segphos	70 (**3an**)	81 (*R*)
8	**1d**	**2n**	CsO*t*Bu	segphos	91 (**3dn**)	90 (*R*)
9	**1a**	**2o**	CsO*t*Bu	segphos	72 (**3ao**)	62 (*R*)
10	**1b**	**2o**	CsO*t*Bu	segphos	75 (**3bo**)	80 (*R*)
11	**1d**	**2o**	CsO*t*Bu	segphos	85 (**3do**)	87 (*R*)

[a] The reaction was carried out with **1** (0.50 mmol) and **2** (0.55 mmol) in THF in the presence of base (0.55 mmol) and a Pd catalyst (10 mol-%) generated from $Pd(dba)_2$ and a chiral phosphane. [b] Isolated yield after chromatography on alumina. [c] Determined by chiral HPLC analysis with a chiral stationary phase column (Chiralpak AD-H for **3am**, **3cm**, **3ao**, **3bo**, and **3do**; Chiralcel OD-H for **3bm**, **3dm**, **3an**, and **3dn**). [d] The absolute configuration was deduced by the Lowe–Brewster rule (ref.[18]).

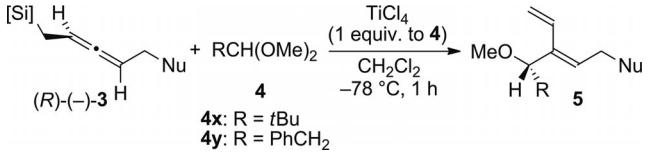
tively (Table 2, Entries 4–6). Likewise, the enantioselectivity of 81%*ee* for **3an**, which was obtained from **1a** and **2n**/CsO*t*Bu, could be improved to 90%*ee* for **3dn** under identical conditions (Table 2, Entries 7 and 8). The same trend was observed for reactions of **1a**–**d** with **2o**/CsO*t*Bu; the *ee* values for **3ao**, **3bo**, and **3do** were 62, 80, and 87%*ee*, respectively (Table 2, Entries 9–11). In all the cases examined here, the isolated yields of the allenic species were within the range of 70 to 91%, and no apparent deviation was seen with regard to the choice of the silyl groups.

All the allenic products shown in Table 2 are levorotatory, and their absolute configurations were deduced to be (*R*) by the Lowe–Brewster rule.[18] Because all the allenes are not crystalline, X-ray crystal structure analysis could not be used to determine their absolute configurations.

Substituent Effects on Enantioselective S_E2' Chirality Transfer Reactions

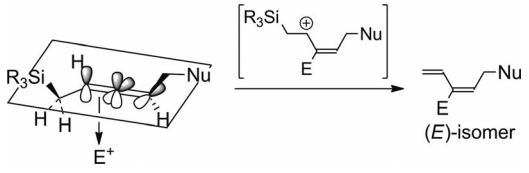
Axially chiral (allenylmethyl)silanes (*R*)-**3** obtained above were applied to the $TiCl_4$-promoted S_E2' reaction with an appropriate acetal. The results are summarized in Table 3. In all cases, the reactions proceeded cleanly and dienes **5** were obtained with the (*E*) configuration exclusively.[7,11a] The (*E*) configuration of the internal double bond in **5mx** was assigned on the basis of ^1H NMR nOe experiments. An nOe was detected between MeOC*H*- and $NuCH_2CH$=C-, whereas no nOe was observed between $NuCH_2CH$=C- and CH_2=C*H*-. Other conjugated dienes **5** showed similar ^1H NMR behavior. The exclusive formation of the (*E*)-diene indicates that the electrophile approaches the central carbon of the allene from the side opposite to the sterically demanding $NuCH_2$- substituent (Scheme 3). The same stereochemical outcome was reported in the protodesilylation of (allenylmethyl)silanes.[11a]

Table 3. $TiCl_4$-promoted S_E2' reaction of (allenylmethyl)silanes **3** with $RCH(OMe)_2$ **4**.[a]



Entry	3	*ee* of **3** [%]	Acetal **4**	Yield of **5** [%][b]	*ee* of **5** [%][c]	Chirality transfer [%][d]
1	**3am**	79	**4x**	87 (**5mx**)	70 (*S*)	88
2	**3bm**	80	**4x**	71 (**5mx**)	71 (*S*)	89
3	**3dm**	87	**4x**	71 (**5mx**)	80 (*S*)	92
4	**3an**	81	**4x**	97 (**5nx**)	50[e] (*S*)	62
5	**3dn**	90	**4x**	95 (**5nx**)	75[e] (*S*)	83
6	**3am**	79	**4y**	89 (**5my**)	21 (nd)[f]	26
7	**3dm**	87	**4y**	36 (**5my**)	15 (nd)[f]	17

[a] The reaction was carried out with **3** (0.35 mmol), **4** (0.53 mmol), and $TiCl_4$ (0.53 mmol) in CH_2Cl_2 for 1 h. [b] Isolated yield after silica gel chromatography. [c] Determined by chiral HPLC analysis with a chiral stationary phase column (Chiralcel OD-H). [d] Chirality transfer = (*ee* of **5**)/(*ee* of **3**) × 100. [e] The *ee* value was determined on the diol obtained by $LiAlH_4$ reduction of **5nx**. [f] Absolute configuration was not determined.

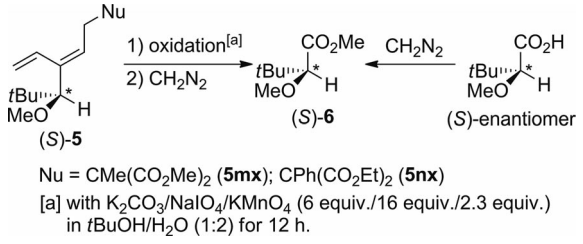


Scheme 3. Stereochemistry producing (*E*)-dienes in the S_E2' reactions between **3** and **4**.

Diene products **5** possess a newly formed stereogenic carbon atom, and axis-to-center chirality transfer takes place during the transformation.[6,7] The chirality transfer is highly effective in the reactions with pivalaldehyde dimethyl acetal (**4x**). Allene **3am** (79%*ee*) containing a Me_3Si group gave diene **5mx** in 87% yield with 70%*ee*. The chirality transfer efficiency of this transformation was calculated to be 88% (Table 3, Entry 1). With the bulkier silyl groups in **3**, the chirality transfer becomes more effective. Et_3Si-allene **3bm** with 80%*ee* afforded diene **5mx** in 71%*ee* (89% chirality transfer; Table 3, Entry 2). The chirality transfer was

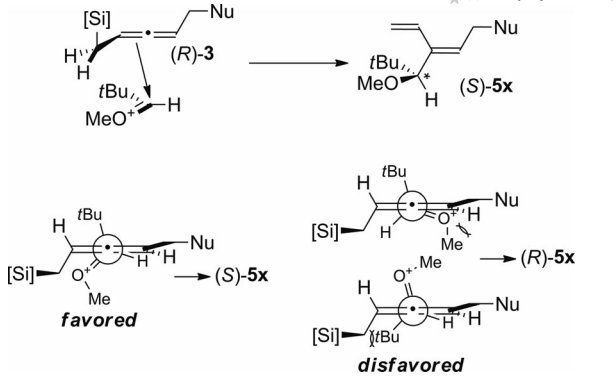
further improved to 92% in the reaction of **3dm** (87%*ee*), which contains an *i*Pr_3Si substituent, and **4x** gave **5mx** with 80%*ee* (Table 3, Entry 3). The effect of the silyl group is more evident for the reactions of **3an/3dn** with **4x**. Whereas Me_3Si-allene **3an** (81%*ee*) afforded diene **5nx** with 50%*ee* and with 62% chirality transfer (Table 3, Entry 4), *i*Pr_3Si analogue **3dn** (90%*ee*) gave **5nx** with 75%*ee* and 83% transfer (Table 3, Entry 5). On the other hand, the S_E2' reactions with phenylacetaldehyde dimethyl acetal (**4y**) showed inadequate chirality transfer in all cases. The reaction between **3am** (79%*ee*) and **4y** gave diene **5my** with 21%*ee* with a chirality transfer of only 26% (Table 3, Entry 6). Similarly, **5my** obtained from **3dm** (87%*ee*) and **4y** was as low as 15%*ee* (17% transfer; Table 3, Entry 7).

The absolute configurations of **5mx** and **5nx** were determined as follows. 1,3-Dienes **5mx** and **5nx** were converted into *t*BuCH(OMe)CO_2Me (**6**) by successive oxidation and diazomethane treatment (Scheme 4), and the absolute configuration of both **5mx** and **5nx** was determined to be (*S*) by correlation with an authentic sample of (*S*)-**6**, which was prepared from commercially available (*S*)-*t*BuCH(OH)CO_2H.[7]



Scheme 4. Determination of the absolute configurations of **5mx** and **5nx**.

The stereochemical pathway for the reaction of (*R*)-**3** with **4x** to give (*S*)-(*E*)-**5x** is shown in Schemes 3 and 5. On the basis of the *anti* stereochemistry observed for the S_E2' reactions of allylsilanes,[19] the electrophile *t*BuCH=O^+Me, which is generated in situ from **4x** and $TiCl_4$, approaches the C=C bond in **3** from the side opposite to the silyl group. Subsequently, nucleophilic attack takes place onto the *Re* face of the electrophile. Steric interactions between the electrophile and (*R*)-**3** are minimized in the relative orientation of the two reactants, which is illustrated in Scheme 5 (bottom left). In this synclinal-like transition state,[19d] the bulkiest substituent in the electrophile (*t*Bu group) occupies the sterically least congested position, whereas the smallest one (methine hydrogen) possesses a position adjacent to the =C*H*CH_2Nu hydrogen in (*R*)-**3**, which sticks out toward the electrophile. An antiperiplanar-like transition state and a second synclinal-like transition state (Scheme 5, bottom right), which would lead to (*R*)-**5x**, are unfavorable due to steric repulsions between =C*H*CH_2Nu and the OMe group or between =CHCH_2[*Si*] and the *t*Bu substituent. The bulkier silyl substituent in (*R*)-**3** further destabilizes one of the disfavored transition states (Scheme 5, far bottom right), which leads to better chirality transfer with (*R*)-**3dm** and (*R*)-**3dn**.



Scheme 5. Stereochemistry producing (*S*)-dienes in the S_E2' reactions between **3** and **4x**.

The bulky *t*Bu substituent in **4x** is important for the effective chirality transfer in the S_E2' reaction. With the sterically more compact acetal **4y**, the chirality transfer efficiency in **5my** was considerably diminished due to ineffective discrimination between the two enantiotopic faces in the electrophile. Because the relative steric proportions between -CH_2Ph and -OMe are not so different, effective chirality transfer in the present S_E2' reaction is inherently difficult with **4y**, and thus, the positive effects from the bulkier silyl groups in **3** are not visible using **4y**.

The conversion of achiral bromodienes **1** into centrally chiral **5** is the process of the two subsequent enantioselective reactions. Whereas bulkier silyl groups induce higher enantioselectivity in both enantioselective reactions, final products **5** of much higher optical purity are obtained starting with **1d**, which contains a Si*i*Pr_3 group, without any appreciable loss in the chemical yields. Starting substrates **1** with various silyl groups provide identical products **5** in the end of the two-step reaction sequence, because the silyl groups are the leaving groups in the S_E2' reaction.

Conclusions

The substituent effects of the silyl groups were studied in the palladium-catalyzed asymmetric synthesis of (allenylmethyl)silanes and their S_E2' chirality transfer reactions. It is found that as the steric bulk of the silyl groups in the 3-bromo-5-silylpenta-1,3-dienes increased from -$SiMe_3$ to -Si*i*Pr_3, the enantioselectivity of the two enantioselective processes also improved remarkably.

Experimental Section

General Methods: All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glove box techniques under prepurified argon. ^{1}H NMR and ^{13}C NMR were measured with a JEOL JNM-ECX400 spectrometer; chemical shifts are reported in ppm downfield of internal tetramethylsilane. Tetrahydrofuran and hexane (homogenized with tetraglyme) were distilled from benzophenone-ketyl under an atmosphere of nitrogen prior to use. The second generation Grubbs catalyst,[14] 1,4-disilyl-2-butenes (**6a**–**c**),[13] 3-

bromo-5-trimethylsilylpenta-1,3-diene (**1a**),[12] [PdCl(π-allyl)]$_2$,[20] dpbp,[15] Pd(dba)$_2$,[21] (*R*)-segphos,[16] (*S*)-*t*Bu-segphos,[17] *t*BuCH(OMe)$_2$,[22] and (MeO)$_2$CHCH$_2$CH(CO$_2$Me)$_2$[23] were prepared as reported. All other chemicals were obtained from commercial sources and used without additional purification.

(*E*/*Z*)-1,4-Bis(triisopropylsilyl)-2-butene (6d): Allyltriisopropylsilane (5.47 g, 27.6 mmol) was dissolved in CH_2Cl_2 together with the second generation Grubbs catalyst (0.59 g, 0.69 mmol, 2.5 mol-%) under an atmosphere of nitrogen. The solution was heated at reflux for 12 h with stirring. The solution was cooled to room temperature, then filtered through a short pad of SiO_2. After removing the solvent under reduced pressure, vacuum transfer of the residue gave **6d** as a mixture of two isomers (*E*/*Z* = 72:28) in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99–1.10 (m, 42 H of both isomers), 1.51 (d, *J* = 6.0 Hz, 4 H of *E*-isomer), 1.54 (d, *J* = 6.4 Hz, 4 H of *Z*-isomer), 5.30–5.35 (m, 2 H of both isomers) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *E*-isomer): δ = 11.1, 15.3, 18.8, 125.3 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *Z*-isomer): δ = 10.2, 11.3, 18.8, 123.9 ppm. HRMS (EI): calcd. for $C_{22}H_{48}Si_2$ 368.3295; found 368.3293.

3-Bromo-5-silylpenta-1,3-dienes (1a–c):[10] To a suspension of disilylbutene **6** (10 mmol) and KO*t*Bu (3.4 g, 30 mmol) in dry hexane (20 mL) was added bromoform (7.6 g, 30 mmol) slowly at 0 °C. The mixture was stirred for 1 h at 0 °C and 1 h at room temperature. The mixture was then filtered through Celite, and the filtrate was washed with saturated aqueous NaCl. The aqueous phase was extracted with diethyl ether, and the combined organic layer was dried with $MgSO_4$. After removing the solvent, the crude dibromocyclopropane was heated at 100–150 °C (bath temperature) under vacuum in a distillation assembly to afford a crude product, which was with the eliminated bromosilane and bromoform. The pure product was obtained by a second distillation of the crude product. Bromodiene (*Z*)-**1a**, obtained in 71% isolated yield, was characterized by comparison of its spectroscopic data with those reported previously.[10] The characterization data of (*Z*)-**1b** and (*Z*)-**1c** are listed below.

(*Z*)-3-Bromo-5-triethylsilylpenta-1,3-diene (1b): B.p. (bath temp.) = 60–65 °C (0.2 Torr). Yield: 59%. ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 0.58 (q, *J* = 7.8 Hz, 6 H), 0.96 (t, *J* = 7.8 Hz, 9 H), 1.86 (d, *J* = 8.7 Hz, 2 H), 5.06 (d, *J* = 10.6 Hz, 1 H), 5.42 (d, *J* = 16.5 Hz, 1 H), 6.03 (t, *J* = 8.7 Hz, 1 H), 6.31 (dd, *J* = 10.6, 16.5 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 3.5, 7.3, 18.8, 115.1, 123.6, 132.8, 136.0 ppm. HRMS (EI): calcd. for $C_{11}H_{21}BrSi$ 260.0596; found 260.0591.

(*Z*)-3-Bromo-5-dimethylphenylsilylpenta-1,3-diene (1c): B.p. (bath temp.) = 80–90 °C (0.2 Torr). Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.34 (s, 6 H), 2.07 (d, *J* = 8.7 Hz, 2 H), 5.07 (d, *J* = 10.1 Hz, 1 H), 5.43 (d, *J* = 16.0 Hz, 1 H), 5.98 (t, *J* = 8.7 Hz, 1 H), 6.29 (dd, *J* = 10.1, 16.0 Hz, 1 H), 7.35–7.39 (m, 3 H), 7.51–7.54 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = –2.8, 22.9, 115.6, 124.5, 128.0, 129.4, 132.0, 133.6, 136.1, 138.2 ppm. HRMS (EI): calcd. for $C_{13}H_{17}BrSi$ 280.0283; found 280.0286.

(*Z*)-3-Bromo-5-triisopropylsilylpenta-1,3-diene (1d): Thermolysis of the dibromocyclopropane, which was obtained from **6d** as above, gave 1,5-bis(triisopropylsilyl)-3-bromopenta-1,3-diene (**7d**). Crude **7d** was dissolved in CH_2Cl_2 containing 1% CF_3CO_2H, and the solution was stirred at room temperature for 1 h. After removing all the volatiles under vacuum, **1d** was purified by vacuum distillation. B.p. (bath temp.) = 110–120 °C (0.2 Torr). Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02–1.11 (m, 21 H), 1.92 (d, *J* = 8.2 Hz, 2 H), 5.06 (d, *J* = 10.5 Hz, 1 H), 5.42 (d, *J* = 16.5 Hz, 1 H), 6.08 (t, *J* = 8.2 Hz, 1 H), 6.31 (dd, *J* = 10.5, 16.5 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 11.4, 16.4, 18.7, 115.3, 123.9, 133.4, 136.2 ppm. HRMS (EI): calcd. for $C_{14}H_{27}BrSi$ 302.1065; found 302.1074.

Palladium-Catalyzed Synthesis of (Allenylmethyl)silanes 3: Preparation of racemic (allenylmethyl)silanes **3** was conducted according to a reported procedure.[7] The reaction conditions and results are summarized in Table 1. A mixture of [PdCl(π-allyl)]$_2$ (1.8 mg, 10 μmol/Pd), dpbp (5.7 mg, 11 μmol), and **1** (0.50 mmol) was dissolved in THF (5 mL), and the solution was added to a mixture of **2** (0.55 mmol) and NaH (0.55 mmol) by cannula under an atmosphere of nitrogen. The mixture was stirred at the appropriate temperature for 12 h, then filtered through a short pad of SiO_2 to remove the precipitated inorganic salts. The silica gel pad was washed with a small amount of Et_2O (3×), and the combined solution was evaporated to dryness under reduced pressure. The yellow residue was chromatographed on silica gel to give allene **3** in pure form. Allenes **3am**,[7] **3ao**,[9g] **3bo**,[9g] and **3do**[9g] were characterized by comparison of their spectroscopic data with those reported previously. The characterization data of the other allenic products are listed below.

Dimethyl 2-Methyl-2-[5-(triethylsilyl)penta-2,3-dienyl]propane-1,3-dioate (3bm): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.54 (q, *J* = 8.0 Hz, 6 H), 0.94 (t, *J* = 8.0 Hz, 9 H), 1.31–1.32 (m, 1 H), 1.33–1.34 (m, 1 H), 1.44 (s, 3 H), 2.53 (d, *J* = 2.3 Hz, 1 H), 2.55 (d, *J* = 2.3 Hz, 1 H), 3.721 (s, 3 H), 3.724 (s, 3 H), 4.86–4.92 (m, 1 H), 5.02–5.09 (m, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 3.2, 7.4, 12.7, 19.8, 36.2, 52.5, 52.6, 54.0, 84.5, 87.4, 172.38, 172.45, 206.3 ppm. HRMS (EI): calcd. for $C_{17}H_{30}O_4Si$ 326.1913; found 326.1918.

Dimethyl 2-[5-(Dimethylphenylsilyl)penta-2,3-dienyl]-2-methylpropane-1,3-dioate (3cm): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.30 (s, 6 H), 1.39 (s, 3 H), 1.51–1.53 (m, 1 H), 1.54–1.55 (m, 1 H), 2.47–2.49 (m, 2 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 4.84–4.91 (m, 1 H), 5.00–5.07 (m, 1 H), 7.33–7.37 (m, 3 H), 7.49–7.52 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = –3.32, –3.25, 17.2, 19.8, 36.2, 52.5, 52.6, 54.0, 84.8, 86.9, 127.9, 129.1, 133.7, 138.5, 172.3, 172.4, 206.6 ppm. HRMS (EI): calcd. for $C_{19}H_{26}O_4Si$ 346.1600; found 346.1605.

Dimethyl 2-Methyl-2-[5-(triisopropylsilyl)penta-2,3-dienyl]propane-1,3-dioate (3dm): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01–1.08 (m, 21 H), 1.41–1.42 (m, 1 H), 1.43–1.44 (m, 1 H), 1.44 (s, 3 H), 2.54 (d, *J* = 1.8 Hz, 1 H), 2.56 (d, *J* = 1.8 Hz, 1 H), 3.718 (s, 3 H), 3.724 (s, 3 H), 4.85–4.91 (m, 1 H), 5.09–5.15 (m, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.6, 11.0, 18.8 (unresolved diastereotopic -SiCH*Me*$_2$), 19.8, 36.0, 52.5, 52.6, 54.0, 84.6, 88.2, 172.39, 172.44, 206.3 ppm. HRMS (EI): calcd. for $C_{20}H_{36}O_4Si$ 368.2383; found 368.2387.

Diethyl 2-Phenyl-2-[5-(trimethylsilyl)penta-2,3-dienyl]propane-1,3-dioate (3an): ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.02 (s, 9 H), 1.17–1.20 (m, 2 H), 1.245 (t, *J* = 7.3 Hz, 3 H), 1.249 (t, *J* = 7.1 Hz, 3 H), 2.99 (d, *J* = 2.8 Hz, 1 H), 3.01 (d, *J* = 2.8 Hz, 1 H), 4.17–4.27 (m, 4 H), 4.91–5.00 (m, 2 H), 7.26–7.35 (m, 3 H), 7.42–7.44 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = –1.9, 14.1 (unresolved diastereotopic -$CO_2CH_2CH_3$), 17.6, 36.7, 61.6, 61.7, 63.0, 85.0, 87.2, 127.5, 128.1, 128.4, 136.7, 170.3, 170.4, 206.3 ppm. HRMS (EI): calcd. for $C_{21}H_{30}O_4Si$ 374.1913; found 374.1915.

Diethyl 2-Phenyl-2-[5-(triethylsilyl)penta-2,3-dienyl]propane-1,3-dioate (3bn): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50 (q, *J* = 8.0 Hz, 6 H), 0.91 (t, *J* = 8.0 Hz, 9 H), 1.22–1.24 (m, 2 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 2.94–3.05 (m, 2 H), 4.19–4.27 (m, 4 H), 4.92–4.97 (m, 2 H), 7.26–7.35 (m, 3 H), 7.42–7.44 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 3.2, 7.4, 12.5,

14.1 (unresolved diastereotopic -$CO_2CH_2CH_3$), 36.5, 61.61, 61.64, 62.9, 85.0, 87.3, 127.5, 128.1, 128.4, 136.7, 170.3, 170.4, 206.1 ppm. HRMS (EI): calcd. for $C_{24}H_{36}O_4Si$ 416.2383; found 416.2390.

Diethyl 2-[5-(Dimethylphenylsilyl)penta-2,3-dienyl]-2-phenylpropane-1,3-dioate (3cn): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.248 (s, 3 H), 0.251 (s, 3 H), 1.23 (t, J = 7.3 Hz, 3 H), 1.24 (t, J = 7.3 Hz, 3 H), 1.42–1.45 (m, 2 H), 2.92–2.95 (m, 2 H), 4.17–4.25 (m, 4 H), 4.91–4.97 (m, 2 H), 7.25–7.40 (m, 8 H), 7.46–7.49 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = –3.4, –3.3, 14.1 (unresolved diastereotopic -$CO_2CH_2CH_3$), 16.8, 36.5, 61.6, 61.7, 62.9, 85.3, 86.8, 127.5, 127.8, 128.1, 128.4, 129.1, 133.7, 136.7, 138.5, 170.3, 170.4, 206.5 ppm. HRMS (EI): calcd. for $C_{26}H_{32}O_4Si$ 436.2070; found 436.1956.

Diethyl 2-Phenyl-2-[5-(triisopropylsilyl)penta-2,3-dienyl]propane-1,3-dioate (3dn): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (br., 21 H), 1.24 (t, J = 7.3 Hz, 3 H), 1.25 (t, J = 7.4 Hz, 3 H), 1.31 (d, J = 2.5 Hz, 1 H), 1.33 (d, J = 2.5 Hz, 1 H), 2.94–3.05 (m, 2 H), 4.16–4.28 (m, 4 H), 4.90–5.03 (m, 2 H), 7.25–7.34 (m, 3 H), 7.41–7.43 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 10.3, 11.0, 14.1 (unresolved diastereotopic -$CO_2CH_2CH_3$), 18.8 (unresolved diastereotopic -SiCHMe_2), 36.3, 61.61, 61.64, 62.9, 85.1, 88.0, 127.5, 128.1, 128.4, 136.7, 170.3, 170.4, 206.1 ppm. HRMS (EI): calcd. for $C_{27}H_{42}O_4Si$ 458.2852; found 458.2834.

Palladium-Catalyzed Asymmetric Synthesis of (Allenylmethyl)silanes 3: Asymmetric synthesis of (allenylmethyl)silanes (*R*)-**3** was conducted according to the reported method.[7] The reaction conditions and the results are summarized in Table 2. A typical procedure is given for the preparation of (*R*)-**3am**: A mixture of $Pd(dba)_2$ (28.8 mg, 50.0 μmol), (*R*)-segphos (34.2 mg, 56.0 μmol), and **2m** (101 mg, 0.600 mmol) was dissolved in THF (5 mL). After stirring the solution at 40 °C for 15 min, (*Z*)-**1a** (110 mg, 0.500 mmol) was added by syringe. The mixture was stirred at this temperature for 24 h, then cooled to room temperature and filtered through a short pad of alumina to remove the precipitated inorganic salts. The alumina pad was washed with a small amount of Et_2O (3×), and the combined solution was evaporated to dryness under reduced pressure. The residue was purified by chromatography on alumina (hexane/Et_2O = 4:1) to afford allene (*R*)-**3am** (107 mg, 75%) as a colorless oil.

The enantiopurity of **3** was determined by HPLC analysis with a chiral stationary phase column. The HPLC analysis conditions and the specific optical rotation data are listed below.

(*R*)-3am: HPLC (Daicel Chiralpak AD-H, hexane/*i*PrOH = 200:1, 0.3 mL/min): t_R = 23.2 min, t_S = 29.4 min. $[\alpha]_D^{20}$ = –60.0 (c = 0.99, $CHCl_3$ for a sample of 79%*ee*).

(*R*)-3bm: HPLC (Daicel Chiralcel OD-H, hexane/*i*PrOH = 1000:1, 0.5 mL/min): t_S = 25.7 min, t_R = 28.4 min. $[\alpha]_D^{26}$ = –62.4 (c = 0.89, $CHCl_3$ for a sample of 80%*ee*).

(*R*)-3cm: HPLC (Daicel Chiralpak AD-H, hexane/*i*PrOH = 400:1, 0.5 mL/min): t_R = 23.9 min, t_S = 27.2 min. $[\alpha]_D^{25}$ = –60.2 (c = 0.97, $CHCl_3$ for a sample of 80%*ee*).

(*R*)-3dm: HPLC (Daicel Chiralcel OD-H, hexane/*i*PrOH = 1000:1, 0.5 mL/min): t_S = 24.0 min, t_R = 26.1 min. $[\alpha]_D^{26}$ = –132 (c = 1.00, $CHCl_3$ for a sample of 87%*ee*).

(*R*)-3an: HPLC (Daicel Chiralcel OD-H, hexane/*i*PrOH = 400:1, 0.5 mL/min): t_R = 25.8 min, t_S = 30.8 min. $[\alpha]_D^{26}$ = –57.8 (c = 1.01, $CHCl_3$ for a sample of 81%*ee*).

(*R*)-3dn: HPLC (Daicel Chiralcel OD-H, hexane/*i*PrOH = 1000:1, 1.0 mL/min): t_S = 22.7 min, t_R = 26.4 min. $[\alpha]_D^{25}$ = –118 (c = 0.86, $CHCl_3$ for a sample of 90%*ee*).

(*R*)-3ao: HPLC (Daicel Chiralpak AD-H, hexane/*i*PrOH = 100:1, 0.5 mL/min): t_R = 29.7 min, t_S = 32.8 min. $[\alpha]_D^{25}$ = –56.0 (c = 1.03, $CHCl_3$ for a sample of 62%*ee*).

(*R*)-3bo: HPLC (Daicel Chiralpak AD-H, hexane/*i*PrOH = 200:1, 0.5 mL/min): t_R = 54.3 min, t_S = 62.8 min. $[\alpha]_D^{25}$ = –87.2 (c = 1.01, $CHCl_3$ for a sample of 80%*ee*).

(*R*)-3do: HPLC (Daicel Chiralpak AD-H, hexane/*i*PrOH = 200:1, 0.5 mL/min): t_R = 21.7 min, t_S = 24.8 min. $[\alpha]_D^{27}$ = –109 (c = 0.95, $CHCl_3$ for a sample of 87%*ee*).

$TiCl_4$-Promoted S_E2' Reaction of (Allenylmethyl)silanes 3 with $RCH(OMe)_2$ 4: The reaction was performed according to a reported method[7] with slight modifications. The reaction conditions and results are summarized in Table 3. A typical procedure is given for the preparation of (*E*)-dimethyl 2-[3-(1-methoxy-2,2-dimethylpropyl)penta-2,4-dienyl]-2-methylpropane-1,3-dioate (**5mx**): Under a nitrogen atmosphere, to a solution of *t*BuCH(OMe)$_2$ (**4x**, 92.6 mg, 0.7 mmol) in CH_2Cl_2 (2 mL) was added a CH_2Cl_2 solution of $TiCl_4$ (1.0 M, 0.7 mL, 0.7 mmol). The solution was cooled to –78 °C and to this was added a CH_2Cl_2 solution (2 mL) of (allenylmethyl)silane (*R*)-**3am** (99.6 mg, 0.35 mmol, 78% *ee*) by cannula. The solution was stirred at this temperature for 1 h and then quenched with water. The reaction mixture was extracted with diethyl ether (3×), and the combined organic solution was washed with saturated aqueous NaCl and dried with anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (hexane/Et_2O = 4:1) to give diene **5mx** as a colorless oil.

The enantiopurity of **5mx** and **5my** was determined by HPLC analysis with a chiral stationary phase column. The HPLC analysis conditions and the specific optical rotation data are listed below.

(*S*)-5mx: HPLC (Daicel Chiralcel OD-H, double columns connected in series, hexane/*i*PrOH = 500:1, 0.8 mL/min): t_S = 71.3 min, t_R = 74.6 min. $[\alpha]_D^{20}$ = –1.1 (c = 1.01, $CHCl_3$ for a sample of 80%*ee*).

5my: HPLC (Daicel Chiralcel OD-H, hexane/*i*PrOH = 200:1, 1.0 mL/min): t_1 = 68.1 min, t_2 = 74.1 min. $[\alpha]_D^{20}$ = –10.4 (c = 0.99, $CHCl_3$ for a sample of 26%*ee*).

For the determination of the enantiopurity of (*S*)-**5nx**, the compound was derivatized by $LiAlH_4$ reduction in THF into the corresponding diol, which was analyzed by chiral HPLC (Daicel Chiralcel OD-H, double columns connected in series, hexane/*i*PrOH = 50:1, 1.0 mL/min): t_S = 182.6 min, t_R = 193.4 min.

The absolute configurations of both **5mx** and **5nx** were determined as follows.[7] Diene **5** was treated with a mixture of K_2CO_3/$NaIO_4$/$KMnO_4$ (6 equiv./16 equiv-/2.3 equiv.) in *t*BuOH/H_2O (1:2) for 12 h. By this treatment, both **5mx** and **5nx** were converted into *t*BuCH(OMe)CO_2H. The crude carboxylic acid was treated with etherial CH_2N_2, and then the obtained methyl ester was purified by vacuum transfer. The absolute configuration of the ester from both **5mx** and **5nx**, *t*BuCH(OMe)CO_2Me, was determined to be (*S*) by comparison of retention time on the chiral HPLC with that of an authentic sample (*S*)-*t*BuCH(OMe)CO_2Me, which was prepared from commercially available (*S*)-*t*BuCH(OH)CO_2H (Aldrich). The methyl ester *t*BuCH(OH)CO_2Me was too volatile to be purified in a small scale, and thus determination of the absolute configuration by the signs of optical rotation was abandoned.

Dienes **5mx** and **5my** were characterized by comparison of its spectroscopic data with those reported previously.[7] The characterization data of **5nx** and the diol derived from **5nx** are listed below.

(*S*)-(*E*)-Diethyl 2-[3-(1-Methoxy-2,2-dimethylpropyl)penta-2,4-dienyl]-2-phenylpropane-1,3-dioate (5nx): ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 0.79 (s, 9 H), 1.239 (t, J = 7.3 Hz, 3 H), 1.242 (t, J = 7.3 Hz, 3 H), 3.04 (s, 3 H), 3.25 (dd, J = 6.9, 16.1 Hz, 1 H), 3.34 (dd, J = 7.6, 16.1 Hz, 1 H), 3.41 (s, 1 H), 4.16–4.28 (m, 4 H), 5.17 (d, J = 11.4 Hz, 1 H), 5.25 (d, J = 18.3 Hz, 1 H), 5.42 (t, J = 7.1 Hz, 1 H), 6.53 (dd, J = 11.4, 18.3 Hz, 1 H), 7.24–7.33 (m, 3 H), 7.40–7.42 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.0 (unresolved diastereotopic -$CO_2CH_2CH_3$), 26.8, 34.2, 35.7, 56.6, 61.7 (unresolved diastereotopic -$CO_2CH_2CH_3$), 62.5, 89.7, 116.1, 126.1, 127.6, 128.2, 128.4, 134.0, 136.6, 137.5, 170.5 (unresolved diastereotopic -$CO_2CH_2CH_3$) ppm. HRMS (EI): calcd. for $C_{24}H_{34}O_5$ 402.2406; found 402.2406. $C_{24}H_{34}O_5$ (402.53): calcd. C 71.61, H 8.51; found C 71.54, H 8.59. $[a]_D^{25}$ = –6.2 (c = 1.02, $CHCl_3$ for a sample of 75%*ee*).

(*S*)-(*E*)-2-[3-(1-Methoxy-2,2-dimethylpropyl)penta-2,4-dienyl]-2-phenylpropane-1,3-diol: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.74 (s, 9 H), 2.52 (br., 2 H), 2.61 (dd, J = 7.4, 15.1 Hz, 1 H), 2.69 (dd, J = 7.8, 15.1 Hz, 1 H), 3.00 (s, 3 H), 3.40 (s, 1 H), 3.91–3.94 (m, 2 H), 4.06–4.09 (m, 2 H), 5.14 (d, J = 11.4 Hz, 1 H), 5.22 (d, J = 17.4 Hz, 1 H), 5.25 (t, J = 7.8 Hz, 1 H), 6.56 (dd, J = 11.4, 17.4 Hz, 1 H), 7.19–7.23 (m, 1 H), 7.30–7.35 (m, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 26.8, 32.0, 35.7, 47.9, 56.7, 68.2, 68.3, 89.5, 115.7, 126.7, 126.8, 127.1, 128.8, 134.3, 137.0, 141.2 ppm. HRMS (FAB): calcd. for $C_{20}H_{30}NaO_3$ $[M + Na]^+$ 341.2093; found 341.2103.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and ^{13}C NMR spectra for all new compounds and key known compounds.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformations of Carbon Resources" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Received: November 11, 2011
Published Online: January 30, 2012

