CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200601326

Titanocene(II)-Promoted Multicomponent Reactions Utilizing Alkynyl Sulfones, Alkenyl Sulfones, and Carbonyl Compounds: A Novel Method for the Synthesis of Vinylallenes

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Abstract: Titanocene(II)-promoted cross coupling of alkynyl- and (*Z*)-alkenyl sulfones affords α-(phenylsulfonyl)alkenyltitanium species. Further treatment of these species with the titanocene(II) reagent generates titanium vinylvinylidene complexes, which react with carbonyl compounds in one pot to produce substituted vinylallenes with complete stereoselectivity. By using α,β-unsaturated ketones, 1,3,4,6-tetraenes are also obtained stereoselectively.

Keywords: allenes · cross-coupling · ketones · multicomponent reactions · olefination

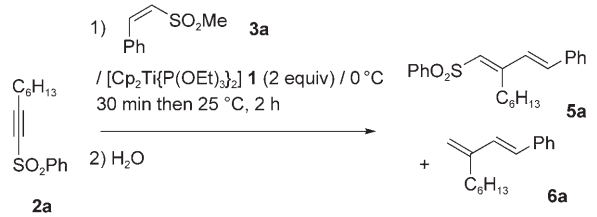
Introduction

Multicomponent reactions are useful and efficient methods in organic synthesis.[1] The major advantages of these reactions are 1) a single purification step, 2) higher yields than the stepwise assembly, 3) the use of simple and diverse modules to construct complex molecules, and 4) the use of only a single promoter or catalyst. These advantages make this approach suitable for combinatorial synthesis. In the last decade, late transition-metal-catalyzed (Pd,[2] Rh,[3] Ni,[4] and Ru[5]) multicomponent reactions have been extensively studied. The low-valent group 4 metal species were also employed for the multicomponent reactions.[6] For example, preparations of aromatic and heteroaromatic compounds have been achieved by divalent titanium[7] and zirconium[8] species-mediated couplings of alkynes and nitriles, which involve the cycloaddition of intermediary five-membered metallacycles with multiple bonds.

Recently we disclosed a novel methodology for the cross-coupling of unsaturated compounds promoted by the titanocene(II) species $[Cp_2Ti\{P(OEt)_3\}_2]$ **1** (Scheme 1) via the formation of five-membered titanacycles.[9] Alkenylation of carbonyl compounds with vinyl pivalate or (*Z*)-alkenyl sulfones proceeds by simply mixing these compounds with **1**, and conjugated dienes are obtained with high stereoselectivity by the reaction of the alkenyl sulfones with alkynes. Considering its reaction pathway, we expected that this new cross-coupling would have the potential for a wide variety of applications. Here we describe synthesis of vinylallenes by the three-component reaction of alkynyl sulfones **2**, (*Z*)-alkenyl sulfones **3**, and carbonyl compounds **4** promoted by the low-valent titanium species **1**.

Results and Discussion

When the alkynyl phenyl sulfone **2a** was treated with a small excess of (*Z*)-alkenyl methyl sulfone **3a** at 0 to 25 °C for 2.5 h, the (*E*,*E*)-dienyl sulfone **5a** was produced with complete stereoselectivity along with a small amount of the conjugated diene **6a** (Scheme 1; entry 1, Table 1). The yield



Scheme 1. Titanocene(II) **1**-promoted cross-coupling of the alkynyl- and (*Z*)-alkenyl sulfones **2a** and **3a**.

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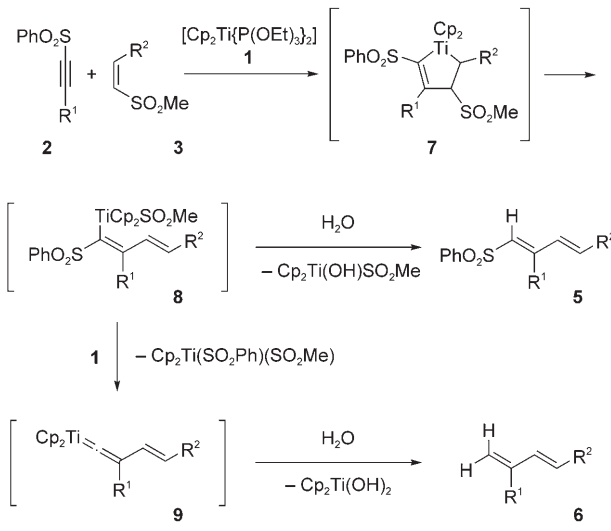
Table 1. Titanocene(II) **1**-promoted reaction of **2a** with **3a**.

Entry	**2a** [equiv]	**3a** [equiv]	Yield **5a** [%]	Yield **6a** [%]
1	1.0	1.2	35	8
2	1.0	1.5	54	6
3	1.0	2.0	51	6
4[a]	1.2	1.0	38	6

[a] (*E*)-2-Hexyl-1-(phenylsulfonyl)-1-decen-3-yne was produced in 24% yield.

of **5a** was significantly increased by the use of an excess amount of the (*Z*)-alkenyl sulfone **3a** (entry 2, Table 1). On the contrary, the use of an excess amount of **2a** gave a rather complex mixture and the yield of the coupling product **5a** was decreased due to the concomitant formation of the self-coupling product of **2a**, (*E*)-2-hexyl-1-(phenylsulfonyl)-1-decen-3-yne (entry 4, Table 1).

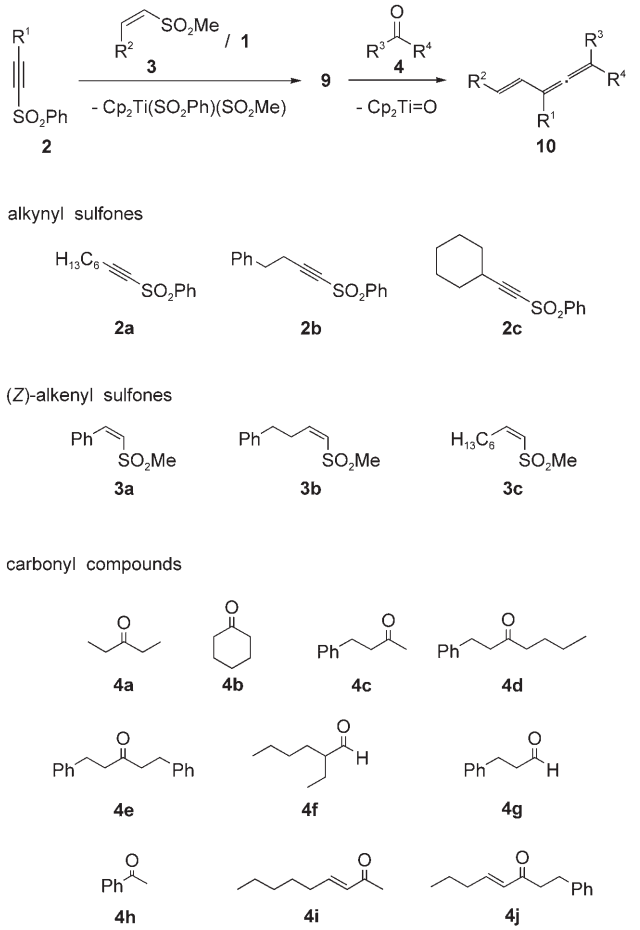
The formation of dienyl sulfone **5** is explained by the regioselective construction of the titanacyclopentene intermediate **7** (Scheme 2). The following elimination of the



Scheme 2. Plausible pathway for the cross-coupling of alkynyl- and (*Z*)-alkenyl sulfones **2** and **3** in the presence of the titanocene(II) reagent **1**.

methylsulfonyl group from **7** produces the α-(phenylsulfonyl)dienyltitanium species **8** which affords the dienyl sulfone **5** on hydrolysis. The formation of the conjugated diene **6** is of great interest because it suggests that the vinylvinylidene complex of titanium **9** can be produced by further reaction of **8** with the titanocene(II) reagent **1**.

Above results indicate that the titanocene(II) reagent **1** promotes both the tandem cross-coupling of unsaturated sulfones **2** and **3** and the reductive desulfurization of the resulting 1-titanio-1-(phenylsulfonyl)-1,3-dienes **8** to produce the titanium vinylvinylidene complexes **9**. Preparation and reactions of nucleophilic titanium carbene complexes have been extensively studied, and these organotitanium species are employed as synthetic reagents or catalysts in a wide range of organic syntheses, such as carbonyl olefination[10] and olefin metathesis.[11] Recently, we reported that titanium vinylvinylidene complexes, generated from the reaction of 1,1-dichloro-1,3-dienes with **1**, reacted with ketones[12] and alkynes[13] to produce vinylallenes and conjugated trienes, respectively. On the basis of the above, we, therefore, examined one-pot assembly of vinylallenes **10** by using unsaturated sulfones **2**, **3** and carbonyl compounds **4** (Scheme 3).



Scheme 3. Formation of vinylallenes by the titanocene(II) **1**-promoted three-component reaction.

As was expected, the reaction of the organotitanium species, generated by the treatment of the sulfones **2a** and **3c** with **1** at 0 to 25°C for 1.5 h, with a small excess of 1,5-diphenylpentan-3-one **4e** gave the vinylallene **10h** (entry 1, Table 2). A slight increase of the yield of **10h** was observed when two equivalents of **4e** and six equivalents of **1** were used (entry 3, Table 2).

In a similar fashion, various vinylallenes **10** were readily obtained by the successive addition of different alkynyl phenyl sulfones **2**, (*Z*)-alkenyl methyl sulfones **3**,[14] and carbonyl compounds **4** to a THF solution of the titanocene(II) reagent **1** (Tables 3 and 4). Although (*Z*)-alkenyl phenyl sulfones can also be employed in this reaction, their preparation is troublesome because of photoisomerization of their

Table 2. Three-component reaction between **2a**, **3c**, and **4e**.[a]

Entry	**1** [equiv]	**4e** [equiv]	Yield **10h** [%]
1	5.0	1.2	59
2	5.0	2.0	55
3	6.0	2.0	65
4	6.0	4.0	64

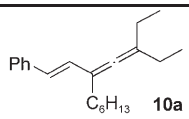
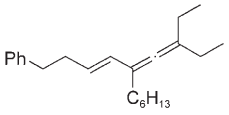
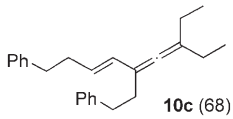
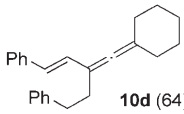
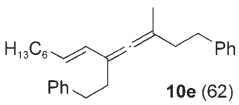
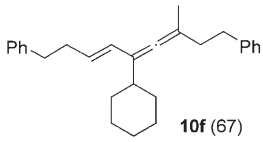
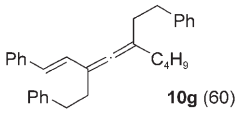
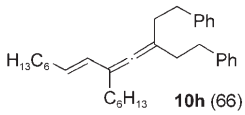
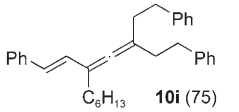
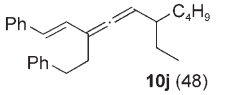
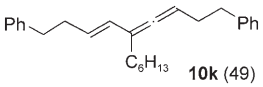
[a] The coupling of **2a** and **3c** (1.5 equiv) was carried out at 0 °C for 30 min and then at 25 °C for 1 h. The resulting organotitanium species was treated with **4e** at 25 °C for 1 h.

precursors, (*Z*)-alkenyl sulfides.[15] Trisubstituted allenes **10j** and **10k** were also obtained by the use of aldehydes **4f** and **4g** as the third components, though the yields were moderate (entries 10 and 11, Table 3). The aromatic and α,β-unsaturated ketones **4h–j** can be employed for the assembly of doubly conjugated allenes **10l–n** (Table 4).

As listed in Tables 3 and 4, all the vinylallenes **10** were obtained with complete stereoselectivity; the configuration of the double bond originating from (*Z*)-alkenyl sulfones is *E*, suggesting that the formation of the titanacycle **7** proceeds with retention of configuration of **3**. The subsequent *syn* elimination of the methylsulfonyl group via the conformation **7A** affords the dienyltitanium species **8A** stereoselectively (Scheme 4). Preferential *syn* elimination over *anti* elimination could be due to the intramolecular coordination of the sulfonyl oxygen to the titanium atom.

Vinylallenes are useful synthetic intermediates for the construction of a variety of cyclic compounds by Diels–Alder reactions,[16] transition-metal-catalyzed cycloadditions,[17] thermal electrocyclic reactions,[18] and cheletropic SO_2 addition.[19] The major route to vinylallenes utilizes substitution of α-[16e,20] or γ-ethynylallyl alcohol derivatives.[18a,21] γ-Vinylpropargyl alcohol derivatives are also employed as starting materials for this preparation.[16f,g,h,22] Synthesis of vinylallenes by the reaction of vinylmetals with propargyl alcohol derivatives,[18b,23] conjugate addition of organocuprates to acetylenic Michael acceptors,[16d] palladium-catalyzed coupling of alkenyl halides with allenylindium reagents,[17f,24] and the Wittig–Horner reaction using 1-lithio-1,3-dienyl phosphine oxides[25] have also been reported. These preparations, however, sometimes suffer from the difficulties in obtaining appropriate starting materials. The present one-pot assembly of vinylallenes enjoys the advantage that a variety of vinyl- and divinylallenes are obtained by using readily available starting materials.

Table 3. Preparation of vinylallenes by using aliphatic ketones and aldehydes.

Entry	**2**	**3**	**4**	Yield **10** [%]
1[a]	**2a**	**3a**	**4a**	 **10a** (73)
2[a]	**2a**	**3b**	**4a**	 **10b** (74)
3[a]	**2b**	**3b**	**4a**	 **10c** (68)
4[a]	**2b**	**3a**	**4b**	 **10d** (64)
5[a]	**2b**	**3c**	**4c**	 **10e** (62)
6[a]	**2c**	**3b**	**4c**	 **10f** (67)
7[a]	**2b**	**3a**	**4d**	 **10g** (60)
8[a]	**2a**	**3c**	**4e**	 **10h** (66)
9[a]	**2a**	**3a**	**4e**	 **10i** (75)
10[b]	**2b**	**3a**	**4f**	 **10j** (48)
11[b]	**2a**	**3b**	**4g**	 **10k** (49)

[a] Performed with the general procedure A described in the Experimental Section. [b] Performed with the general procedure B described in the Experimental Section.

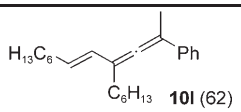
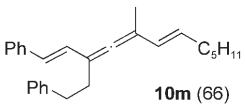
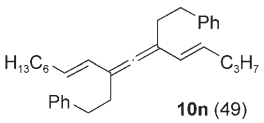
Conclusion

We have established a novel multicomponent reaction promoted by the low-valent titanium species **1**, which consists of 1) cross-coupling of alkynyl- and (*Z*)-alkenyl sulfones, 2) generation of the titanium vinylvinylidene complexes, and 3) olefination of carbonyl compounds. Since titanium carbene complexes are versatile tools for organic synthesis,[26] the present formation of vinylvinylidene complexes provides a novel approach for the construction of acyclic unsaturated systems.

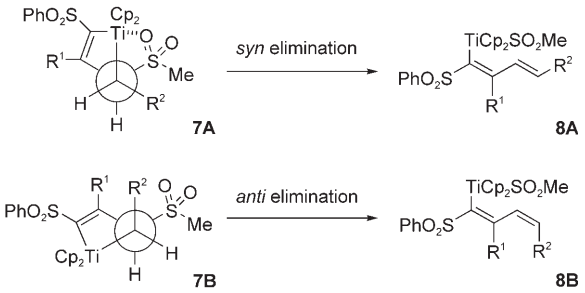
Experimental Section

General considerations: ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ by using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are quoted in parts per million from TMS

Table 4. Preparation of vinylallenes by using aromatic and α,β-unsaturated ketones.[a]

Entry	2	3	4	Yield 10 [%]
1	**2a**	**3c**	**4h**	 **10l** (62)
2	**2b**	**3a**	**4i**	 **10m** (66)
3	**2b**	**3c**	**4j**	 **10n** (49)

[a] Performed with the general procedure C described in the Experimental Section.



Scheme 4. Stereochemistry of elimination.

for ^{1}H and $CDCl_3$ for ^{13}C spectroscopy. IR absorptions are reported in cm^{-1}. All reactions were performed under an argon atmosphere in dried glassware. THF was distilled from sodium and benzophenone. Preparative thin layer chromatography (PTLC) was carried out by using Wakogel B-5F.

Reaction of 1-(phenylsulfonyl)-1-octyne (2a) with (*Z*)-1-(methylsulfonyl)-2-phenylethene (3a): Finely powdered molecular sieves 4 Å (60 mg), magnesium turnings (16 mg, 0.66 mmol), and $[Cp_2TiCl_2]$ (149 mg, 0.6 mmol) were placed in a flask and dried by heating with a heat gun in vacuo (2–3 mmHg). After cooling, THF (1.5 mL) and $P(OEt)_3$ (0.21 mL, 1.2 mmol) were added successively with stirring at 25 °C. After 3 h, the reaction mixture was cooled to 0 °C. A THF (1 mL) solution of **3a** (82 mg, 0.45 mmol) was added dropwise over 5 min to the mixture and then the mixture was stirred for 30 min. Next, a THF (1 mL) solution of **2a** (75 mg, 0.3 mmol) was added dropwise over 10 min, stirring was continued for 30 min at 0 °C and then for 2 h at 25 °C. The reaction was quenched by addition of 1 M NaOH, and the insoluble materials were filtered off through Celite and washed with ether. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were dried (Na_2SO_4) and the solvent was evaporated. Purification of the residue by PTLC (hexane/AcOEt 4:1) gave (1*E*,3*E*)-2-hexyl-4-phenyl-1-(phenylsulfonyl)buta-1,3-diene (**5a**) (57 mg, 54%) and (*E*)-3-hexyl-1-phenylbuta-1,3-diene (**6a**) (4 mg, 6%).

Compound ***5a***: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.96$ (d, $J = 7.0$ Hz, 2H), 7.65–7.49 (m, 3H), 7.46–7.24 (m, 5H), 6.93 (d, $J = 16.1$ Hz, 1H), 6.57 (d, $J = 16.1$ Hz, 1H), 6.36 (s, 1H), 2.83 (t, $J = 7.7$ Hz, 2H), 1.60–1.15 (m, 8H), 0.90 ppm (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.4$, 142.5, 135.6, 135.4, 133.0, 129.13, 129.09, 128.8, 128.3, 128.0, 127.2, 127.1, 31.5, 29.7, 29.6, 27.4, 22.5, 14.0 ppm; IR (neat): $\tilde{\nu} = 2928$, 2858, 1622, 1568, 1447, 1305, 1146, 1085, 964, 752, 720, 688, 648 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{26}O_2S$: C 74.54, H 7.39; found: C 74.50, H 7.63.

Compound ***6a***: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.48$–7.14 (m, 5H), 6.81 (d, $J = 16.1$ Hz, 1H), 6.58 (d, $J = 16.3$ Hz, 1H), 5.13 (d, $J = 1.6$ Hz, 1H), 5.05 (d, $J = 1.1$ Hz, 1H), 2.32 (dt, $J = 0.4$, 7.7 Hz, 2H), 1.47–1.14 (m, 8H), 0.90 ppm (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.4$, 137.5, 131.2, 128.6, 127.9, 127.3, 126.4, 116.0, 32.1, 31.7, 29.3, 28.3, 22.6, 14.1 ppm; IR (neat): $\tilde{\nu} = 3026$, 2927, 2857, 1729, 1603, 1494, 1449, 1072, 961, 886, 753, 693 cm^{-1}.

Preparation of vinylallenes 10

General procedure A: THF (1.5 mL) and $P(OEt)_3$ (0.41 mL, 2.4 mmol) were added successively with stirring at 25 °C to a flask charged with finely powdered molecular sieves 4 Å (120 mg), magnesium turnings (32 mg, 1.3 mmol), and $[Cp_2TiCl_2]$ (299 mg, 1.2 mmol). After 3 h, the reaction mixture was cooled to 0 °C. A THF (1 mL) solution of **3a** (55 mg, 0.3 mmol) was added dropwise over 5 min to the mixture and it was stirred for 15 min. Next, a THF (1 mL) solution of **2a** (50 mg, 0.2 mmol) was added dropwise over 10 min, stirring was continued for 30 min at 0 °C and then for 1 h at 25 °C. A THF (1 mL) solution of **4a** (35 mg, 0.4 mmol) was added to the reaction mixture, which was further stirred for 1 h. The reaction was quenched by addition of 1 M NaOH, and the insoluble materials were filtered off through Celite and washed with ether. The layers were separated, and the aqueous layer was extracted with ether. After the combined organic extracts were dried (K_2CO_3), the solvent was evaporated. Purification of the residue by PTLC (hexane) gave (*E*)-5-ethyl-3-hexyl-1-phenylhepta-1,3,4-triene (**10a**) (41 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.10 (m, 5H), 6.69 (d, $J = 16.3$ Hz, 1H), 6.43 (d, $J = 16.3$ Hz, 1H), 2.23 (t, $J = 7.5$ Hz, 2H), 2.03 (q, $J = 7.4$ Hz, 4H), 1.59–1.23 (m, 8H), 1.01 (t, $J = 7.3$ Hz, 6H), 0.90 ppm (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 204.1$, 138.0, 129.4, 128.5, 126.7, 126.0, 125.3, 109.2, 107.6, 31.9, 29.4, 29.1, 28.0, 26.0, 22.7, 14.1, 12.5 ppm; IR (neat): $\tilde{\nu} = 3025$, 2928, 1938, 1621, 1599, 1494, 1456, 1376, 1323, 1072, 957, 747, 691 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{30}$: C 89.29, H 10.71; found: C 89.34, H 11.07.

(*E*)-3-Ethyl-5-hexyl-9-phenylnona-3,4,6-triene (10b): The reaction was carried out according to general procedure A by using **2a** (50 mg, 0.2 mmol), **3b** (63 mg, 0.3 mmol), and **4a** (35 mg, 0.4 mmol) to produce **10b** (46 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$–7.11 (m, 5H), 5.95 (d, $J = 15.8$ Hz, 1H), 5.57 (dt, $J = 15.6$, 6.9 Hz, 1H), 2.73 (t, $J = 7.9$ Hz, 2H), 2.47–2.30 (m, 2H), 2.08 (t, $J = 7.4$ Hz, 2H), 1.98 (q, $J = 7.4$ Hz, 4H), 1.55–1.19 (m, 8H), 0.97 (t, $J = 7.3$ Hz, 6H), 0.89 ppm (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 202.1$, 142.1, 130.0, 128.5, 128.2, 126.3, 125.7, 108.7, 106.8, 36.2, 35.0, 31.9, 29.4, 29.3, 28.0, 26.0, 22.7, 14.1, 12.6 ppm; IR (neat): $\tilde{\nu} = 3026$, 2927, 1941, 1604, 1496, 1454, 1376, 1324, 1031, 962, 745, 698 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{34}$: C 88.96, H 11.04; found: C 89.33, H 10.82.

(*E*)-3-Ethyl-5-phenethyl-9-phenylnona-3,4,6-triene (10c): The reaction was carried out according to general procedure A by using **2b** (54 mg, 0.2 mmol), **3b** (63 mg, 0.3 mmol), and **4a** (35 mg, 0.4 mmol) to produce **10c** (45 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.09 (m, 10H), 5.98 (d, $J = 15.8$ Hz, 1H), 5.60 (dt, $J = 15.8$, 6.9 Hz, 1H), 2.85–2.61 (m, 4H), 2.54–2.33 (m, 4H), 1.95 (q, $J = 7.3$ Hz, 4H), 0.94 ppm (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 202.1$, 142.6, 142.0, 129.7, 128.43, 128.36, 128.3, 128.2, 126.5, 125.73, 125.65, 109.5, 106.3, 36.2, 35.0, 34.3, 31.1, 26.0, 12.5 ppm; IR (neat): $\tilde{\nu} = 3085$, 3061, 3026, 2963, 2929, 1941, 1604, 1496, 1454, 1374, 1324, 1077, 1030, 962, 746, 698 cm^{-1}; elemental analysis calcd (%) for $C_{25}H_{30}$: C 90.85, H 9.15; found: C 90.94, H 9.54.

[2-Phenethyl-2-(*E*)-(phenylethenyl)ethenylidene]cyclohexane (10d): The reaction was carried out according to general procedure A by using **2b** (54 mg, 0.2 mmol), **3a** (55 mg, 0.3 mmol), and **4b** (39 mg, 0.4 mmol) to produce **10d** (40 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.08 (m, 10H), 6.71 (d, $J = 16.3$ Hz, 1H), 6.43 (d, $J = 16.3$ Hz, 1H), 2.83 (t, $J = 7.8$ Hz, 2H), 2.55 (t, $J = 7.8$ Hz, 2H), 2.08 (t, $J = 5.5$ Hz, 4H), 1.72–1.44 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 201.9$, 142.3, 137.9, 128.9, 128.5, 128.4, 128.2, 126.8, 126.0, 125.7, 125.6, 104.1, 102.6, 34.0, 31.5, 30.6, 27.6, 26.1 ppm; IR (neat): $\tilde{\nu} = 3025$, 2927, 2852, 1942, 1621, 1599, 1496, 1446, 1265, 958, 908, 747, 693 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{26}$: C 91.67, H 8.33; found: C 91.73, H 8.51.

(*E*)-3-Methyl-5-phenethyl-1-phenyltrideca-3,4,6-triene (10e): The reaction was carried out according to general procedure A by using **2b**

(54 mg, 0.2 mmol), **3c** (57 mg, 0.3 mmol), and **4c** (59 mg, 0.4 mmol) to produce **10e** (46 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.10 (m, 10H), 5.81 (d, J = 15.8 Hz, 1H), 5.53 (dt, J = 15.8, 6.9 Hz, 1H), 2.75–2.56 (m, 4H), 2.45–2.30 (m, 2H), 2.24 (t, J = 7.8 Hz, 2H), 2.07 (dt, J = 7.0, 6.7 Hz, 2H), 1.65 (s, 3H), 1.45–1.19 (m, 8H), 0.89 ppm (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.1, 142.5, 142.2, 128.5, 128.4, 128.3, 128.2, 125.7, 125.6, 104.1, 100.1, 36.0, 34.0, 33.0, 31.7, 30.8, 29.6, 28.9, 22.6, 19.2, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 3061, 3026, 2925, 2854, 1945, 1604, 1496, 1454, 1367, 1194, 1076, 1031, 963, 746, 697 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{36}$: C 90.26, H 9.74; found: C 90.33, H 10.03.

(*E*)-5-Cyclohexyl-3-methyl-1,9-diphenylnona-3,4,6-triene (10f): The reaction was carried out according to general procedure A by using **2c** (50 mg, 0.2 mmol), **3b** (63 mg, 0.3 mmol) and **4c** (59 mg, 0.4 mmol) to produce **10f** (50 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.12 (m, 10H), 5.73 (d, J = 15.8 Hz, 1H), 5.58 (dt, J = 15.8, 6.6 Hz, 1H), 2.79–2.62 (m, 4H), 2.43–2.22 (m, 4H), 2.01 (tt, J = 11.4, 3.0 Hz, 1H), 1.85–1.58 (m, 5H), 1.73 (s, 3H), 1.38–0.90 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.0, 142.3, 142.1, 128.5, 128.41, 128.37, 128.3, 128.2, 127.0, 125.73, 125.67, 110.5, 100.7, 37.8, 36.2, 36.1, 35.0, 34.1, 33.1, 32.9, 26.71, 26.69, 26.4, 19.4 ppm; IR (neat): $\tilde{\nu}$ = 3085, 3061, 3026, 2924, 2850, 1942, 1604, 1496, 1451, 1367, 1336, 1199, 1177, 1076, 1031, 964, 746, 698 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{34}$: C 90.75, H 9.25; found: C 90.65, H 9.19.

(*E*)-3,5-Diphenethyl-1-phenylnona-1,3,4-triene (10g): The reaction was carried out according to general procedure A by using **2b** (54 mg, 0.2 mmol), **3a** (55 mg, 0.3 mmol), and **4d** (76 mg, 0.4 mmol) to produce **10g** (49 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.06 (m, 15H), 6.56 (d, J = 16.3 Hz, 1H), 6.42 (d, J = 16.3 Hz, 1H), 2.85–2.58 (m, 4H), 2.52 (t, J = 7.4 Hz, 2H), 2.30 (t, J = 7.8 Hz, 2H), 2.00 (t, J = 7.0 Hz, 2H), 1.44–1.19 (m, 4H), 0.89 ppm (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.8, 142.3, 142.0, 137.8, 128.7, 128.5, 128.41, 128.39, 128.3, 128.2, 126.8, 126.1, 125.80, 125.77, 125.7, 106.2, 105.6, 34.4, 34.0, 33.9, 32.7, 30.7, 29.9, 22.5, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 3083, 3060, 3026, 2925, 2856, 1939, 1621, 1602, 1495, 1453, 1073, 1030, 958, 747, 695 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{34}$: C 91.57, H 8.43; found: C 91.56, H 8.28.

(*E*)-5-Hexyl-3-phenethyl-1-phenyltrideca-3,4,6-triene (10h): The reaction was carried out according to general procedure A by using **2a** (50 mg, 0.2 mmol), **3c** (57 mg, 0.3 mmol), and **4e** (95 mg, 0.4 mmol) to produce **10h** (58 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.10 (m, 10H), 5.72 (d, J = 15.8 Hz, 1H), 5.50 (dt, J = 15.8, 6.8 Hz, 1H), 2.70 (t, J = 7.9 Hz, 4H), 2.31 (t, J = 7.7 Hz, 4H), 2.13–1.92 (m, 4H), 1.45–1.17 (m, 16H), 0.89 ppm (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.8, 142.3, 128.7, 128.4, 128.2, 128.1, 125.7, 106.9, 103.9, 34.9, 34.2, 33.0, 31.9, 31.8, 29.6, 29.4, 29.2, 29.0, 27.9, 22.7, 22.6, 14.15, 14.12 ppm; IR (neat): ν = 3085, 3062, 3026, 2925, 1941, 1604, 1496, 1454, 1378, 1336, 1196, 1072, 1031, 963, 905, 745, 698 cm^{-1}; elemental analysis calcd (%) for $C_{33}H_{46}$: C 89.53, H 10.47; found: C 89.61, H 10.84.

(*E*)-3-Hexyl-5-phenethyl-1,7-diphenylhepta-1,3,4-triene (10i): The reaction was carried out according to general procedure A by using **2a** (50 mg, 0.2 mmol), **3a** (55 mg, 0.3 mmol), and **4e** (95 mg, 0.4 mmol) to produce **10i** (65 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.12 (m, 15H), 6.43 (d, J = 16.3 Hz, 1H), 6.36 (d, J = 16.3 Hz, 1H), 2.74 (t, J = 7.8 Hz, 4H), 2.37 (t, J = 7.6 Hz, 4H), 2.15 (t, J = 7.1 Hz, 2H), 1.46–1.18 (m, 8H), 0.90 ppm (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.0, 142.0, 137.9, 128.7, 128.46, 128.42, 128.2, 126.8, 126.1, 125.8, 125.7, 107.5, 104.2, 34.7, 34.0, 31.8, 29.4, 29.0, 27.9, 22.7, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 3060, 3026, 2925, 2855, 1939, 1620, 1602, 1496, 1453, 1073, 1030, 959, 747, 696 cm^{-1}; elemental analysis calcd (%) for $C_{33}H_{38}$: C 91.19, H 8.81; found: C 91.08, H 8.83.

General procedure B: THF (1.5 mL) and $P(OEt)_3$ (0.34 mL, 2.0 mmol) were added successively with stirring at 25°C to a flask charged with finely powdered molecular sieves 4 Å (100 mg), magnesium turnings (27 mg, 1.1 mmol), and [Cp_2TiCl_2] (249 mg, 1.0 mmol). After 3 h, the reaction mixture was cooled to 0°C. A THF (1 mL) solution of **3a** (55 mg, 0.3 mmol) was added dropwise over 5 min to the mixture and it was stirred for 15 min. Next, a THF (1 mL) solution of **2b** (54 mg, 0.2 mmol) was added dropwise over 10 min, stirring was continued for 30 min at 0°C and then for 2 h at 25°C. A THF (1 mL) solution of **4f** (103 mg, 0.8 mmol) was added to the reaction mixture, which was further stirred for 1 h. The usual workup and purification gave (*E*)-6-ethyl-3-phenethyl-1-phenyldeca-1,3,4-triene (**10j**) (33 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.14 (m, 10H), 6.69 (d, J = 16.3 Hz, 1H), 6.47 (d, J = 16.3 Hz, 1H), 5.18 (d, J = 7.9 Hz, 1H), 2.84 (t, J = 8.1 Hz, 2H), 2.62–2.48 (m, 2H), 2.02–1.87 (m, 1H), 1.56–1.17 (m, 8H), 1.03–0.79 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.0, 142.3, 137.7, 128.6, 128.4, 128.3, 128.0, 127.9, 127.0, 126.4, 126.1, 125.8, 104.8, 97.0, 41.6, 34.7, 34.5, 34.3, 30.9, 29.6, 29.5, 28.2, 28.1, 22.8, 22.7, 14.2, 14.1, 11.9, 11.7 ppm; IR (neat): $\tilde{\nu}$ = 3026, 2956, 2926, 2857, 1939, 1602, 1495, 1453, 958, 746, 693 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{32}$: C 90.64, H 9.36; found: C 90.60, H 9.63.

(*E*)-5-Hexyl-1,9-diphenylnona-3,4,6-triene (10k): The reaction was carried out according to general procedure B by using **2a** (50 mg, 0.2 mmol), **3b** (63 mg, 0.3 mmol), and **4g** (107 mg, 0.8 mmol) to produce **10k** (35 mg, 49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.08 (m, 10H), 5.85 (d, J = 15.8 Hz, 1H), 5.70–5.46 (m, 1H), 5.36–5.19 (m, 1H), 2.72 (t, J = 7.0 Hz, 2H), 2.69 (t, J = 6.8 Hz, 2H), 2.48–2.22 (m, 4H), 2.13–1.92 (m, 2H), 1.46–1.15 (m, 8H), 0.89 ppm (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.7, 142.0, 141.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.5, 125.8, 125.7, 105.2, 91.1, 36.1, 35.5, 34.9, 31.8, 30.9, 29.2, 28.8, 27.7, 22.7, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 3062, 3026, 2925, 2855, 1942, 1604, 1496, 1454, 1030, 963, 744, 698 cm^{-1}; elemental analysis calcd (%) for $C_{27}H_{34}$: C 90.44, H 9.56; found: C 90.13, H 9.60.

General procedure C: THF (1.5 mL) and $P(OEt)_3$ (0.34 mL, 2.0 mmol) were added successively with stirring at 25°C to a flask charged with finely powdered molecular sieves 4 Å (100 mg), magnesium turnings (27 mg, 1.1 mmol), and [Cp_2TiCl_2] (249 mg, 1.0 mmol). After 3 h, the reaction mixture was cooled to 0°C. A THF (1 mL) solution of **3c** (57 mg, 0.3 mmol) was added dropwise over 5 min to the mixture and it was stirred for 15 min. Next, a THF (1 mL) solution of **2a** (50 mg, 0.2 mmol) was added dropwise over 10 min, stirring was continued for 30 min at 0°C and then for 2 h at 25°C. After the reaction mixture had been cooled to 0°C, a THF (1 mL) solution of **4h** (96 mg, 0.8 mmol) was added to the reaction mixture, which was further stirred for 13 h at 0°C. The usual workup and purification gave (*E*)-4-hexyl-2-phenyldodeca-2,3,5-triene (**10l**) (40 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.11 (m, 5H), 5.96 (d, J = 15.6 Hz, 1H), 5.67 (dt, J = 15.6, 6.9 Hz, 1H), 2.28–2.18 (m, 2H), 2.16–2.04 (m, 2H), 2.10 (s, 3H), 1.56–1.16 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H), 0.85 ppm (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.7, 137.8, 129.7, 128.2, 127.2, 126.3, 125.7, 106.9, 101.1, 33.1, 31.8, 31.7, 29.5, 29.3, 29.2, 29.0, 27.7, 22.7, 22.6, 17.1, 14.10, 14.08 ppm; IR (neat): $\tilde{\nu}$ = 2955, 2925, 2855, 1929, 1599, 1493, 1464, 1377, 1065, 1027, 962, 724, 692 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{36}$: C 88.82, H 11.18; found: C 89.14, H 11.49.

(1*E*,6*E*)-5-Methyl-3-phenethyl-1-phenyldodeca-1,3,4,6-tetraene (10m): The reaction was carried out according to general procedure C by using **2b** (54 mg, 0.2 mmol), **3a** (55 mg, 0.3 mmol), and **4i** (112 mg, 0.8 mmol) to produce **10m** (47 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.10 (m, 10H), 6.68 (d, J = 16.3 Hz, 1H), 6.48 (d, J = 16.3 Hz, 1H), 5.86 (d, J = 15.6 Hz, 1H), 5.56 (dt, J = 15.6, 7.0 Hz, 1H), 2.82 (t, J = 7.6 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H), 2.09 (dt, J = 6.9, 6.9 Hz, 2H), 1.76 (s, 3H), 1.47–1.19 (m, 6H), 0.90 ppm (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.8, 142.1, 137.6, 130.1, 128.53, 128.48, 128.2, 127.6, 127.4, 127.0, 126.8, 126.1, 125.8, 104.0, 101.7, 33.9, 32.9, 31.5, 30.8, 29.2, 22.5, 15.5, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 3060, 3026, 2925, 2855, 1922, 1622, 1601, 1495, 1453, 1377, 1074, 1030, 960, 747, 693 cm^{-1}; elemental analysis calcd (%) for $C_{27}H_{32}$: C 90.95, H 9.05; found: C 91.17, H 9.43.

(4*E*,9*E*)-6,8-Diphenethylhexadeca-4,6,7,9-tetraene (10n): The reaction was carried out according to general procedure C by using **2b** (54 mg, 0.2 mmol), **3c** (57 mg, 0.3 mmol), and **4j** (162 mg, 0.8 mmol) to produce **10n** (42 mg, 49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.12 (m, 10H), 5.802 (d, J = 15.8 Hz, 1H), 5.798 (d, J = 15.8 Hz, 1H), 5.67–5.51 (m, 2H), 2.78–2.57 (m, 4H), 2.52–2.31 (m, 4H), 2.14–1.98 (m, 4H), 1.49–1.18 (m, 10H), 0.91 (t, J = 7.3 Hz, 3H), 0.89 ppm (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.2, 142.3, 129.2, 128.9, 128.5, 128.2, 127.7, 127.4, 125.7, 105.67, 105.66, 35.1, 34.0, 33.0, 31.7, 31.0, 29.5, 28.9, 22.7, 22.6, 14.1,

13.7 ppm; IR (neat): $\tilde{\nu}$ = 3026, 2956, 2925, 2856, 1926, 1604, 1496, 1454, 1378, 1189, 1075, 963, 744, 697 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{42}$: C 90.08, H 9.92; found: C 90.26, H 10.21.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research (No. 18350018) and Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformations of Carbon Resources" (No. 18037017) from the Ministry of Education, Culture, Sports, Science and Technology (Japan). This work was carried out under the 21st Century COE program of "Future Nanomaterials" in Tokyo University of Agriculture & Technology.

[1] a) A. Dömling, I. Ugi, *Angew. Chem.* **2000**, *112*, 3300–3344; *Angew. Chem. Int. Ed.* **2000**, *39*, 3168–3210; b) D. J. Ramón, M. Yus, *Angew. Chem.* **2005**, *117*, 1628–1661; *Angew. Chem. Int. Ed.* **2005**, *44*, 1602–1634; c) A. Ulaczyk-Lesanko, D. G. Hall, *Curr. Opin. Chem. Biol.* **2005**, *9*, 266–276; d) *Multicomponent Reactions* (Eds.: Z. Jieping, B. Hugues), Wiley-VCH, Weinheim, **2005**.

[2] For recent examples see a) M. Yoshida, M. Ihara, *Angew. Chem.* **2001**, *113*, 636–639; *Angew. Chem. Int. Ed.* **2001**, *40*, 616–619; b) G. Balme, E. Bossharth, N. Monterio, *Eur. J. Org. Chem.* **2003**, 4101–4111; c) R. Dhawan, B. A. Arndtsen, *J. Am. Chem. Soc.* **2004**, *126*, 468–469; d) L. F. Tietze, K. M. Sommer, J. Zinngrebe, F. Stecker, *Angew. Chem.* **2005**, *117*, 262–264; *Angew. Chem. Int. Ed.* **2005**, *44*, 257–259; e) K. C. Nicolaou, W. Tang, P. Dagneau, R. Faraoni, *Angew. Chem.* **2005**, *117*, 3942–3947; *Angew. Chem. Int. Ed.* **2005**, *44*, 3874–3879; f) O. Jiménez, G. Rosa, R. Lavilla, *Angew. Chem.* **2005**, *117*, 6679–6683; *Angew. Chem. Int. Ed.* **2005**, *44*, 6521–6525; g) A. S. Karpov, E. Merkul, F. Rominger, T. J. J. Müller, *Angew. Chem.* **2005**, *117*, 7112–7117; *Angew. Chem. Int. Ed.* **2005**, *44*, 6951–6956; h) H. A. Dondas, C. W. G. Fishwick, X. Gai, R. Grigg, C. Kilner, N. Dumrongchai, B. Kongkathip, N. Kongkathip, C. Polysuk, V. Sridharan, *Angew. Chem.* **2005**, *117*, 7742–7746; *Angew. Chem. Int. Ed.* **2005**, *44*, 7570–7574; i) D. J. Knapton, T. Y. Meyer, *J. Org. Chem.* **2005**, *70*, 785–796; j) A. Arefalk, M. Larhed, A. Hallberg, *J. Org. Chem.* **2005**, *70*, 938–942; k) C. Zhou, R. C. Larock, *J. Org. Chem.* **2005**, *70*, 3765–3777; l) G. Abbiati, A. Arcadi, V. Canevari, L. Capezzuto, E. Rossi, *J. Org. Chem.* **2005**, *70*, 6454–6460; m) C. D. Hopkins, L. Guan, H. C. Malinakova, *J. Org. Chem.* **2005**, *70*, 6848–6862; n) K. Shibata, T. Satoh, M. Miura, *Org. Lett.* **2005**, *7*, 1781–1783; o) M. S. M. Ahmed, K. Kobayashi, A. Mori, *Org. Lett.* **2005**, *7*, 4487–4489.

[3] For recent examples see a) H. Huang, Y. Wang, Z. Chen, W. Hu, *Adv. Synth. Catal.* **2005**, *347*, 531–534; b) S. Torssell, M. Kienle, P. Somfai, *Angew. Chem.* **2005**, *117*, 3156–3159; *Angew. Chem. Int. Ed.* **2005**, *44*, 3096–3099; c) A. M. Schmidt, P. Eilbracht, *J. Org. Chem.* **2005**, *70*, 5528–5535.

[4] For recent examples see a) M. Kimura, A. Miyachi, K. Kojima, S. Tanaka, Y. Tamaru, *J. Am. Chem. Soc.* **2004**, *126*, 14360–14361; b) M. Kimura, A. Ezoe, M. Mori, Y. Tamaru, *J. Am. Chem. Soc.* **2005**, *127*, 201–209; c) P. G. Cozzi, E. Rivalta, *Angew. Chem.* **2005**, *117*, 3666–3669; *Angew. Chem. Int. Ed.* **2005**, *44*, 3600–3603.

[5] For recent examples see a) H. Lee, H. Y. Kim, H. Tae, B. G. Kim, J. Lee, *Org. Lett.* **2003**, *5*, 3439–3442; b) L. Deng, A. J. Giessert, O. O. Gerlitz, X. Dai, S. T. Diver, H. M. L. Davies, *J. Am. Chem. Soc.* **2005**, *127*, 1342–1343.

[6] a) Y. Liu, F. Song, L. Cong, *J. Org. Chem.* **2005**, *70*, 6999–7002; b) R. Cannella, A. Clerici, N. Pastori, E. Regolini, O. Porta, *Org. Lett.* **2005**, *7*, 645–648.

[7] a) D. Suzuki, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 7925–7926; b) D. Suzuki, R. Tanaka, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2002**, *124*, 3518–3519; c) R. Tanaka, Y. Nakano, D. Suzuki, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2002**, *124*, 9682–9683; d) K. Mitsui, T. Sato, H. Urabe, F. Sato. *Angew. Chem.* **2004**, *116*, 496–498; *Angew. Chem. Int. Ed.* **2004**, *43*, 490–492; e) R. Tanaka, A. Yuza, W. Yuko, D. Suzuki, Y. Takayama, F. Sato, H. Urabe, *J. Am. Chem. Soc.* **2005**, *127*, 7774–7780.

[8] a) T. Takahashi, F. Tsai, M. Kotora, *J. Am. Chem. Soc.* **2000**, *122*, 4994–4995; b) T. Takahashi, *Pure Appl. Chem.* **2001**, *73*, 271–274; c) T. Takahashi, M. Ishikawa, S. Huo, *J. Am. Chem. Soc.* **2002**, *124*, 388–389; d) T. Takahashi, Y. Li, P. Stepnicka, M. Kitamura, Y. Liu, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **2002**, *124*, 576–582; e) T. Takahashi, Y. Li, T. Ito, F. Xu, K. Nakajima, Y. Liu, *J. Am. Chem. Soc.* **2002**, *124*, 1144–1145; f) T. Takahashi, F. Tsai, Y. Li, H. Wang, Y. Kondo, M. Yamamoto, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **2002**, *124*, 5059–5067; g) X. Zhou, Z. Li, H. Wang, M. Kitamura, K. Kanno, K. Nakajima, T. Takahashi, *J. Org. Chem.* **2004**, *69*, 4559–4562.

[9] A. Ogata, M. Nemoto, K. Arai, K. Kobayashi, A. Tsubouchi, T. Takeda, *Eur. J. Org. Chem.* **2006**, 878–880.

[10] T. Takeda, A. Tsubouchi, in *Modern Carbonyl Olefination* (Ed.: T. Takeda), Wiley-VCH, Weinheim, **2004**, pp. 151–199.

[11] T. Takeda in *Titanium and Zirconium in Organic Synthesis* (Ed.: I. Marek), Wiley-VCH, Weinheim, **2002**, pp. 480–500.

[12] T. Shono, K. Ito, A. Tsubouchi, T. Takeda, *Org. Biomol. Chem.* **2005**, *3*, 2914–2916.

[13] T. Shono, Y. Hayata, A. Tsubouchi, T. Takeda, *Tetrahedron Lett.* **2006**, *47*, 1257–1260.

[14] (*E*)-Alkenyl sulfones are completely inactive for the present reaction.

[15] Y. Yatsumonji, O. Okada, A. Tsubouchi, T. Takeda, *Tetrahedron* **2006**, *62*, 9981–9987.

[16] a) B. B. Snider, B. W. Burbaum, *J. Org. Chem.* **1983**, *48*, 4370–4374; b) H. J. Reich, E. K. Eisenhart, W. L. Whipple, M. J. Kelly, *J. Am. Chem. Soc.* **1988**, *110*, 6432–6442; c) W. H. Okamura, M. L. Curtin, *Synlett* **1990**, 1–9; d) U. Koop, G. Handke, N. Krause, *Liebigs Ann. Chem.* **1996**, 1487–1499; e) C. Spino, C. Thibault, S. Gingras, *J. Org. Chem.* **1998**, *63*, 5283–5287; f) D. Regás, M. M. Afonso, A. Galindo, J. A. Palenzuela, *Tetrahedron Lett.* **2000**, *41*, 6781–6784; g) D. Regás, J. M. Ruiz, M. M. Afonso, A. Galindo, J. A. Palenzuela, *Tetrahedron Lett.* **2003**, *44*, 8471–8474; h) D. Regás, M. M. Afonso, M. L. Rodríguez, J. A. Palenzuela, *J. Org. Chem.* **2003**, *68*, 7845–7852; i) D. Regás, M. M. Afonso, J. A. Palenzuela, J. Antonio, *Synthesis* **2004**, 757–760.

[17] a) M. Murakami, K. Itami, Y. Ito, *Angew. Chem.* **1998**, *110*, 3616–3619; *Angew. Chem. Int. Ed.* **1998**, *37*, 3418–3420; b) M. Murakami, K. Itami, Y. Ito, *J. Am. Chem. Soc.* **1999**, *121*, 4130–4135; c) M. Murakami, K. Itami, Y. Ito, *Synlett* **1999**, 951–953; d) A. S. K. Hashmi, *Angew. Chem.* **2000**, *112*, 3737–3740; *Angew. Chem. Int. Ed.* **2000**, *39*, 3590–3593; e) M. Murakami, R. Minamida, K. Itami, M. Sawamura, Y. Ito, *Chem. Commun.* **2000**, 2293–2294; f) P. H. Lee, K. Lee, Y. Kang, *J. Am. Chem. Soc.* **2006**, *128*, 1139–1146.

[18] a) S. López, J. Rodríguez, J. G. Rey, A. R. Lera, *J. Am. Chem. Soc.* **1996**, *118*, 1881–1891; b) C. Delas, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 7937–7938; c) M. Murakami, S. Ashida, T. Matsuda, *J. Am. Chem. Soc.* **2004**, *126*, 10838–10839.

[19] J. A. Souto, C. S. López, O. N. Faza, R. Alvarez, A. R. Lera, *Org. Lett.* **2005**, *7*, 1565–1568.

[20] a) J. P. Dulcère, J. Gore, M. L. Roumestant, *Bull. Soc. Chim. Fr.* **1974**, 1119–1123; b) T. Konoike, Y. Araki, *Tetrahedron Lett.* **1992**, *33*, 5093–5096.

[21] a) M. Purpura, N. Krause, *Eur. J. Org. Chem.* **1999**, 267–275; b) N. Krause, M. Purpura, *Angew. Chem.* **2000**, *112*, 4512–4514; *Angew. Chem. Int. Ed.* **2000**, *39*, 4355–4356.

[22] A. G. Myers, B. Zheng, *J. Am. Chem. Soc.* **1996**, *118*, 4492–4493.

[23] R. Baudouy, J. Goré, *J. Chem. Res. (S)* **1981**, 278–279.

[24] K. Lee, D. Seomoon, P. H. Lee, *Angew. Chem.* **2002**, *114*, 4057–4059; *Angew. Chem. Int. Ed.* **2002**, *41*, 3901–3903.

[25] Z. Xi, W. Zhang, Z. Song, W. Zheng, F. Kong, T. Takahashi, *J. Org. Chem.* **2005**, *70*, 8785–8789.

[26] T. Takeda, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 195–217.

Received: September 15, 2006
Published online: October 30, 2006

