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Facile Synthesis and Palladium-Catalyzed Cross-Coupling Reactions of 2,3-Bis(pinacolatoboryl)-1,3-butadiene

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In memory of Professor Yoshihiko Ito

Abstract: Treatment of 1,1-bis(pinacolatoboryl)ethene with an excess of 1-bromo-1-lithioethene gave 2,3-bis(pinacolatoboryl)-1,3-butadiene in high yield. Palladium-catalyzed cross-coupling of the resulting diborylbutadiene with aryl iodides took place smoothly in the presence of a catalytic amount of $Pd(OAc)_2/PPh_3$ and aqueous KOH to give 2,3-diaryl-1,3-butadienes in good yields. The coupling reaction with commercially available 4-acetoxyphenylmethyl chloride under the same conditions followed by hydrolysis of the acetyl groups gave anolignan B in a one-pot manner. A variety of [3]- to [6]dendralenes were synthesized by palladium-catalyzed coupling of the diene or 1,1-bis(pinacolato)borylethene with alkenyl or dienyl halides, respectively, in good yields.

Keywords: alkenes · boron · conjugation · cross-coupling · synthetic methods

Introduction

Polyfunctionalized conjugate molecules such as 2,3-disubstituted 1,3-butadienes serve as useful intermediates for biologically active compounds and as functionalized monomers for polybutadienes and their copolymers.[1] Among these compounds, a 1,3-butadien-2,3-diyl skeleton is found in dendralenes, a class of acyclic cross-conjugated polyenes that exhibit unique electronic properties not found in linear conjugated organic compounds.[2] Although cross-conjugated polyenes such as radialenes have been extensively studied,[3] dendralenes remain unexplored probably due to limited preparation methods. Organodimetallic compounds have emerged as a versatile class of reagents in organic synthesis, because these compounds have been demonstrated to perform efficiently two carbon–carbon bond formations in one vessel by a single operation or stepwise manipulations to achieve rapid and efficient syntheses of target carbon frameworks.[4] Given that the transition-metal-catalyzed cross-coupling reaction is one of the most valuable methods for bond formation at sp^2-hybridized carbon atoms,[5] 2,3-dimetalated 1,3-butadienes appear to be highly attractive reagents for the convenient synthesis of 2,3-disubstituted 1,3-butadienes, although they have remained unexplored except for 2,3-bis(trimethylstannyl)-1,3-butadiene.[6] We report herein the facile synthesis of 2,3-bis(pinacolatoboryl)-1,3-butadiene (**3**) and its Pd-catalyzed cross-coupling reactions with aryl iodides, benzyl chloride, and alkenyl iodides to provide a concise synthesis of 2,3-diaryl-1,3-butadienes **4**, anolignan B (**5**), and functionalized dendralenes **6**, respectively (Scheme 1).[7]

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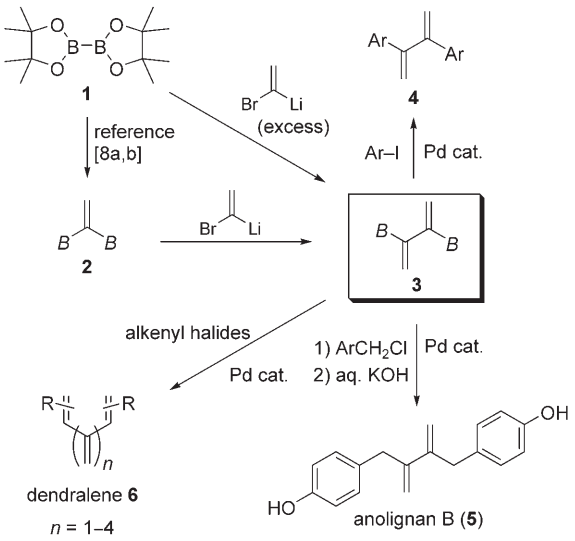
Results and Discussion

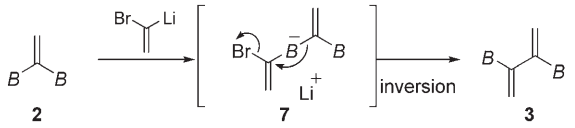
Facile Synthesis of 2,3-Diboryl-1,3-dienes

During the course of our studies on the *gem*-diborylation of alkylidene-type lithium carbenoids with bis(pinacolato)diboron (**1**),[8] we found that 2,3-bis(pinacolatoboryl)-1,3-butadiene (**3**) was produced when **1** was treated with 1-bromo-1-lithioethene in excess. Formation of **3** was ascribed to the reaction of 1,1-bis(pinacolatoboryl)ethene (**2**), the initial *gem*-diborylated product, with another 1-bromo-1-lithioethene to give a borate intermediate **7**, followed by 1,2-migration of the 1-borylethenyl group (Scheme 2).[9]

To clarify the assumed reaction sequence, we examined the reaction of **2** with 1-bromo-1-lithioethene. The results



Scheme 1. Synthesis and cross-coupling reactions of **3**. *B* = pinacolatoboryl.



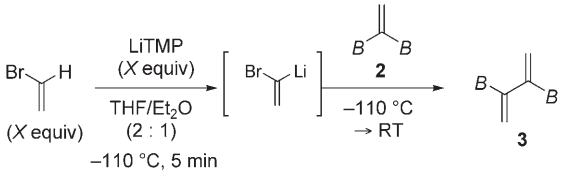
Scheme 2. Mechanism of 2,3-diboryl-1,3-butadiene formation.

are shown in Table 1. Compound **2** was added to a solution of 1-bromo-1-lithioethene (1 equiv) in THF/Et_2O (2:1), which was generated from vinyl bromide and lithium 2,2,6,6-tetramethylpiperidide (LiTMP), at −110 °C to give **3** in only 7% yield (Table 1, entry 1). Given that **1** reacted with an equimolar amount of 1-bromo-1-lithioethene to give **2** in 91% yield,[8a,b] the low yield here indicates that the reaction of the lithium carbenoid with **2** is slower than that with **1** and apparently competes with carbenoid decomposition. Next, we increased the amount of 1-bromo-1-lithioethene (Table 1, entries 2–4). The highest yield of **3** was obtained when 5 equivalents of vinyl bromide and LiTMP were employed (Table 1, entry 3).[10] Notably, although 2-(pinacolatoboryl)-1,3-butadiene is reportedly susceptible to dimerization,[11] **3** can be purified by column chromatography on silica gel. Carbenoid generation carried out in the presence of **2** resulted in a lower yield (59%) of **3**, whereas reaction of 2-substituted 1-bromo-1-lithioethene with **2** did not proceed at all.

Abstract in Japanese:

1,1-ビス（ピナコラートボリル）エテンを過剰量の 1-ブロモ-1-リチオエテンで処理すると，2,3-ビス（ピナコラートボリル）-1,3-ブタジエンが高収率で得られた。このジボリルブタジエンとヨウ化アリールとの交差カップリング反応は，酢酸パラジウム／トリフェニルホスフィン触媒および水酸化カリウム水溶液存在下円滑に進行し，対応する 2,3-ジアリール-1,3-ブタジエンを収率よく与えた。同条件下，市販の塩化（4-アセトキシフェニル）メチルをカップリングさせ，つづけてアセトキシ基を加水分解することにより，アノリグナン B をワンポットで簡便合成した。ジボリルブタジエンとハロゲン化アルケニルやジエニルとの交差カップリング反応を検討し，デンドラレンの簡便合成法を開発した。

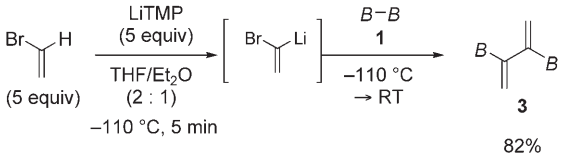
Table 1. Preparation of **3** from **2**.[a]



Entry	LiTMP [equiv]	Yield [%][b]
1	1	7
2	3	46
3	5	72
4	10	60

[a] A solution of **2** (0.5 mmol) in THF (0.1 mL) was added to a solution of 1-bromo-1-lithioethene (*X* equiv) in THF (2 mL) and Et_2O (1 mL) at −110 °C. After 5 min, the reaction mixture was gradually warmed to room temperature. [b] Yield of isolated product.

The one-pot synthesis of **3** from **1** is also possible. As shown in Scheme 3, treatment of vinyl bromide (5 equiv) with LiTMP (5 equiv) at −110 °C followed by the addition of **1** gave **3** in 82% yield.



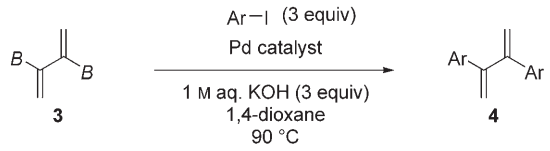
Scheme 3. One-pot synthesis of **3** from **1**.

Palladium-Catalyzed Double-Cross-Coupling Reaction of 2,3-Bis(pinacolatoboryl)-1,3-butadiene with Organic Halides

With **3** in hand, we scrutinized its Pd-catalyzed double-cross-coupling reactions with organic halides.[14] First, we chose iodobenzene as a model electrophile for the preparation of 2,3-diaryl-1,3-butadienes and screened Pd catalysts with aqueous KOH as a base in 1,4-dioxane.[15] The results are summarized in Table 2. Among the tested palladium catalysts (Table 2, entries 1–5), $Pd(OAc)_2$ (10 mol%)/PPh_3 (40 mol%) gave the highest yield of **4a** (Table 2, entry 5). Under the same conditions, 4-methyl-, 4-trifluoromethyl-, 4-methoxy-, and 4-phenyliodobenzene coupled with **3** to produce the corresponding 2,3-diaryl-1,3-butadienes (**4b**–**e**) in good yields (Table 2, entries 6–9).

Anolignan A and B were isolated from *Anogeissus acuminata*; these compounds are the active inhibitory constituents of HIV-1 reverse transcriptase in the plant (Scheme 4).[16] Meanwhile, a bioactivity-guided fractionation of an extract from *Terminalia bellerica* led to the isolation of termilignan, which exhibits anti-HIV-1, antimalarial, and antifungal activities.[17] A structural feature of these lignans is that they have a 2,3-bis(arylmethyl)-1,3-butadiene moiety that can be prepared by the double-coupling reaction of **3** with aryl-

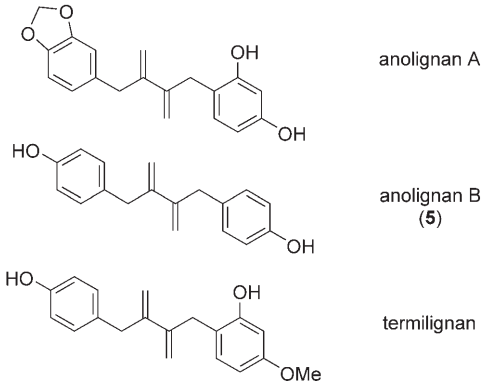
Table 2. Cross-coupling reaction of **3** with an aryl iodide.[a]



3 **4**

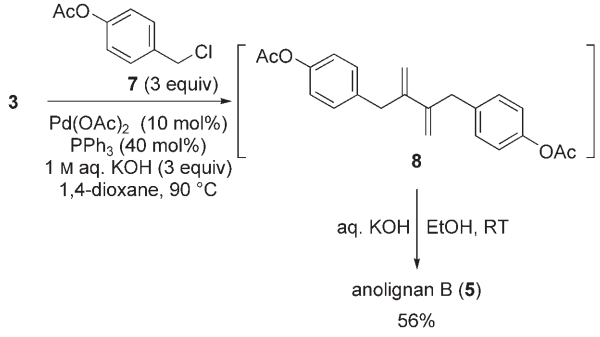
Entry	Ar	Pd catalyst (quantity [mol%])	4	Yield [%][b]
1	C_6H_5	$[Pd(PPh_3)_4]$ (1)	**4a**	71
2	C_6H_5	$[PdCl_2(PPh_3)_2]$ (10)	**4a**	62
3[c]	C_6H_5	$[Pd_2(dba)_3]$ (1.5)/P(*t*Bu)$_3$ (3.6)	**4a**	31
4	C_6H_5	$[Pd_2(dba)_3]$ (10)	**4a**	37
5	C_6H_5	$Pd(OAc)_2$ (10)/PPh_3 (40)	**4a**	75
6	4-Me-C_6H_4	$Pd(OAc)_2$ (10)/PPh_3 (40)	**4b**	75
7	4-MeO-C_6H_4	$Pd(OAc)_2$ (10)/PPh_3 (40)	**4c**	81
8	4-CF_3-C_6H_4	$Pd(OAc)_2$ (10)/PPh_3 (40)	**4d**	68
9	4-C_6H_5-C_6H_4	$Pd(OAc)_2$ (10)/PPh_3 (40)	**4e**	65

[a] Aqueous KOH (1 M, 1.5 mL) was added to a solution of **3** (0.50 mmol), the aryl iodide (1.5 mmol), $Pd(OAc)_2$ (10 mol%), and PPh_3 (40 mol%) in 1,4-dioxane (2 mL). The resulting mixture was stirred at 90 °C for 2 h. [b] Yield of isolated product. [c] The coupling reaction was carried out at room temperature.



Scheme 4. 2,3-Bis(arylmethyl)-1,3-butadiene-type lignans.

methyl halides. We applied the optimized conditions for aryl iodides to the reaction with commercially available chloride **7** to demonstrate a facile synthesis of anolignan B (**5**). Treatment of **3** with **7** under these conditions produced diacetate **8**, which was directly treated with aqueous KOH without isolation to give **5** in 56% overall yield (Scheme 5). This is the shortest and most facile method for the synthesis of anolignan B.



Scheme 5. Facile and short total synthesis of anolignan B.

Growing interest has been focused on cross-conjugated nonaromatic compounds as a potent platform for versatile π-conjugated systems owing to their unique electronic structures and properties, which are not exhibited in linearly conjugated π systems (Scheme 6).[18] Whereas the electronic

radialenes fulvenes dendralenes

Scheme 6. Cross-conjugated molecules.

properties of radialenes and fulvenes have been extensively studied so far, dendralenes, acyclic cross-conjugated polyenes based on a 3-methylene-1,4-pentadiene unit, remains yet to be studied, probably because synthetic methods of dendralenes are quite limited. For example, [*n*]dendralenes ($n>4$) were unknown until the recent study by Sherburn and co-workers, who succeeded in preparing [5]- to [8]dendralenes by the coupling of 2,3-bis(trimethylstannyl)-1,3-butadiene with 3-iodosulfol-3-ene followed by cheletropic elimination of SO_2 upon heating at 450 °C.[6b] Therefore, development of a facile synthetic method for functionalized dendralenes is of significant importance in organic synthesis.[19]

We envisioned that the Pd-catalyzed coupling of **3** with functionalized alkenyl or dienyl halides would become a new and concise synthetic method for symmetrical [4]- and [6]dendralenes and unsymmetrical [3]- and [5]dendralenes (Scheme 7). Furthermore, the coupling reaction of **2** with dienyl halides is expected to open a way to symmetrical [5]- and unsymmetrical [4]dendralenes.

At first, we examined the double cross-coupling of **3** with 3 equivalents of α-bromostyrene. The results are summarized in Table 3. The coupling reaction in the presence of $[Pd(PPh_3)_4]$, $[PdCl_2(dppf)]$, or $[Pd_2(dba)_3]$/P(*t*Bu)$_3$ with aqueous KOH in THF at 50 °C resulted in low yields of [4]**6a** (Table 3, entries 1–3), whereas $[Pd\{P(tBu)_3\}_2]$ catalyzed the reaction smoothly to give [4]**6a** in 60% yield (Table 3, entry 4). Use of aqueous Cs_2CO_3 in THF gave comparable results to the aqueous KOH/THF system (Table 3, entry 5). Finally, the combination of aqueous Cs_2CO_3/1,4-dioxane was found to be best: it gave **2a** in 73% yield (Table 3, entry 6). Under the optimized conditions, cross-coupling of **1b** with 1-bromo-1-(4-nitrophenyl)ethene gave the corresponding [4]**6b** in good yield (Table 3, entry 8), but the conditions were not applicable to the reaction with 1-bromo-1-trimethylsilylethene (Table 3, entry 9). In this case, the aqueous KOH/THF system was effective and gave [4]**6c** in 37% yield (Table 3, entry 10). On the other hand, the cross-coupling of **3** with α-iodostyrene and 1-(4-fluorophenyl)-1-iodoethene in the presence of $[Pd_2(dba)_3]$/P(*t*Bu)$_3$ proceeded at room temperature to give [4]**6a** and [4]**6d** in 63 and 47% yield, respectively (Table 3, entries 12 and 13). In these cases, the $[Pd_2(dba)_3]$/P(*t*Bu)$_3$ combination was better than $[Pd\{P(tBu)_3\}_2]$, which was good for the coupling with α-bro-

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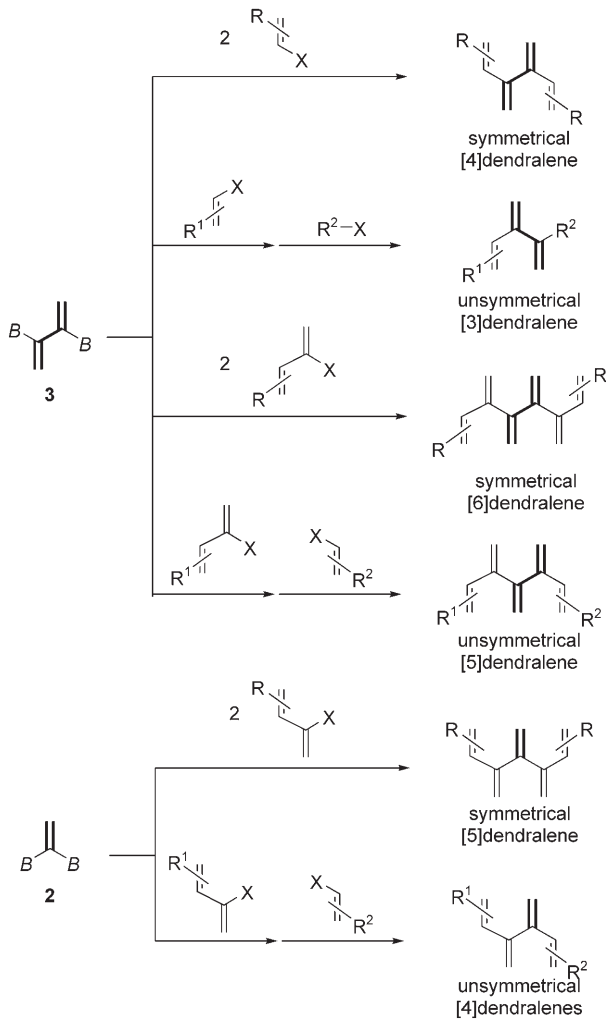
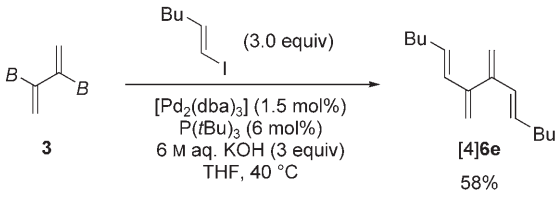


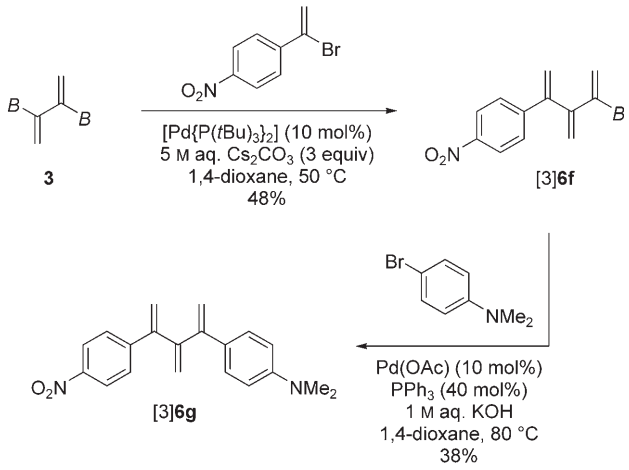
Scheme 7. Synthetic plan for [3]- to [6]dendralenes from **2** or **3**.

mostyrene. Similarly, **3** coupled with 1-iodohex-1-ene upon heating at 40 °C in the presence of $[Pd_2(dba)_3]/P(tBu)_3$ to give [4]**6e** in 58 % yield [Eq. (1)].



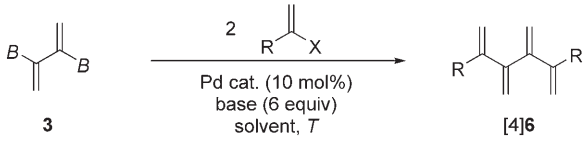
(1)

Unsymmetrical [3]dendralene is accessible by stepwise coupling with alkenyl and aryl bromides. At first, monocoupled [3]**6f** was obtained in 48 % yield by the reaction of **3** with one equivalent of 4-(1-bromoethenyl)nitrobenzene. Subsequent coupling of [3]**6f** with 4-(dimethylamino)bromobenzene gave [3]**6g**, which has a donor–π-acceptor electronic structure (Scheme 8).



Scheme 8. Synthesis of unsymmetrical [3]dendralenes.

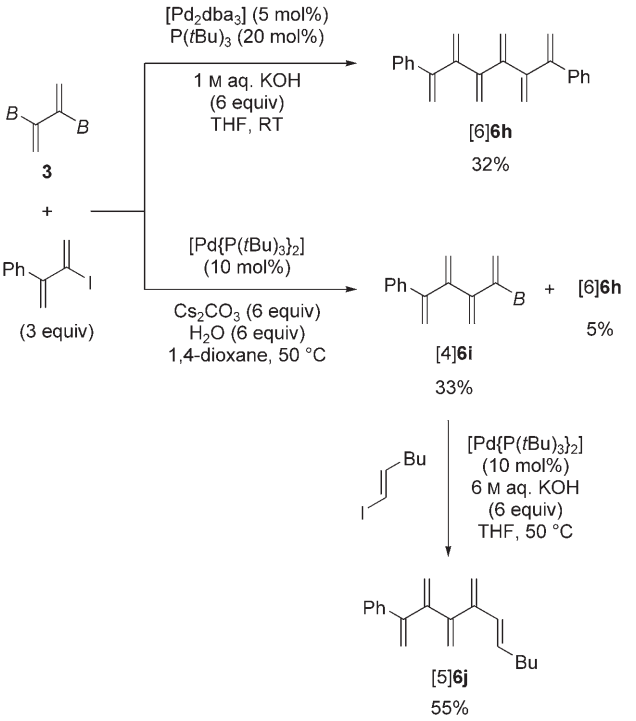
Table 3. Synthesis of symmetrical [4]dendralenes by cross-coupling of **3** with alkenyl halides.[a]



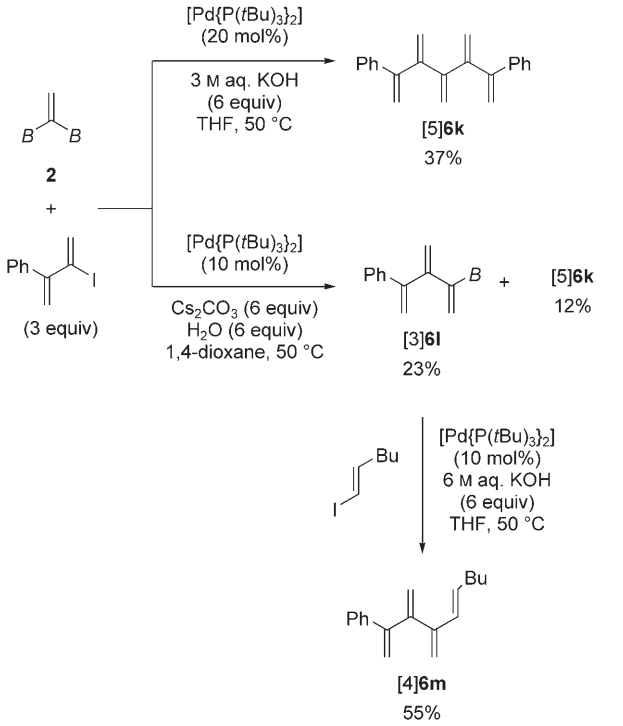
Entry	R	X	Pd cat.	Base	Solvent	T [°C]	[4]**6**	Yield [%][b]
1	C_6H_5	Br	$[Pd(PPh_3)_4]$	6 M aq. KOH	THF	50	[4]**6a**	20
2	C_6H_5	Br	$[PdCl_2(dppf)]$	6 M aq. KOH	THF	50	[4]**6a**	6
3	C_6H_5	Br	$[Pd_2(dba)_3]/P(tBu)_3$[c]	6 M aq. KOH	THF	50	[4]**6a**	22
4	C_6H_5	Br	$[Pd\{P(tBu)_3\}_2]$	6 M aq. KOH	THF	50	[4]**6a**	60
5	C_6H_5	Br	$[Pd\{P(tBu)_3\}_2]$	5 M aq. Cs_2CO_3	THF	50	[4]**6a**	56
6	C_6H_5	Br	$[Pd\{P(tBu)_3\}_2]$	5 M aq. Cs_2CO_3	1,4-dioxane	50	[4]**6a**	73
7	C_6H_5	Br	$[Pd\{P(tBu)_3\}_2]$	5 M aq. Cs_2CO_3	DME	50	[4]**6a**	trace
8	p-NO_2-C_6H_4	Br	$[Pd\{P(tBu)_3\}_2]$	5 M aq. Cs_2CO_3	1,4-dioxane	50	[4]**6b**	74
9	$SiMe_2Ph$	Br	$[Pd\{P(tBu)_3\}_2]$	5 M aq. Cs_2CO_3	1,4-dioxane	50	[4]**6c**	trace
10	$SiMe_2Ph$	Br	$[Pd\{P(tBu)_3\}_2]$	6 M aq. KOH	THF	50	[4]**6c**	37
11	C_6H_5	I	$[Pd\{P(tBu)_3\}_2]$	6 M aq. KOH	THF	RT	[4]**6a**	23
12	C_6H_5	I	$[Pd_2(dba)_3]/P(tBu)_3$[c]	6 M aq. KOH	THF	RT	[4]**6a**	63
13	p-F-C_6H_4	I	$[Pd_2(dba)_3]/P(tBu)_3$[c]	6 M aq. KOH	THF	RT	[4]**6d**	47

[a] A solution of **3** (0.13 mmol), alkenyl halide (0.31 mmol), Pd catalyst (13 μmol), and base (0.78 mmol) in solvent (1.0 mL) was stirred at room temperature or 50 °C. [b] Yield of isolated product. [c] $[Pd_2(dba)_3]$ (5 mol %) and $P(tBu)_3$ (20 mol %) were used.

Higher homologues of dendralenes are available by the use of dienyl iodide as a coupling partner of **3**. For example, treatment of **3** with 3 equivalents of 2-iodo-3-phenylbuta-1,3-diene in the presence of $[Pd_2(dba)_3]/P(tBu)_3$ and aqueous KOH in THF at room temperature gave [6]**6h** as the sole product in 32 % yield (Scheme 9); use of $[Pd\{P(tBu)_3\}_2]$ as the catalyst gave [6]**6h** in only 19 % yield. On the other hand, when the same reaction was carried out with Cs_2CO_3/H_2O as a base in 1,4-



Scheme 9. Synthesis of symmetrical [6]- and unsymmetrical [5]dendralenes.



Scheme 10. Synthesis of symmetrical [5]- and unsymmetrical [4]dendralenes.

dioxane, monocoupled product [4]**6i** was obtained as the major product in 33% yield along with 5% of [6]**6h**. Subsequent reaction of [4]**6i** with 1-iodohex-1-ene provided easy access to unsymmetrical [5]dendralene [5]**6j**.

The preparation of symmetrical [5]- and unsymmetrical [4]dendralenes is also possible by double or stepwise coupling of **2**. Thus, treatment of a mixture of **2** in THF and 2-iodo-3-phenylbuta-1,3-diene with [Pd{P(*t*Bu)$_3$}$_2$] and aqueous KOH in THF gave only [5]**6k** in 37% yield, whereas the use of Cs_2CO_3/H_2O as a base in 1,4-dioxane afforded boryl-substituted [3]dendralene [3]**6l** as the major product, which reacted with 1-iodohex-1-ene to give [4]**6m** in 55% yield (Scheme 10).

UV/Vis Spectra of Dendralenes

UV/Vis spectra of phenyl-substituted dendralenes **4a**, [4]**6a**, and [6]**6h** were recorded in cyclohexane (1×10^{-5} M) at room temperature; the absorption maxima were at 243 ($\varepsilon=$ 24200) for **4a**, 231 ($\varepsilon=42600$) for [4]**6a**, and 225 nm ($\varepsilon=$ 30000 M^{-1}cm^{-1}) for [6]**6h** (Figure 1). Notably, all the absorption maxima exhibited blue shifts in proportion to the number of *exo*-methylene bonds, which indicates that the *exo*-methylene bonds prefer a twisted conformation rather than a coplanar one.[20] Fluorescence emission was not observed for these dendralenes in cyclohexane, in contrast to the conjugated counterparts.[21]

The UV/Vis spectra of *p*-nitrophenyl-substituted dendralenes recorded in cyclohexane (1×10^{-5} M) at room temperature showed absorption maxima at 288 nm for [4]**6b** and at 291 nm for [3]**6g** (Figure 2). The absorption maxima appeared at almost the same wavelength as that of *p*-nitrostyrene (290 nm). These results mean that the effective π-conjugation lengths in [3]**6g** and [4]**6b** are effectively similar to that of *p*-nitrostyrene. No fluorescence emission was observed with a solution of the dendralenes in cyclohexane.

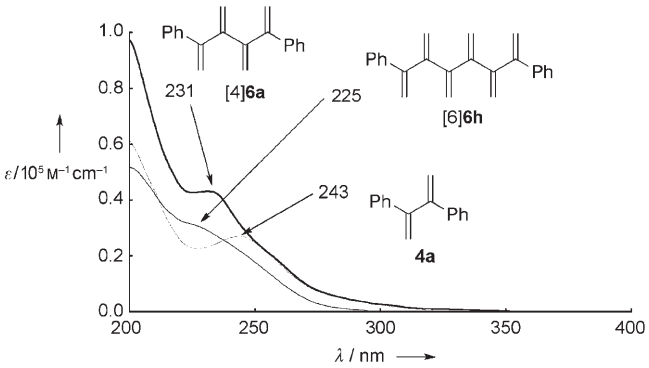


Figure 1. UV/Vis spectra of **4a**, [4]**6a**, and [6]**6h** recorded in cyclohexane.

Conclusions

We have established a facile synthesis of 2,3-bis(pinacolatoboryl)-1,3-butadiene from 1,1-bis(pinacolatoboryl)ethene or

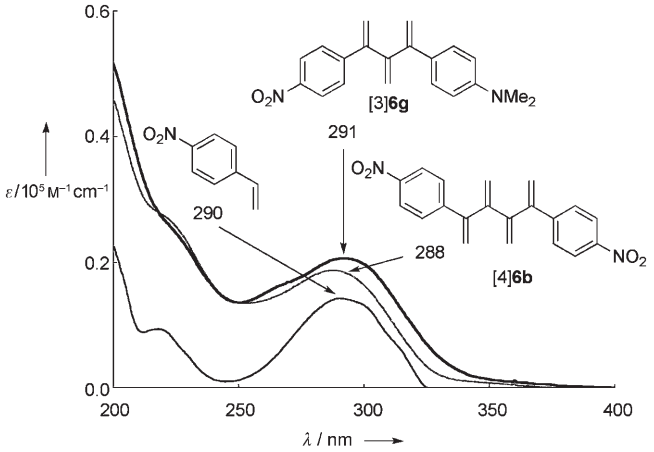


Figure 2. UV/Vis spectra of *p*-nitrophenyl-substituted dendralenes recorded in cyclohexane.

bis(pinacolato)diboron with 1-bromo-1-lithioethene. The methylene insertion was extended to the preparation of 2,3-diboryl-1,3-dienes. The palladium-catalyzed cross-coupling reaction of 2,3-bis(pinacolatoboryl)-1,3-butadiene with electrophiles such as aryl iodides, a benzyl chloride, and alkenyl halides was demonstrated to be a powerful strategy for the convenient synthesis of 2,3-diaryl-1,3-butadiene, 1,3-butadien-2,3-diyl-containing lignans, and functionalized dendralenes.

Experimental Section

General

All manipulations of oxygen- and moisture-sensitive materials were conducted with standard Schlenk techniques under argon atmosphere. Melting points were determined with a Yanagimoto Micro melting-point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian Mercury 200 (200 MHz), 300 (300 MHz), and 400 (400 MHz) spectrometers with tetramethylsilane ($\delta=0$ ppm) or chloroform ($\delta=7.26$ ppm) as an internal standard. Splitting patterns are indicated as s = singlet, d = doublet, t = triplet, q = quartet, and br s = broad singlet. ^{13}C NMR spectra were recorded on Varian Mercury 400 (100 MHz) and JEOL EX-270 (67.8 MHz) spectrometers with tetramethylsilane ($\delta=0$ ppm) or [D]chloroform ($\delta=77.0$ ppm) as an internal standard. Owing to quadrupolar relaxation, the carbon nucleus substituted by the boron atom was not detected. ^{19}F NMR spectra were recorded on a Varian Mercury 200 (188 MHz) spectrometer with $CFCl_3$ as an internal standard ($\delta=0$ ppm). ^{29}Si NMR spectra were recorded on a Varian Mercury 400 (80 MHz) spectrometer with tetramethylsilane as an internal standard ($\delta=0$ ppm). All chemical shifts are given in parts per million relative to the internal standard. IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer. GC–MS analysis was performed with a JEOL JMS-700 spectrometer with electron ionization at 70 eV. Elemental analysis was carried out with a YANAKO MT2 CHN CORDER machine at the Elemental Analysis Center of Kyoto University. TLC analysis was performed by means of Merck Kieselgel 60 F_{254}. Column chromatography was carried out with Wako gel C-200 or silica gel 60 (Kanto Chemical Co., Inc.). Solvents such as THF, 1,4-dioxane, diethyl ether, and 1,2-dimethoxyethane (DME) were distilled from benzophenone ketyl under argon atmosphere. Butyllithium was purchased from Sigma–Aldrich Co., Inc. Bis(pinacolato)diboron was purchased from Boron Molecular Co., Inc.

Syntheses

Synthesis of **3** from **2**: Butyllithium in hexane (1.56 M, 0.32 μL, 0.49 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.084 μL, 0.50 mmol) in THF (1 mL) and diethyl ether (0.5 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 5 min. A solution of vinyl bromide (1.00 M, 0.50 mL, 0.50 mmol) in THF and 1,1-[bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)]ethene (**2**; 25 mg, 0.10 mmol) in THF (0.1 mL) were added successively to this solution at −110 °C. The resulting mixture was allowed to warm gradually to room temperature and stirred for 12 h. The reaction was quenched with 3 drops of saturated aqueous NH_4Cl, and the mixture was diluted with diethyl ether (10 mL) and water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give a colorless solid, which was purified by column chromatography (200-mesh silica gel, hexane/ethyl acetate = 10:1) to give **3** (22 mg, 72 %). $R_f=0.33$ (hexane/ethyl acetate = 10:1); m.p.: 140 °C (decomp.); IR (Nujol): $\tilde{\nu}=1460$, 1375, 1340, 1300, 1277, 1218, 1120, 1102, 959, 880, 847, 740, 682 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.28$ (s, 24H), 5.85 (d, $J=3.9$ Hz, 2H), 5.96 ppm (d, $J=3.9$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=24.8$, 83.5, 130.6 ppm; MS (EI): *m/z* (%) = 307 $[M+1]^+$ (7), 306 $[M]^+$ (40), 305 $[M-1]^+$ (20), 291 $[M-Me]^+$ (9), 165 (100); elemental analysis: calcd (%) for $C_{16}H_{28}B_2O_4$: C 62.80, H 9.22; found: C 62.53, H 9.42.

One-pot synthesis of **3**: Butyllithium in hexane (1.56 M, 0.32 μL, 0.49 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (84 μL, 0.50 mmol) in THF (1 mL) and diethyl ether (0.5 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 5 min. This solution was added to a solution of vinyl bromide (1.00 M, 0.50 μL, 0.50 mmol) in THF at −110 °C, followed by **1** (25 mg, 0.10 mmol) in THF (0.1 mL). The resulting mixture was allowed to warm gradually to room temperature and stirred for 12 h. The reaction was quenched with 3 drops of saturated aqueous NH_4Cl, and the mixture was diluted with diethyl ether (10 mL) and water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give a colorless solid, which was purified by column chromatography (200-mesh silica gel, hexane/ethyl acetate = 10:1) to give **3** (25 mg, 82 %).

General procedure for cross-coupling of **3** with an aryl iodide: A mixture of **3** (31 mg, 0.10 mmol), iodobenzene (61 mg, 0.30 mmol), $Pd(OAc)_2$ (2.3 mg, 10 μmol), PPh_3 (11 mg, 40 μmol), and aqueous KOH (1 M, 0.30 mL, 0.30 mmol) in 1,4-dioxane (2 mL) was heated at 90 °C for 2 h. Workup and purification by column chromatography (silica gel) gave 2,3-diphenylbuta-1,3-diene (**4a**, CAS No. 2548–47–2) as a white solid (15 mg, 75 %). $R_f=0.43$ (hexane); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=5.32$ (d, $J=1.0$ Hz, 2H), 5.55 (d, $J=1.0$ Hz, 2H), 7.20–7.50 ppm (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=105.3$, 126.2, 127.7, 128.4, 134.9, 149.4 ppm; MS (EI): *m/z* (%) = 207 $[M+1]^+$ (3), 206 $[M]^+$ (32), 205 $[M-1]^+$ (94), 218 (100).

4b: 2,3-Bis(4-methylphenyl)buta-1,3-diene (CAS No. 75416–81–8): Yield: 75 %. $R_f=0.35$ (hexane); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=2.33$ (s, 6H), 5.28–5.30 (m, 2H), 5.53–5.55 (m, 2H), 7.06–7.12 (m, 4H), 7.27–7.34 ppm (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=21.2$, 115.2, 127.2, 128.8, 137.1, 137.2, 149.6 ppm; MS (EI): *m/z* (%) = 235 $[M+1]^+$ (3), 234 $[M]^+$ (32), 233 $[M-1]^+$ (94), 218 (100).

4c: 2,3-Bis(4-methoxyphenyl)buta-1,3-diene (CAS No. 52255–88–6): Yield: 81 %. $R_f=0.32$ (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=3.77$ (s, 6H), 5.24 (d, $J=1.6$ Hz, 2H), 5.45 (d, $J=1.6$ Hz, 2H), 6.78–6.81 (m, 4H), 7.31–7.34 ppm (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=55.2$, 113.5, 114.3, 128.4, 132.5, 149.2, 158.9 ppm; MS (EI): *m/z* (%) = 267 $[M+1]^+$ (42), 266 $[M]^+$ (100), 265 $[M-1]^+$ (47), 251 (49), 234 (77), 121 (52).

4d: 2,3-Bis(4-trifluoromethylphenyl)buta-1,3-diene (CAS No. 839718–77–4): Yield: 68 %. $R_f=0.45$ (hexane); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=5.43$ (d, $J=1.1$ Hz, 2H), 5.64 (d, $J=1.1$ Hz, 2H), 7.48 (d, $J=8.1$ Hz, 4H), 7.55 ppm (d, $J=8.1$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=118.6$, 124.0 (q, $J=271.0$ Hz), 125.3 (q, $J=3.3$ Hz), 127.7, 129.8 (q, $J=32.3$ Hz), 143.2, 148.1 ppm; MS (EI): *m/z* (%) = 343 $[M+1]^+$ (3), 342 $[M]^+$ (13), 341 $[M-1]^+$ (2), 253 (100).

5: A mixture of **3** (70 mg, 0.23 mmol), **7** (0.13 g, 0.69 mmol), $Pd(OAc)_2$ (5.2 mg, 23 μmol), PPh_3 (24 mg, 92 μmol), and aqueous KOH (1 M,

0.70 mL, 0.69 mmol) in 1,4-dioxane (2 mL) was heated at 90 °C for 2 h. The resulting mixture was poured into aqueous KOH (150 mg, 0.3 mL), and the residue was rinsed with EtOH (2 mL). The solution was stirred at room temperature for 14 h. The reaction mixture was diluted with diethyl ether (3 mL) at 0 °C and then acidified with HCl (1 M, 1 mL). The aqueous layer was extracted with diethyl ether (2×20 mL). The combined organic layer was washed with water (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated by a rotary evaporator. Purification of the crude product by preparative HPLC gave **5** as a white solid (35 mg, 56 %). R_f = 0.21 (hexane/ethyl acetate = 9:1); ^{1}H NMR (200 MHz, CD_3OD): δ = 3.37 (s, 4H), 4.81 (s, 2H), 5.12 (s, 2H), 6.55 (d, J = 8.5 Hz, 4H), 6.83 ppm (d, J = 8.5 Hz, 4H); ^{13}C NMR (50 MHz, CD_3OD): δ = 40.9, 115.3, 130.6, 131.9, 147.8, 156.4 ppm; MS (EI): m/z (%) = 267 $[M+1]^+$ (5), 266 $[M]^+$ (10), 159 (100).

General procedure for Pd-catalyzed cross-coupling of **3** with an alkenyl halide: 1-Bromo-(4-nitrophenyl)styrene (77 mg, 0.31 mmol) and aqueous Cs_2CO_3 (5 M, 66 μL) were added to a solution of **3** (41 mg, 0.13 mmol) and [Pd{P(tBu$_3$)}$_2$] (6.8 mg, 13 μmol) in 1,4-dioxane (1 mL) at room temperature. The mixture was stirred at 50 °C for 5 h before the reaction was quenched with saturated aqueous NH_4Cl (20 mL). The resulting mixture was diluted with ethyl acetate (3×20 mL) at 0 °C. The combined organic layer was washed with saturated aqueous NaCl (20 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified by preparative TLC (hexane/ethyl acetate = 5:1) to give 3,4-bis(methylidene)-2,5-(4-nitrophenyl)hexa-1,5-diene ([4]**6b**) as a yellow solid (34 mg, 74 %). R_f = 0.33 (hexane/ethyl acetate = 5:1); m.p.: 110 °C (hexane); IR (neat): $\tilde{\nu}$ = 3099, 2926, 2853, 1595, 1516, 1344, 1109, 914, 860, 706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.24 (d, J = 1.6 Hz, 2H), 5.35 (d, J = 1.4 Hz, 2H), 5.44 (d, J = 1.2 Hz, 2H), 5.53 (d, J = 1.2 Hz, 2H), 7.38–7.50 (m, 4H), 8.12–8.26 ppm (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 119.2, 120.3, 123.5, 127.9, 146.6, 147.1, 147.2, 147.3 ppm; MS (FAB): m/z (%) = 349 $[M+1]^+$ (27), 348 $[M]^+$ (100); HRMS (FAB): m/z calcd for $C_{20}H_{16}N_2O_4$: 349.1188; found: 349.1187.

[4]**6a**: 2,5-Diphenyl-3,4-bis(methylidene)hexa-1,5-diene: Colorless oil, yield: 73 %. R_f = 0.55 (hexane/ethyl acetate = 10:1); IR (neat): $\tilde{\nu}$ = 3088, 3055, 3024, 1585, 1576, 1493, 1445, 1028, 905, 779, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.18 (d, J = 2.0 Hz, 2H), 5.30 (d, J = 2.0 Hz, 2H), 5.32 (d, J = 1.6 Hz, 2H), 5.40 (d, J = 1.6 Hz, 2H), 7.28–7.33 ppm (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 115.9, 119.1, 127.5 (2C), 128.0, 140.6, 148.8, 149.2 ppm; MS (EI): m/z (%) = 258 $[M]^+$ (99), 257 $[M-1]^+$ (100); HRMS (EI): m/z calcd for $C_{20}H_{18}$: 258.1409 $[M]^+$; found: 258.1408.

[4]**6c**: 2,5-(4-Dimethylphenylsilyl)-3,4-bis(methylidene)hexa-1,5-diene: Colorless oil, yield: 37 %. R_f = 0.52 (hexane/ethyl acetate = 10:1); IR (neat): $\tilde{\nu}$ = 3069, 2957, 1576, 1427, 1248, 1115, 988, 905, 847, 837, 816, 731, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.33 (s, 12H), 5.14 (d, J = 2.2 Hz, 2H), 5.28 (d, J = 2.0 Hz, 2H), 5.89 (s, 1H), 5.98 (s, 1H), 6.60 (s, 1H), 6.69 (s, 1H), 7.27–7.43 (m, 6H), 7.43–7.57 ppm (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = −2.4, 118.6, 127.6, 128.8, 130.2, 133.7, 138.6, 145.7, 148.0 ppm; ^{29}Si NMR (80 MHz, $CDCl_3$): δ = −10.7 ppm; MS (EI): m/z (%) = 375 $[M+1]^+$ (8), 374 $[M]^+$ (20), 135 $[PhMe_2Si]^+$ (100); HRMS (EI): m/z calcd for $C_{24}H_{30}Si_2$: 374.1886 $[M]^+$; found: 374.1897.

[4]**6d**: 2,5-(4-Fluorophenyl)-3,4-bis(methylidene)hexa-1,5-diene: Colorless oil, yield: 47 %. R_f = 0.55 (hexane/ethyl acetate = 10:1); IR (neat): $\tilde{\nu}$ = 3092, 1603, 1508, 1231, 1159, 907, 841 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.18 (d, J = 2.2 Hz, 2H), 5.27 (d, J = 1.4 Hz, 2H), 5.29 (d, J = 2.0 Hz, 2H), 5.33 (d, J = 1.6 Hz, 2H), 6.94–7.05 (m, 4H), 7.18–7.28 ppm (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 114.8 (d, J = 21.2 Hz), 115.8, 119.1, 129.0 (d, J = 7.8 Hz), 136.4 (d, J = 3.4 Hz), 148.0, 148.6, 162.2 ppm (d, J = 245.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ = −115.4 ppm; MS (EI): m/z (%) = 294 $[M]^+$ (100); HRMS (EI): m/z calcd for $C_{20}H_{16}F_2$: 294.1220 $[M]^+$; found: 294.1223.

[4]**6e**: 7,8-Bis(methylidene)tetradeca-5,9-diene: Colorless oil, yield: 58 %. R_f = 0.70 (hexane); IR (neat): $\tilde{\nu}$ = 2959, 2926, 2956, 1458, 1379, 1261, 1095, 1024, 964, 891, 802, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.2 Hz, 6H), 1.27–1.39 (m, 8H), 2.05–2.12 (m, 4H), 4.90 (d, J = 2.0 Hz, 2H), 5.01 (d, J = 2.0 Hz, 2H), 5.63 (dt, J = 15.6, 7.2 Hz, 2H), 6.08 ppm (d, J = 15.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.4, 31.5, 32.5, 114.5, 130.5, 133.9, 147.3 ppm; MS (EI): m/z (%) = 219 $[M+1]^+$ (1), 218 $[M]^+$ (6), 161 (100); HRMS (EI): m/z calcd for $C_{16}H_{26}$: 218.2035 $[M]^+$; found: 218.2037.

[3]**6f**: 3-Methylidene-2-(4-nitrophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,4-diene: Colorless oil, yield: 48 %. R_f = 0.40 (hexane/ethyl acetate = 5:1); IR (neat): $\tilde{\nu}$ = 3082, 2978, 2934, 1595, 1520, 1344, 1313, 1221, 1148, 968, 914, 860, 851, 706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.29 (s, 12H), 5.17 (d, J = 1.2 Hz, 1H), 5.39 (d, J = 1.0 Hz, 1H), 5.56 (d, J = 1.4 Hz, 1H), 5.62–5.67 (m, 2H), 5.87 (d, J = 2.8 Hz, 1H), 7.51–7.59 (m, 2H), 8.12–8.20 ppm (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 24.8, 83.7, 117.9, 118.7, 123.4, 128.0, 132.0, 146.9, 147.0, 148.2, 149.2 ppm; MS (EI): m/z (%) = 327 $[M]^+$ (38), 310 (100); HRMS (EI): m/z calcd for $C_{18}H_{22}BNO_4$: 327.1642 $[M]^+$; found: 327.1627.

[3]**6g**: 4-(4-Dimethylaminophenyl)-3-methylidene-2-(4-nitrophenyl)penta-1,4-diene: Orange solid, yield: 38 %. R_f = 0.35 (hexane/ethyl acetate = 5:1); m.p.: 79 °C (hexane); IR (KBr): $\tilde{\nu}$ = 3090, 2924, 2853, 2804, 1611, 1595, 1520, 1344, 1165, 910, 860, 822, 706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.97 (s, 6H), 5.11 (d, J = 1.4 Hz, 1H), 5.27–5.29 (m, 2H), 5.41–5.42 (m, 2H), 5.47 (d, J = 1.2 Hz, 1H), 6.67 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 8.17 ppm (d, J = 8.8 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 40.5, 111.9, 114.0, 119.1, 119.3, 123.3, 127.8, 128.1, 128.4, 146.9, 147.4, 147.6, 148.0, 149.3, 149.9 ppm; MS (EI): m/z (%) = 320 $[M]^+$ (95), 319 $[M-1]^+$ (100); HRMS (EI): m/z calcd for $C_{20}H_{20}N_2O_2$: 320.1525 $[M]^+$; found: 320.1517.

[6]**6h**: 3,4,5,6-Tetrakis(methylidene)-2,7-diphenylocta-1,7-diene: Colorless oil, yield: 32 %. R_f = 0.58 (hexane/ethyl acetate = 10:1); IR (neat): $\tilde{\nu}$ = 3090, 3055, 3024, 1576, 1493, 1445, 1028, 903, 779, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.19–5.22 (br s, 6H), 5.26 (d, J = 1.6 Hz, 2H), 5.32 (d, J = 2.0 Hz, 2H), 5.38 (d, J = 1.6 Hz, 2H), 7.25–7.34 (m, 6H), 7.37–7.43 ppm (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 116.0, 118.4, 118.7, 127.4, 127.5, 128.0, 140.7, 147.8, 149.0, 149.2 ppm; MS (EI): m/z (%) = 310 $[M]^+$ (100), 309 $[M-1]^+$ (59); HRMS (EI): m/z calcd for $C_{24}H_{22}$: 310.1721 $[M]^+$; found: 310.1722.

[4]**6i**: 3,4-Bis(methylidene)-2-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-diene: Colorless oil, yield: 33 %. R_f = 0.50 (hexane/ethyl acetate = 10:1); IR (neat): $\tilde{\nu}$ = 2978, 2926, 2855, 2363, 1583, 1493, 1371, 1312, 1259, 1215, 1144, 1115, 1028, 968, 900, 864, 758, 700, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 12H), 5.02 (s, 1H), 5.20 (s, 2H), 5.26 (s, 1H), 5.28 (s, 1H), 5.42 (s, 1H), 5.85 (d, J = 3.2 Hz, 1H), 5.90 (d, J = 3.2 Hz, 1H), 7.26–7.30 (m, 3H), 7.50–7.52 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 83.6, 114.8, 117.7, 127.2 (2C), 127.9, 131.5, 140.4, 149.8, 150.2 ppm; MS (EI): m/z (%) = 310 $[M+2]^+$ (4), 309 $[M+1]^+$ (22), 308 $[M]^+$ (100), 307 $[M-1]^+$ (32), 306 $[M-2]^+$ (3); HRMS (EI): m/z calcd for $C_{20}H_{25}BO_2$: 308.1948 $[M]^+$; found: 308.1949.

[5]**6j**: 3,4,5-Tris(methylidene)-2-phenylundeca-1,6-diene: Colorless oil, yield: 55 %. R_f = 0.31 (hexane); IR (neat): $\tilde{\nu}$ = 3086, 3022, 2957, 2926, 2856, 1811, 1578, 1493, 1379, 964, 903, 783, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.0 Hz, 3H), 1.20–1.47 (m, 4H), 2.09 (dt, J = 7.0, 6.4 Hz, 2H), 4.94 (d, J = 2.2 Hz, 1H), 5.05–5.07 (m, 1H), 5.10 (d, J = 2.2 Hz, 1H), 5.14–5.20 (m, 2H), 5.26 (d, J = 1.8 Hz, 1H), 5.35 (d, J = 2.0 Hz, 1H), 5.45 (d, J = 1.6 Hz, 1H), 5.70 (dt, J = 15.6, 7.0 Hz, 1H), 6.11 (d, J = 15.6 Hz, 1H), 7.22–7.48 ppm (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 14.1, 22.3, 31.5, 32.5, 115.0, 115.5, 117.8, 118.2, 126.9, 127.4, 127.9, 128.0, 130.5, 133.7, 147.1, 147.4, 148.6, 149.0 ppm; MS (EI): m/z (%) = 264 $[M]^+$ (20), 263 $[M-1]^+$ (32), 207 $[M-Bu]^+$ (100); HRMS (EI): m/z calcd for $C_{20}H_{24}$: 264.1878 $[M]^+$; found: 264.1881.

[5]**6k**: 3,4,5-Tris(methylidene)-2,6-diphenylhepta-1,6-diene: Colorless oil, yield: 37 %. R_f = 0.75 (hexane/ethyl acetate = 10:1); IR (neat): $\tilde{\nu}$ = 3057, 3024, 2962, 2923, 1491, 1445, 1406, 1325, 1261, 2070, 2026, 907, 756, 700, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.17 (d, J = 2.0 Hz, 2H), 5.21–5.24 (m, 1H), 5.28 (d, J = 2.0 Hz, 2H), 5.31 (d, J = 2.0 Hz, 2H), 5.36–5.39 (m, 1H), 5.39 (d, J = 2.0 Hz, 2H), 7.26–7.30 ppm (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.9, 118.5, 119.2, 127.3, 127.4, 127.9, 140.4, 147.6, 148.8, 149.1 ppm; MS (EI): m/z (%) = 285 $[M+1]^+$ (13), 284 $[M]^+$ (65), 283 (100); HRMS (EI): m/z calcd for $C_{22}H_{20}$: 284.1565 $[M]^+$; found: 284.1565.

[3]**6l**: 3-Methylidene-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,4-diene: Colorless oil, yield: 23 %. R_f = 0.50 (hexane/ethyl acetate = 10:1); IR (neat): $\tilde{\nu}$ = 2978, 2928, 1576, 1493, 1389, 1371, 1311,

1261, 1221, 1148, 1132, 1119, 968, 900, 783, 700, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (s, 12H), 5.15 (d, $J = 2.4$ Hz, 1H), 5.20 (d, $J = 2.4$ Hz, 1H), 5.42 (d, $J = 1.6$ Hz, 1H), 5.56 (d, $J = 1.6$ Hz, 1H), 5.70 (d, $J = 2.8$ Hz, 1H), 5.84 (d, $J = 2.8$ Hz, 1H), 7.20–7.41 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.8$, 83.6, 114.8, 117.7, 127.2, 127.2, 127.9, 127.9, 131.5, 149.7, 150.2 ppm; MS (EI): m/z (%) = 283 $[M+1]^+$ (8), 282 $[M]^+$ (40), 281 $[M-1]^+$ (23), 154 (100); HRMS (EI): m/z calcd for $C_{18}H_{23}BO_2$: 282.1791 $[M]^+$; found: 282.1787.

[4]**6m**: (*E*)-3,4-Bis(methylidene)-2-phenyldeca-1,5-diene: Colorless oil, yield: 55%. $R_f = 0.33$ (hexane); IR (neat): $\tilde{\nu} = 3024$, 2957, 2926, 1585, 1493, 1445, 1379, 1028, 964, 899, 779, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 6.8$ Hz, 3H), 1.27–1.42 (m, 4H), 2.10 (dt, $J = 6.8$, 6.4 Hz, 2H), 4.99 (d, $J = 2.2$ Hz, 1H), 5.11 (d, $J = 2.2$ Hz, 1H), 5.15 (d, $J = 2.0$ Hz, 1H), 5.25–5.29 (m, 2H), 5.30 (d, $J = 1.6$ Hz, 1H), 5.82 (dt, $J = 15.4$, 6.8 Hz, 1H), 6.11 (dd, $J = 15.4$, 0.6 Hz, 1H), 7.23–7.43 (m, 5H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 14.1$, 22.4, 31.5, 32.6, 115.5, 116.2, 117.6, 127.2, 127.9, 127.9, 130.1, 133.7, 140.7, 146.9, 148.8, 148.9 ppm; MS (EI): m/z (%) = 238 $[M]^+$ (5), 237 $[M-1]^+$ (3), 181 $[M-Bu]^+$ (100); HRMS (EI): m/z calcd for $C_{18}H_{22}$: 238.1721 $[M]^+$; found: 238.1724.

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[1] a) T. Yamamoto, T. Yasuda, K. Kobayashi, I. Yamaguchi, T. Koizumi, D. Ishii, M. Nakagawa, Y. Mashiko, N. Shimizu, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 498–500; b) I. H. Paik, S. Xie, T. A. Shapiro, T. Labonte, A. A. Narducci Sarjeant, A. C. Baege, G. H. Posner, *J. Med. Chem.* **2006**, *49*, 2731–2734; c) Z. Ikeda, K. Oshima, S. Matsubara, *Org. Lett.* **2005**, *7*, 4859–4861; d) M. D. Beery, M. K. Rath, V. V. Sheares, *Macromolecules* **2001**, *34*, 2469–2475; e) X. Han, E. J. Corey, *Org. Lett.* **1999**, *1*, 1871–1872; f) A. Hirao, Y. Sakano, K. Takenaka, S. Nakahama, *Macromolecules* **1998**, *31*, 9141–9145; g) H. Wang, A. B. Padias, H. K. Hall, Jr., *Macromolecules* **1998**, *31*, 3247–3250; h) L. Zhu, R. D. Rieke, *Tetrahedron Lett.* **1991**, *32*, 2865–2866; i) B. Gordon III, M. Blumenthal, *Polym. Bull.* **1985**, *14*, 69–72.

[2] a) H. Hopf, *Angew. Chem.* **1984**, *96*, 947–958; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 948–960; b) N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten, S. Karabunarliev, *Chem. Phys.* **1994**, *189*, 83–97; c) M. H. Palmer, J. A. Blair-Fish, P. Sherwood, *J. Mol. Struct.* **1997**, *412*, 1–18; d) M. R. Bryce, M. A. Coffin, P. J. Skabara, A. J. Moore, A. S. Batsanov, J. A. K. Howard, *Chem. Eur. J.* **2000**, *6*, 1955–1962; e) J. R. Dias, *Croat. Chem. Acta* **2004**, *77*, 325–330; f) B. C. Van Der Wiel, R. M. Williams, C. A. Van Walree, *Org. Biomol. Chem.* **2004**, *2*, 3432–3433.

[3] Reviews on radialenes: a) H. Hopf, G. Maas, *Angew. Chem.* **1992**, *104*, 953–977; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 931–954; b) F. Geneste, A. Moradpour, *Org. Prep. Proced. Int.* **1999**, *31*, 507–536; c) T. Höpfner, P. G. Jones, B. Ahrens, I. Dix, L. Ernst, H. Hopf, *Eur. J. Org. Chem.* **2003**, 2596–2611.

[4] Reviews on *gem*-diorganometallics: a) I. Marek, J.-F. Normant, *Chem. Rev.* **1996**, *96*, 3241–3267; b) I. Marek, J. F. Normant in *Organozinc Reagents: A Practical Approach* (Eds.: P. Knochel, P. Jones), Oxford University Press, Oxford, **1999**, pp. 119–137; c) I. Marek, *Chem. Rev.* **2000**, *100*, 2887–2900; d) S. Matsubara, K. Oshima, K. Utimoto, *J. Organomet. Chem.* **2001**, *617–618*, 39–46; e) V. M. Dembitsky, M. Srebnik in *Titanium and Zirconium in Organic Synthesis* (Ed.: I. Marek), Wiley-VCH, Weinheim, **2002**, pp. 230–281; reviews on *vic*-diorganometallics: f) I. Beletskaya, C. Moberg, *Chem. Rev.* **1999**, *99*, 3435–3461; g) L.-B. Han, M. Tanaka, *Chem. Commun.* **1999**, 395–402; h) M. Suginome, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221–3256; i) I. Beletskaya, C. Moberg, *Chem. Rev.* **2006**, *106*, 2320–2354; reviews on dianion chemistry: j) C. M. Thompson, *Dianion Chemistry in Organic Synthesis*, CRC Press, Boca Raton, **1994**; k) P. Langer, W. Freiberg, *Chem. Rev.* **2004**, *104*, 412–4149; l) F. Foubelo, M. Yus, *Curr. Org. Chem.* **2005**, *9*, 459–490; review on bisborylated compounds: m) V. M. Dembitsky, H. A. Ali, M. Srebnik, *Appl. Organomet. Chem.* **2003**, *17*, 327–345; see also: n) *Handbook of Functionalized Organometallics* (Ed.: P. Knochel), Wiley-VCH, Weinheim, **2005**.

[5] Reviews on metal-catalyzed cross-coupling reactions: a) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**; b) *Cross-Coupling Reaction: A Practical Guide*, *Vol. 219* (Ed.: N. Miyaura), Springer, Berlin, **2002**; c) *Handbook of Organopalladium Chemistry for Organic Synthesis* (Ed.: E. Negishi), John Wiley & Sons, New York, **2002**; d) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; e) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489.

[6] Preparation and reactions of 2,3-bis(trimethylstannyl)-1,3-butadiene: a) H. J. Reich, I. L. Reich, K. E. Yelm, J. E. Holladay, D. Gschneidner, *J. Am. Chem. Soc.* **1993**, *115*, 6625–6635; dendralene synthesis with a diene: b) S. Fielder, D. D. Rowan, M. S. Sherburn, *Angew. Chem.* **2000**, *112*, 4501–4503; *Angew. Chem. Int. Ed.* **2000**, *39*, 4331–4333.

[7] Preliminary reports: a) M. Shimizu, T. Kurahashi, T. Hiyama, *Synlett* **2001**, 1006–1008; b) M. Shimizu, K. Tanaka, T. Kurahashi, K. Shimono, T. Hiyama, *Chem. Lett.* **2004**, *33*, 1066–1067.

[8] a) T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu, T. Hiyama, *Angew. Chem.* **2001**, *113*, 812–814; *Angew. Chem. Int. Ed.* **2001**, *40*, 790–792; b) T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu, T. Hiyama, *Tetrahedron* **2002**, *58*, 6381–6395; c) M. Shimizu, C. Nakamaki, K. Shimono, M. Schelper, T. Kurahashi, T. Hiyama, *J. Am. Chem. Soc.* **2005**, *127*, 12506–12507; d) Shimizu, K. Shimono, T. Hiyama, *Chem. Lett.* **2006**, *35*, 838–839; e) M. Shimizu, M. Schelper, I. Nagao, K. Shimono, T. Kurahashi, T. Hiyama, *Chem. Lett.* **2006**, *35*, 1222–1223.

[9] a) D. S. Matteson, *Stereodirected Synthesis with Organoboranes*, Springer, Berlin, **1995**; b) E. Negishi, M. J. Idacavage, *Org. React.* **1985**, *33*, 1–246; c) H. C. Brown, T. Imai, N. G. Bhat, *J. Org. Chem.* **1986**, *51*, 5277–5282.

[10] No further methylene insertion was observed. Although the reason is unclear, borate formation of **3** with 1-bromo-1-lithioethene or 1,2-rearrangement of the 3-boryl-1,3-butadienyl group may be slower because of steric hindrance than the decomposition of the carbenoid.

[11] A. Karambuchi, N. Miyaura, A. Suzuki, *Tetrahedron Lett.* **1993**, *34*, 4827–4828.

[12] Diboryl-1,3-dienes: a) G. Zweifel, N. L. Polston, *J. Am. Chem. Soc.* **1970**, *92*, 4068–4071; b) A. Maercker, W. Brieden, T. Schmidt, H. D. Lutz, *Angew. Chem.* **1989**, *101*, 477–479; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 477–478; c) Y. N. Bubnov, *Pure Appl. Chem.* **1991**, *63*, 361–364; d) M. Enders, A. Kramer, H. Pritzkow, W. Siebert, *Angew. Chem.* **1991**, *103*, 80–81; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 84–85; e) N. Metzler, H. Noth, M. Thomann, *Organometallics* **1993**, *12*, 2423–2425; f) J. Hauss, H. Pritzkow, W. Siebert, *Chem. Ber.* **1995**, *128*, 183–185; g) G. Desurmont, R. Klein, S. Uhlenbrock, E. Laloe, L. Deloux, D. M. Giolando, Y. W. Kim, S. Pereira, M. Srebnik, *Organometallics* **1996**, *15*, 3323–3328.

[13] M. Suginome, Y. Ohmori, Y. Ito, *J. Organomet. Chem.* **2000**, *611*, 403–413.

[14] Reviews on Suzuki–Miyaura coupling reaction: a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; b) A. Suzuki in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, pp. 49–97; c) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147–168; d) N. Miyaura in *Cross-Coupling Reaction: A Practical Guide*, *Vol. 219* (Ed.: N. Miyaura), Springer, Berlin, **2002**, pp. 11–59; e) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633–9695; f) N. Miyaura in *Metal-Catalyzed*

Cross-Coupling Reactions, *Vol. 1* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 41–123.
[15] T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 11018–11019.
[16] Isolation, preparation, and biological activity of anolignan A and B: a) A. M. Rimando, J. M. Pezzuto, N. R. Farnsworth, T. Santisuk, V. Reutrakul, K. Kawanishi, *J. Nat. Prod.* **1994**, *57*, 896–904; b) M. M. Luo, A. Matsui, T. Esumi, Y. Iwabuchi, S. Hatakeyama, *Tetrahedron Lett.* **2000**, *41*, 4401–4402; c) M. Mori, K. Tonogaki, N. Nishiguchi, *J. Org. Chem.* **2002**, *67*, 224–226; d) I. M. S. Eldeen, E. E. Elgorashi, D. A. Mulholland, J. van Staden, *J. Ethnopharmacol.* **2006**, *103*, 135–138.
[17] R. Valsaraj, P. Pushpangadan, U. W. Smitt, A. Adsersen, S. B. Christensen, A. Sittie, U. Nyman, C. Nielsen, C. E. Olsen, *J. Nat. Prod.* **1997**, *60*, 739–742.
[18] Reviews on cross-conjugated compounds: a) M. Gholami, R. R. Tykwinski, *Chem. Rev.* **2006**, *106*, 4997–5027; b) R. R. Tykwinski, Y. Zhao, *Synlett* **2002**, 1939–1953; c) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**, pp. 251–320; d) R. R. Tykwinski, F. Diederich, *Liebigs Ann/Recl.* ***1997***, 649–661; e) N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, *45*, 633–637.
[19] Dendralenes can serve as valuable starting compounds for sequential multiple cycloadditions; for recent examples, see: a) N. A. Miller, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem.* **2007**, *119*, 955–958; *Angew. Chem. Int. Ed.* **2007**, *46*, 937–940; b) A. D. Payne, A. C. Willis, M. S. Sherburn, *J. Am. Chem. Soc.* **2005**, *127*, 12188–12189.
[20] P. T. Brain, B. A. Smart, H. E. Robertson, M. J. Davis, D. W. H. Rankin, W. J. Henry, I. Gosney, *J. Org. Chem.* **1997**, *62*, 2767–2773.
[21] M. T. Allen, D. G. Whitten, *Chem. Rev.* **1989**, *89*, 1691–1702.

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