JOC The Journal of Organic Chemistry

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Stereospecific Cross-Coupling between Alkenylboronates and Alkyl Halides Catalyzed by Iron−Bisphosphine Complexes

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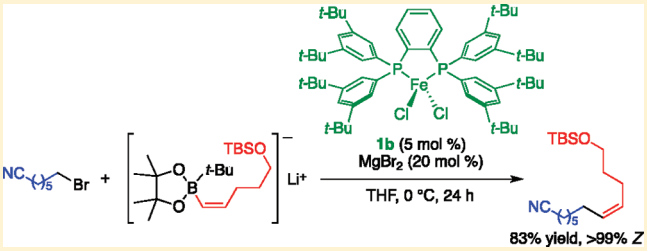
Supporting Information

ABSTRACT: A stereospecific and high-yielding cross-coupling reaction between alkenylboron reagents and alkyl halides is described. The reaction has been achieved by using well-defined iron−bisphosphine complexes such as **1b** $FeCl_2$(3,5-*t*-Bu_2-SciOPP), which was recently developed by the authors' group. Various nonactivated alkyl bromides and chlorides possessing a base/nucleophile-sensitive functional group can participate in the cross-coupling, demonstrating its utility for stereoselective synthesis of functional molecules bearing a carbon−carbon double bond.



Stereoselective synthesis of olefins is of great importance in organic chemistry; therefore, there has been continual effort to develop more efficient synthetic methods for over one hundred years.[1] The metal-catalyzed cross-coupling reaction has emerged as a powerful tool for carbon−carbon bond formation, and hence, various alkenylation reactions based on coupling technology were studied and applied in a number of synthetic studies.[2] Among them, considerable effort has recently been devoted to develop an efficient coupling between alkenylmetal reagents and alkyl halides. Fu developed a series of palladium- and nickel-catalyzed alkenylation reactions of primary and secondary alkyl halides with alkenyltin,[3] zinc,[4] zirconium,[5] and boron reagents.[6] Oshima found that cobalt catalysts were effective for the alkenylation of primary and secondary alkyl halides with 1-(trimethylsilyl)-ethenylmagnesium bromide.[7] Iron-catalyzed cross-coupling[8] has also been applied to the alkenylation of alkyl halides with organomagnesium or zinc reagents: Cossy and Cahiez independently reported the alkenylation of alkyl halides with alkenylmagnesium reagents using $FeCl_3$/TMEDA[9] and Fe(acac)$_3$/TMEDA/HMTA[10] catalyst systems. We also developed the iron-catalyzed coupling reaction of alkyl halides with alkenylzinc reagents using the $FeCl_3$/TMEDA catalyst system, adding an example of a highly stereoselective alkenylation reaction.[11] Despite the apparent advantage of iron catalyst in the cross-coupling of alkyl halides[12,13] and availability of stereochemically pure alkenyl boron compounds, there have been no examples of stereospecific alkenylation of nonactivated alkyl halides with organoboron reagents.[14] Herein, we report an efficient iron-catalyzed Suzuki−Miyaura coupling reaction between *E*- and *Z*-alkenylboronic acid pinacol esters **2** and alkyl halides, which proceeds in a stereospecific manner under mild conditions.

Since our initial screening of inorganic bases to activate alkenylboron reagents did not yield any coupling products, we examined the activation of alkenylboron reagent **2** by using alkyllithium reagents (Scheme 1).[15] As expected from our previous arylation-type coupling reactions, the resulting lithium alkenylborates **3** were found to be effectively coupled with alkyl halides in the presence of a catalytic amount of $MgBr_2$ and divalent iron−bisphosphine complexes **1** [$FeCl_2$(SciOPPs)].[16]

Scheme 1. Cross-Coupling of Alkyl Halides with Alkenylboron Reagents in the Presence of Iron−Bisphosphine Complexes 1

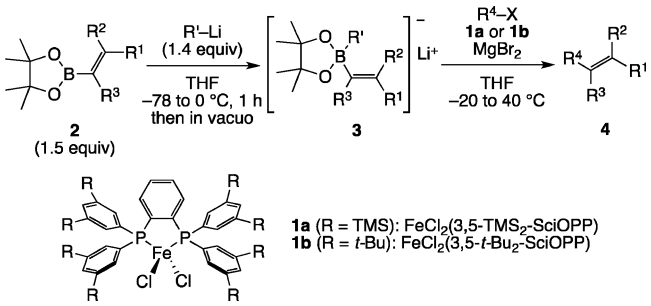
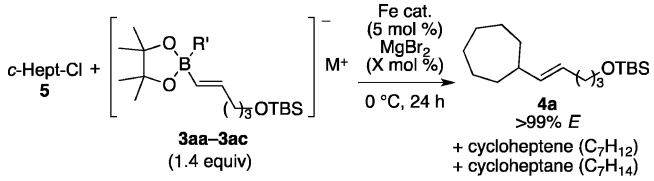


Table 1 summarizes the results of the screening of alkenylborates **3aa**−**3ac**, prepared from the corresponding alkenylboron reagent **2a** using an alkyl lithium or magnesium reagent (see the Experimental Section for the confirmation of their formations), in the coupling reaction with chlorocycloheptane **5**. As shown in entries 1 and 2, the reaction using *t*-BuLi resulted in a slightly better yield (69%) of the coupling product **4a** than that using BuLi (66%), as well as the formation of byproducts (8% cycloheptene and 2% cycloheptane). At an

Received: October 28, 2011
Published: December 8, 2011

dx.doi.org/10.1021/jo202151f | *J. Org. Chem.* 2012, 77, 1168−1173

Table 1. Catalyst and Additive Screening of the Cross-Coupling between Alkenylborate 3aa–3ac and Chlorocycloheptane 5[a]



entry	Fe cat.	R′-M	alkenyl borate	X	yield of **4a**(%)[b]	GC yield (%)[c] C_7H_{12}	GC yield (%)[c] C_7H_{14}	RSM[d] **5**(%)[c]
1	**la**	BuLi	**3aa**	20	66	8	2	15
2	**la**	*t*-BuLi	**3ab**	20	69	7	2	21
3	**la**	*t*-BuLi	**3ab**	20	55	10	3	27
4[e]	**lb**	*t*-BuLi	**3ab**	20	83	5	2	5
5	**lb**	*t*-BuLi	**3ab**	0	0	0	0	97
6	**lb**	*t*-BuMgCl	**3ac**	0	4	12	5	56
7	$FeCl_2(dppbz)_2$	*t*-BuLi	**3ab**	20	0	0	0	92

[a]Reactions were carried out on a 0.4–0.5 mmol scale. [b]NMR yield. [c]Yields of cycloheptene and cycloheptane and recovery of chlorocycloheptane were determined by GC analysis using undecane as an internal standard. [d]Recovery of chlorocycloheptane. [e]The reaction was carried out at 40 °C for 24 h.

elevated temperature (40 °C), the reaction took place in a less selective manner, resulting in a lower yield of **4a** (entry 3). Iron catalyst **1b** was found to be more effective than **1a** to give **4a** in 83% yield (entry 4). In the absence of $MgBr_2$, the coupling reaction did not take place and chlorocycloheptane **5** was recovered quantitatively (entry 5).[15,17] We currently assume that $MgBr_2$ accelerates transmetalation between borate and the iron catalyst.[15] The use of *t*-BuMgCl instead of alkyllithium gave sluggish results, probably owing to instability of the magnesium alkenylborate (entry 6). Interestingly, the parent iron complex $FeCl_2(dppbz)_2$ (R = H in Scheme 1), which is an efficient catalyst for iron-catalyzed Negishi coupling,[18] did not show any catalytic activity (entry 7). The peripheral steric demand[19] of **1a** and **1b** is crucial for the present coupling reaction. It should be noted that the double bond geometry was completely retained in all cases.

Table 2 illustrates the scope of the stereospecific coupling reaction in the presence of iron complexes **1**. As shown in entries 1–10, a variety of primary and secondary alkyl bromides participate in the reaction. *E*- and *Z*-Alkenylboron reagents possessing a silyl ether moiety were coupled with bromocycloheptane at −20 °C to give the corresponding coupling products in 98% and 93% yield, respectively, without any loss of geometrical purity. While the reactions with α-substituted alkenylboron reagents required an elevated temperature (40 °C) and gave the coupling product in modest yield, the trisubstituted olefin was obtained also in a highly stereoselective manner (entry 4). We assume that α-substitution impedes the transmetalation between alkenylboron reagents and iron complexes **1** and the same tendency was found in the reaction with 1-styrylboron reagent (entry 8). As shown in entries 5–10, the coupling reaction is chemoselective: the acetoxy, benzoyl, carbamate, ethoxycarbonyl, cyano, and cyclopropyl groups remained untouched under the reaction conditions. Based on the high functional group compatibility and quantitative formation of lithium borates, the intermediacy of alkenyllithium or magnesium reagents is unlikely. Although no reactions of nonactivated primary alkyl chlorides took place, benzyl and allyl chlorides could participate in the stereospecific coupling reaction. The reaction of methyl 4-(chloromethyl)benzoate took place at −20 °C to give the coupling product in 44% yield along with the dimer of the benzoate (20% yield) and the alkane (<5% yield) (entry 11). Cinnamyl chloride was also coupled with the alkenylboron reagent to give α-attack product **4l** rather than γ-attack product **4m** (entry 12).[20]

We carried out the reaction of *N*-allyl-*N*-(2-bromoethyl)-4-methylbenzenesulfonamide with **3ab** under standard reaction conditions to determine if the radical-mediated cyclization/coupling reaction[21] takes place (Scheme 2). The expected product **4n** was obtained in 56% yield along with byproducts (3-methyl and 3-methylene pyrrolidine derivatives in 25% and 3% yield, respectively, and *N*-allyl-*N*-ethyl-4-methylbenzenesulfonamide in 10% yield), suggesting the intermediacy of an alkyl radical intermediate, as we reported for related reactions.[11,13a,h,i,15,17a,18b] Although the details regarding the reaction mechanism are unclear and need further investigations, it is assumed that the retention of the alkene geometry during radical-mediated cross-coupling is a result of stereospecific transmetalation from boron to iron and stereospecific substitution of the alkenyl ligand on the iron center by the alkyl radical intermediate, which results in the formation of a monohalogenated iron(II) intermediate and the corresponding cross-coupling product.[22]

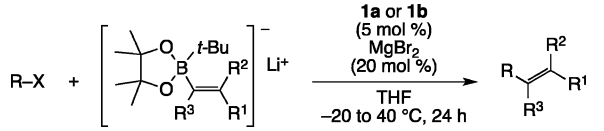
In summary, a stereospecific cross-coupling between various alkenylboron reagents and alkyl halides has been achieved for the first time by using structurally well-defined iron–bisphosphine complexes. The present alkenylation method possesses the following synthetically attractive features: it is stereospecific, high yielding, functional group tolerant, and rare metal free, and has a broad scope for application to alkyl halides.

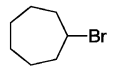
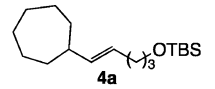
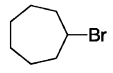
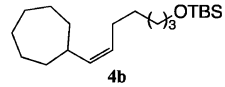
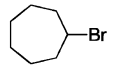
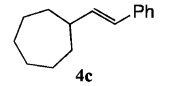
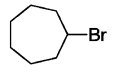
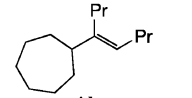
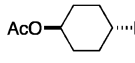
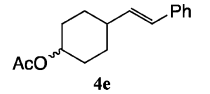
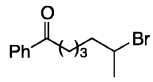
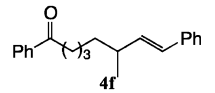
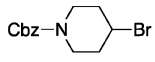
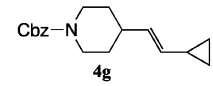
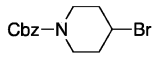
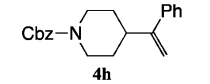
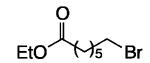
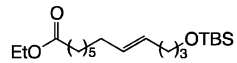
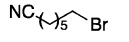
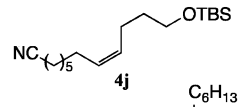
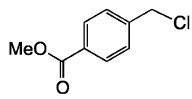
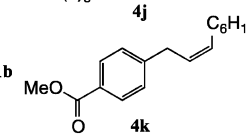
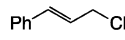
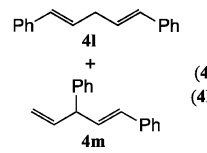
EXPERIMENTAL SECTION

General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Proton nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR) and boron nuclear magnetic resonance (^{11}B NMR) spectra were reported on a NMR spectrometer (392, 98.5, and 96.3 MHz, respectively). Proton, carbon, and boron chemical shift values are reported in parts per million (ppm, δ scale) downfield from Me_4Si, Me_4Si, and BF_3·OEt_2, respectively, and are

dx.doi.org/10.1021/jo202151f | J. Org. Chem. 2012, 77, 1168–1173

Table 2. Cross-Coupling of Alkyl Halides with Alkenylboron Reagents[a,b]

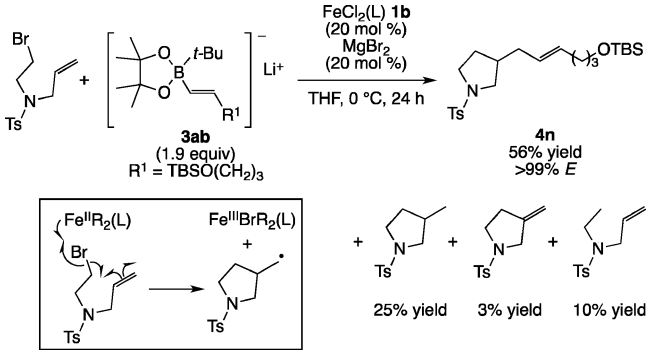


entry	R–X	Fe cat.	coupling product	yield (%) (*E*/*Z*)
1		**1a**	 **4a**	98 (>99% *E*)
2		**1a**	 **4b**	93 (>99% *Z*)
3		**1a**	 **4c**	96 (>99% *E*) 88[c] (>99% *E*)
4[d,e]		**1a**	 **4d**	58 (>99% *E*)
5		**1a**	 **4e**	88[f] (>99% *E*)
6[g]		**1a**	 **4f**	83 (>99% *E*)
7		**1a**	 **4g**	85 (>99% *E*)
8[d,e]		**1a**	 **4h**	77
9		**1b**	 **4i**	73 (>99% *E*)
10		**1b**	 **4j**	83 (>99% *Z*)
11		**1b**	 **4k**	44 (>99% *Z*)
12		**1b**	 **4l** + **4m**	87 (**4l**/**4m** = 89/11) (**4l**,**4m**, >99% *E*)

[a]Reactions were carried out at −20 to 0 °C for 24 h on a 0.4−1.5 mmol scale. Lithium alkenylborates were prepared from corresponding alkenylboron reagents using *t*-BuLi unless otherwise noted. [b]Alkenylboron reagents employed were geometrically pure. [c]10 mmol scale. [d]BuLi was used instead of *t*-BuLi. [e]Reaction was carried out at 40 °C for 24 h. [f]*trans*/*cis* = 57/43. [g]Using 20 mol % **1a**.

referenced to Me_4Si (δ 0.0), $CDCl_3$ (δ 77.0), $BF_3{\cdot}OEt_2$ (δ 0.0), respectively. IR spectra were recorded on an ATR-FTIR spectrometer. Characteristic IR absorptions are reported in cm^{-1}. Gas chromatographic (GC) analysis was performed on a GC system equipped with FID detector and capillary column (30 m × 0.25 mm i.d., 0.25 mm film thickness). NMR yield was determined for a crude product by ^1H NMR analyses by using 1,1,2,2-tetrachloroethane or pyrazine as an internal standard. GC yield was determined upon calibration by using undecane as an internal standard. Purity of isolated compounds was determined by GC analysis and/or ^1H NMR analysis. High-resolution mass spectra (HRMS) were obtained using the electron impact (EI) method. Iron catalysts **1a** and **1b** were prepared as described in the literature.[15]

Scheme 2. Cross-Coupling via Alkyl Radicals



Preparation of Lithium Alkenylborate 3ab from 2-[(1*E*)-5-*tert*-Butyldimethylsilyloxypent-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 2a and *tert*-Butyllithium. To a THF solution (2.0 mL) of 2-[(1*E*)-5-*tert*-butyldimethylsilyloxypent-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2a** (0.196 g, 0.60 mmol) was added *t*-BuLi (0.38 mL, 1.59 M in pentane, 0.60 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 °C for 30 min. The solvent was removed *in vacuo* at 0 °C. Quantitative formation of borate was determined by ^1H and ^{13}C NMR spectra of the residual solid in THF-d_8 (> 97% conversion). ^1H NMR (THF-d_8, 392 MHz) δ 0.03 (s, 6H), 0.64 (s, 9H), 0.89 (s, 9H), 1.05 (s, 6H), 1.08 (s, 6H), 1.55 (tt, *J* = 6.7 and 7.2 Hz, 2H), 1.99 (dt, *J* = 6.7 and 7.2 Hz, 2H), 3.61 (t, *J* = 6.7 Hz, 2H), 5.42 (dt, *J* = 6.7 and 17.2 Hz, 1H), 5.71 (d, *J* = 17.2 Hz, 1H); ^{13}C NMR (THF-d_8, 98.5 MHz) δ −5.1 (2C), 19.0, 26.4 (3C), 28.2 (2C), 28.5 (2C), 30.6 (3C), 33.9, 34.5, 64.1, 78.1 (2C), 130.7; ^{11}B NMR (THF-d_8, 96.3 MHz) δ 5.65 (brs). The ^{13}C NMR signals of the carbons α to the boron were not observed because of the nuclear quadrupole resonance.

Representative Procedure for the Iron-Catalyzed Reaction Shown in Table 1. To a THF solution (2.0 mL) of **2a** (0.75 mmol) was added organometallic reagents (0.70 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 °C for 30 min. The solvent was removed *in vacuo* at 0 °C. To the residual borate were added THF (1.2 mL), undecane (0.25 mmol), chlorocycloheptane (0.50 mmol), $MgBr_2$ (0.10 mmol, 20 mol %), and an iron catalyst (25 μmol, 5.0 mol %) at −78 °C. The coupling reaction was carried out at −20 °C for 24 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with Et_2O. The combined organic extracts were filtered with a pad of Florisil. The yield of **4a** was determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The yields of cycloheptane and cycloheptene, and the recovery of chlorocycloheptane were determined by GC analysis of the crude product using undecane as an internal standard.

Procedure A; A Representative Procedure for the Iron-Catalyzed Reaction Shown in Table 2. *Synthesis of (E)-tert-butyl[(5-cycloheptylpent-4-en-1-yl)oxy]dimethylsilane (**4a**).* To a THF solution (2.0 mL) of **2a** (0.196 g, 0.60 mmol) was added *t*-BuLi (0.35 mL, 1.59 M in pentane, 0.56 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 °C for 30 min. The solvent was removed *in vacuo* at 0 °C. To the residual borate were added THF (1.2 mL), undecane (38.0 mg, 0.24 mmol), bromocycloheptane (71.2 mg, 0.40 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80 μmol), and iron complex **1a** (0.40 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %) at −78 °C. The coupling reaction was carried out at −20 °C for 24 h. After cooling to ambient

dx.doi.org/10.1021/jo202151f | *J. Org. Chem.* 2012, 77, 1168−1173

temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with Et_2O. The combined organic extracts were filtered with a pad of Florisil. The title compound (0.117 g, 98% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane/AcOEt = 50/1). R_f = 0.69 (hexane/AcOEt = 10/1); IR (neat) 2926, 2855, 1461, 1388, 1361, 1256, 1099, 1106, 966, 939, 833, 773, 662; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 0.04 (s, 6H), 0.89 (s, 9H), 1.24−1.33 (m, 2H), 1.39−1.74 (m, 12H), 2.00 (dt, J = 7.2 and 6.3 Hz, 2H), 2.05−2.12 (m, 1H), 3.60 (t, J = 6.3 Hz, 2H), 5.31 (dt, J = 15.4 and 6.3 Hz, 1H), 5.41 (dd, J = 7.2 and 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ −5.3 (2C), 18.4, 26.0 (3C), 26.2 (2C), 28.4 (2C), 28.8, 32.8, 35.0 (2C), 42.8, 62.6, 126.3, 137.7; HRMS (EI) m/z [M − t-Bu]$^+$ calcd for $C_{14}H_{27}OSi$ 239.1831; found 239.1828.

*Synthesis of (Z)-tert-Butyl[(5-cycloheptylpent-4-en-1-yl)oxy]-dimethylsilane (**4b**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using bromocycloheptane (71.6 mg, 0.40 mmol), 2-[(1*Z*)-5-*tert*-butyldimethylsilyloxypent-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.196 g, 0.60 mmol), t-BuLi (0.35 mL, 1.59 M in pentane, 0.56 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80 μmol), and iron complex **1a** (0.40 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %). Conditions: −20 °C, 24 h. The title compound (0.112 g, 93% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane/AcOEt = 50/1). R_f = 0.66 (hexane/AcOEt = 10/1); IR (neat) 2926, 2855, 1471, 1461, 1388, 1361, 1254, 1100, 1006, 988, 939, 833, 773, 728, 679, 662; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 0.05 (s, 6H), 0.90 (s, 9H), 1.23−1.32 (m, 2H), 1.42−1.66 (m, 12H), 2.08 (dt, J = 7.2 and 7.6 Hz, 2H), 2.40−2.49 (m, 1H), 3.61 (t, J = 6.3 Hz, 2H), 5.19 (dt, J = 7.2 and 10.5 Hz, 1H), 5.31 (dd, J = 9.9 and 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ −5.3 (2C), 18.3, 23.6, 26.0 (3C), 26.4 (2C), 28.4 (2C), 33.1, 35.3 (2C), 37.8, 62.7, 125.9, 137.4; HRMS (EI) m/z [M − t-Bu]$^+$ calcd for $C_{14}H_{27}OSi$ 239.1831.; found 239.1832.

*Synthesis of (E)-(2-Cycloheptylethenyl)benzene (**4c**).* The reaction was carried out according to Procedure A on a 0.51 mmol scale by using bromocycloheptane (89.5 mg, 0.51 mmol), (*E*)-4,4,5,5-tetramethyl-2-(2-phenylethenyl)-1,3,2-dioxaborolane (0.173 g, 0.75 mmol), t-BuLi (0.42 mL, 1.65 M in pentane, 0.70 mmol), $MgBr_2$ (1.00 mL, 0.10 M in THF, 0.10 mmol), and iron complex **1a** (0.50 mL, 50.0 mM in THF, 25 μmol, 5.0 mol %). Conditions: −20 °C, 24 h. The title compound (96.8 mg, 96% yield, 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (100% hexane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[11]

*Synthesis of (E)-Oct-4-en-4-ylcycloheptane (**4d**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using bromocycloheptane (71.1 mg, 0.40 mmol), (*Z*)-4,4,5,5-tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (0.191 g, 0.80 mmol), BuLi (0.48 mL, 1.59 M in hexane, 0.76 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80.0 μmol), and iron complex **1a** (0.400 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %). Conditions: 40 °C, 24 h. The title compound (48.6 mg, 58% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (100% hexane). R_f = 0.68 (100% hexane); IR (neat) 2956, 2922, 2858, 1458, 1376, 1260, 1068, 892, 805, 741; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 0.88 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H), 1.25−1.40 (m, 8H), 1.48−1.62 (m, 4H), 1.67−1.71 (m, 4H), 1.92−1.97 (m, 5H), 5.08 (t, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 13.9, 14.5, 22.7, 23.4, 27.2 (2C), 27.9 (2C), 29.8, 32.6, 35.1 (2C), 47.3, 122.5, 146.6; HRMS (EI) m/z [M]$^+$ calcd for $C_{15}H_{28}$ 208.2191; found 208.2185.

*Synthesis of (E)-4-(2-Phenylethenyl)cyclohexyl Acetate (**4e**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using *trans*-4-bromocyclohexyl acetate (88.6 mg, 0.40 mmol), (*E*)-4,4,5,5-tetramethyl-2-(2-phenylethenyl)-1,3,2-dioxaborolane (0.140 g, 0.61 mmol), t-BuLi (0.34 mL, 1.65 M in pentane, 0.56 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80.0 μmol), and iron complex **1a** (0.40 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %). Conditions: −20 °C, 24 h. The title compounds (85.7 mg, 88% yield, > 99% pure on GC analysis, *cis*:*trans* = 43/57) was obtained as a colorless oil after silica gel column chromatography (hexane/AcOEt = 50/1). R_f = 0.48 (hexane/AcOEt = 4/1); mixture of *cis* and *trans* isomers: IR (neat) 3025, 2929, 2859, 1730, 1599, 1492, 1448, 1368, 1233, 1157, 1123, 1090, 1027, 965, 899, 842, 745, 693; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 1.25−1.48 (m, 4H), 1.56−1.69 (m, 2H), 1.89−1.92 (m, 2H), 2.04 (s, 3H), [2.07 (s, 3H)], 2.13−2.16 (m, 1H), [2.23 (br, 1H)], 4.70 (m, 1H), [5.00 (m, 1H)], 6.13 (dd, J = 6.1 and 15.9 Hz, 1H), [6.21 (dd, J = 6.7 and 15.9 Hz, 1H)], 6.37 (d, J = 15.9 Hz, 1H), [6.39 (d, J = 15.9 Hz, 1H)], 7.17−7.21 (m, 1H), 7.26−7.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 21.4, 29.2 (2C) [27.3, 2C], 31.3 (2C) [30.7, 2C], 40.1 [39.5], 72.9 [69.6], 126.0 (2C) [126.0, 2C], 127.0 [126.0], 128.2 [128.0], 128.5 (2C) [128.5, 2C], 134.9 [135.4], 137.6 [137.7], 170.6; HRMS (EI) m/z [M]$^+$ calcd for $C_{16}H_{20}O_2$ 244.1463; found 244.1455. The values in parentheses refer to the minor (*cis*) isomer.

*Synthesis of (E)-6-Methyl-1,8-diphenyloct-7-en-1-one (**4f**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using 6-bromo-1-phenylheptan-1-one (0.107 g, 0.40 mmol), (*E*)-4,4,5,5-tetramethyl-2-(2-phenylethenyl)-1,3,2-dioxaborolane (0.276 g, 1.2 mmol), t-BuLi (0.73 mL, 1.59 M in pentane, 1.16 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80.0 μmol), and iron complex **1a** (1.60 mL, 50.0 mM in THF, 80 μmol, 20.0 mol %). Conditions: −20 °C, 24 h. The title compound (97.3 mg, 83% yield, > 98% pure on GC analysis) was obtained as a colorless oil after purification by GPC (eluent: $CHCl_3$). R_f = 0.47 (hexane/AcOEt = 4/1); IR (neat) 3059, 3024, 2929, 2865, 1739, 1683, 1597, 1579, 1492, 1448, 1409, 1365, 1279, 1217, 1179, 1072, 1001, 966, 912, 848, 746, 690, 657; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 1.08 (d, J = 6.7 Hz, 3H), 1.38−1.46 (m, 4H), 1.70−1.79 (m, 2H), 2.31 (m, 1H), 2.96 (t, J = 7.2 Hz, 2H), 6.08 (dd, J = 8.0 and 15.7 Hz, 1H), 6.34 (d, J = 15.7 Hz, 1H), 7.17−7.21 (m, 1H), 7.26−7.36 (m, 4H), 7.43−7.47 (m, 2H), 7.52−7.57 (m, 1H), 7.93−7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 20.7, 24.4, 27.2, 36.9, 37.2, 38.6, 126.0 (2C), 126.8, 128.0 (2C), 128.2, 128.4 (2C), 128.5 (2C), 132.9, 136.7, 137.0, 137.8, 200.5; HRMS (EI) m/z [M]$^+$ calcd for $C_{21}H_{24}O$ 292.1827; found 292.1828.

*Synthesis of 1-Benzyloxycarbonyl-4-[(1E)-2-cyclopropylvinyl]-piperidine (**4g**).* The reaction was carried out according to Procedure A on a 0.42 mmol scale by using 4-bromo-*N*-(benzyloxycarbonyl)-piperidine (0.125 g, 0.42 mmol), (*E*)-2-(2-cyclopropylethenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.116 g, 0.60 mmol), t-BuLi (0.35 mL, 1.59 M in pentane, 0.56 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80 μmol), and iron complex **1a** (0.40 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %). Conditions: 0 °C, 24 h. The title compound (0.102 g, 85% yield, > 99% pure on GC analysis) was obtained as a white solid after silica gel column chromatography (hexane/AcOEt = 50/1 to 20/1). R_f = 0.42 (hexane/AcOEt = 4/1); IR (neat) 3006, 2932, 2852, 1694, 1498, 1468, 1427, 1363, 1289, 1275, 1246, 1217, 1171, 1118, 1071, 1016, 962, 910, 865, 811, 763, 731, 696; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 0.29−0.33 (m, 2H), 0.64−0.69 (m, 2H), 1.21−1.34 (m, 3H), 1.64−1.67 (m, 2H), 2.02−2.11 (m, 1H), 2.77−2.83 (m, 2H), 4.15 (br, 2H), 4.95 (dd, J = 8.5 and 15.2 Hz, 1H), 5.12 (s, 2H), 5.44 (dd, J = 6.7 and 15.2 Hz, 1H), 7.30−7.32 (m, 1H), 7.35−7.36 (m, 4H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 6.5 (2C), 13.6, 32.0, 38.6 (2C), 44.0 (2C), 66.9, 127.8 (2C), 127.9, 128.4 (2C), 131.8, 132.8, 137.0, 155.3; HRMS (EI) m/z [M]$^+$ calcd for $C_{18}H_{23}NO_2$ 285.1729; found 285.1724.

*Synthesis of 1-Benzyloxycarbonyl-4-(1-phenylvinyl)piperidine (**4h**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using 4-bromo-*N*-(benzyloxycarbonyl)piperidine (0.120 g, 0.40 mmol), 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (0.184 g, 0.80 mmol), BuLi (0.48 mL, 1.59 M in hexane, 0.76 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80 μmol), and iron complex **1a** (0.80 mL, 50.0 mM in THF, 40 μmol, 10.0 mol %). Conditions: 40 °C, 24 h. The title compound (99.1 mg, 77% yield, > 99% pure on GC analysis) was obtained as a white solid after silica gel column chromatography (hexane/AcOEt = 50/1 to 20/1). R_f = 0.38 (hexane/AcOEt = 4/1); IR (neat) 3032, 2939, 2855, 1693, 1626, 1495, 1468, 1427, 1381, 1363, 1318, 1275, 1253, 1217, 1125, 1074, 1027, 943, 900, 865, 776, 763, 732, 696; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 1.34−1.44 (br, 2H), 1.78−1.81 (br, 2H), 2.59 (tt, J = 3.6 and 11.2 Hz, 1H), 2.83 (br, 2H), 4.26 (br, 2H), 5.00 (s, 1H), 5.13 (s, 2H), 5.18 (s, 1H), 7.27−7.36 (m, 10H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 31.4,

dx.doi.org/10.1021/jo202151f | J. Org. Chem. 2012, 77, 1168−1173

40.7 (2C), 44.5 (2C), 67.0, 111.4, 126.6 (2C), 127.3, 127.8 (2C), 127.9, 128.3 (2C), 128.5 (2C), 136.9, 142.0, 152.8, 155.2; HRMS (EI) m/z $[M]^+$ calcd for $C_{21}H_{23}NO_2$ 321.1729; found 321.1741.

*Synthesis of (E)-Ethyl 12-[(tert-Butyldimethylsilyl)oxy]dodec-8-enoate (**4i**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using ethyl 7-bromo-heptanoate (95.1 mg, 0.40 mmol), **2a** (0.261 g, 0.80 mmol), *t*-BuLi (0.48 mL, 1.59 M in pentane, 0.76 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80 μmol), and iron complex **1b** (0.40 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %). Conditions: 0 °C, 24 h. The title compound (0.105 g, 73% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane/AcOEt = 50/1). R_f = 0.61 (hexane/AcOEt = 4/1); IR (neat) 2929, 2856, 1737, 1463, 1371, 1252, 1179, 1099, 1034, 1006, 967, 939, 834, 774, 726, 662; ^{1}H NMR (392 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.89 (s, 9H), 1.23−1.27 (m, 3H), 1.29−1.38 (m, 6H), 1.53−1.66 (m, 4H), 1.94−2.05 (m, 4H), 2.28 (t, J = 7.2 Hz, 2H), 3.60 (t, J = 6.3 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 5.39 (m, 2H); ^{13}C NMR (98.5 MHz, $CDCl_3$) δ −5.3 (2C), 14.2, 18.3, 24.9, 26.0 (3C), 28.7, 28.8, 29.0, 29.4, 32.5, 32.7, 34.4, 60.1, 62.6, 129.8, 130.6, 173.9; HRMS (EI) m/z $[M - t\text{-Bu}]^+$ calcd for $C_{16}H_{31}O_3Si$ 299.2042; found 299.2032.

*Synthesis of (Z)-12-[(tert-Butyldimethylsilyl)oxy]dodec-8-enenitrile (**4j**).* The reaction was carried out according to Procedure A on a 0.41 mmol scale by using 7-bromoheptanenitrile (77.3 mg, 0.41 mmol), 2-[(1*Z*)-5-*tert*-butyldimethylsilyloxypent-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.261 g, 0.80 mmol), *t*-BuLi (0.48 mL, 1.59 M in pentane, 0.76 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80 μmol), and iron complex **1b** (0.40 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %). Conditions: 0 °C, 24 h. The title compound (0.104 g, 83% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane/AcOEt = 25/1). R_f = 0.50 (hexane/AcOEt = 4/1); IR (neat) 2928, 2857, 1734, 1463, 1387, 1361, 1254, 1096, 1006, 966, 939, 834, 774, 715, 661; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 0.05 (s, 6H), 0.90 (s, 9H), 1.32−1.38 (m, 4H), 1.43−1.47 (m, 2H), 1.56 (tt, J = 6.3 and 8.1 Hz, 2H), 1.66 (tt, J = 7.1 and 7.2 Hz, 2H), 2.01−2.10 (m, 4H), 2.33 (t, J = 6.7 Hz, 2H), 3.61 (t, J = 6.3 Hz, 2H), 5.34 (dt, J = 10.8 and 5.8 Hz, 1H), 5.39 (dt, J = 10.8 and 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ −5.3 (2C), 17.1, 18.3, 23.5, 25.4, 25.9 (3C), 27.0, 28.4, 28.6, 29.3, 32.9, 62.6, 119.8, 129.6, 129.8; HRMS (EI) m/z $[M - t\text{-Bu}]^+$ calcd for $C_{14}H_{26}NOSi$ 252.1784; found 252.1781.

*Synthesis of (Z)-Methyl 4-(non-2-en-1-yl)benzoate (**4k**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using methyl 4-(chloromethyl)benzoate (74.7 mg, 0.40 mmol), (*Z*)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (0.191 g, 0.80 mmol), *t*-BuLi (0.48 mL, 1.60 M in pentane, 0.76 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80.0 μmol), and iron complex **1b** (0.40 mL, 50.0 mM in THF, 20 μmol, 5.0 mol %). Conditions: −20 °C, 24 h. The title compound (45.9 mg, 44% yield, > 98% pure on GC analysis) was obtained as a colorless oil after purification by GPC (eluent: $CHCl_3$). R_f = 0.58 (hexane/AcOEt = 4/1); IR (neat) 2954, 2925, 2854, 1722, 1610, 1575, 1508, 1435, 1378, 1309, 1275, 1191, 1107, 1020, 969, 918, 853, 836, 807, 756, 725, 699; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 0.87−0.90 (m, 3H), 1.22−1.41 (m, 8H), 2.14 (dt, J = 6.7 and 7.2 Hz, 2H), 3.45 (d, J = 5.8 Hz, 2H), 3.90 (s, 3H), 5.49−5.59 (m, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 14.1, 22.6, 27.3, 29.0, 29.6, 31.7, 33.5, 51.2, 126.8, 127.8, 128.3 (2C), 129.7 (2C), 131.9, 146.8, 167.1; HRMS (EI) m/z $[M]^+$ calcd for $C_{17}H_{24}O_2$ 260.1776; found 260.1770.

*Synthesis of (1E,4E)-1,5-Diphenylpenta-1,4-diene (**4l**) and (E)-Penta-1,4-diene-1,3-diyldibenzene (**4m**).* The reaction was carried out according to Procedure A on a 1.51 mmol scale by using cinnamyl chloride (0.230 g, 1.51 mmol), (*E*)-4,4,5,5-tetramethyl-2-(2-phenylethenyl)-1,3,2-dioxaborolane (0.518 g, 2.25 mmol), *t*-BuLi (1.32 mL, 1.59 M in pentane, 2.10 mmol), $MgBr_2$ (3.00 mL, 0.10 M in THF, 0.30 mol), and iron complex **1b** (1.50 mL, 50.0 mM in THF, 75 μmol, 5.0 mol %). Conditions: 0 °C, 24 h. The title compounds (0.290 g, 87% yield, > 99% pure on GC analysis, **4l**/**4m** = 89/11) were obtained as a white solid after silica gel column chromatography (100% hexane).[1]H and ^{13}C NMR spectra have been attached. Analytical data for the title compounds have been reported.[23]

*Synthesis of (E)-3-{6-[(tert-Butyldimethylsilyl)oxy]hex-2-en-1-yl}-1-tosylpyrrolidine (**4n**).* The reaction was carried out according to Procedure A on a 0.40 mmol scale by using *N*-allyl-*N*-(2-bromoethyl)-4-methylbenzenesulfonamide (0.127 g, 0.40 mmol), **2a** (0.261 g, 0.80 mmol), *t*-BuLi (0.48 mL, 1.59 M in pentane, 0.76 mmol), $MgBr_2$ (0.80 mL, 0.10 M in THF, 80 μmol), and iron complex **1b** (1.60 mL, 50.0 mM in THF, 80 μmol, 20.0 mol %). Conditions: 0 °C, 24 h. The title compound (97.2 mg, 56% yield, 98% pure on GC analysis) was obtained as a white oil after silica gel column chromatography (hexane/AcOEt = 15/1). R_f = 0.38 (hexane/AcOEt = 4/1); IR (neat) 2928, 2856, 1598, 1471, 1388, 1344, 1305, 1289, 1253, 1160, 1036, 1016, 969, 939, 834, 815, 774, 708, 661; ^{1}H NMR ($CDCl_3$, 392 MHz) δ 0.04 (s, 6H), 0.89 (s, 9H), 1.36−1.46 (m, 1H), 1.50−1.57 (m, 2H), 1.85−1.93 (m, 3H), 1.97−2.10 (m, 3H), 2.43 (s, 3H), 2.82 (dd, J = 8.1 and 9.7 Hz, 1H), 3.19 (dt, J = 9.9 and 7.6 Hz, 1H), 3.29−3.34 (m, 1H), 3.37 (dd, J = 7.2 and 9.7 Hz, 1H), 3.58 (t, J = 6.3 Hz, 2H), 5.26 (dt, J = 15.1 and 6.3 Hz, 1H), 5.36 (dt, J = 15.1 and 6.7 Hz, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ −5.3 (2C), 18.3, 21.5, 25.9(3C), 28.7, 30.9, 32.5, 36.0, 38.7, 47.5, 52.7, 62.5, 127.4, 127.5 (2C), 129.6 (2C), 132.1, 134.0, 143.2; HRMS (EI) m/z $[M - t\text{-Bu}]^+$ calcd for $C_{19}H_{30}NO_3SSi$ 380.1716; found 380.1710.

Large-Scale Procedure for the Cross-Coupling Reaction of Bromocycloheptane and 4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane. To a THF solution (50 mL) of (*E*)-4,4,5,5-tetramethyl-2-(2-phenylethenyl)-1,3,2-dioxaborolane (3.46 g, 15.0 mmol) was added *t*-BuLi (8.80 mL, 1.59 M in pentane, 14.0 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 °C for 30 min. The solvent was removed *in vacuo* at 0 °C. To the residual borate were added THF (50 mL), bromocycloheptane (1.78 g, 10.1 mmol), $MgBr_2$ (368.2 mg, 2.0 mmol), and iron complex **1a** (575.3 mg, 0.50 mmol, 5.0 mol %) at −78 °C. The coupling reaction was carried out at −20 °C for 24 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 10.0 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil. (*E*)-(2-cycloheptylethenyl)benzene (**4c**) (1.79 g, 88% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (100% hexane).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR for all new compounds and ^{11}B NMR for **3ab**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

This research was supported by a grant from the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for Next Generation World-Leading Researchers (NEXT Program)," initiated by the Council for Science and Technology Policy (CRTP). Financial support from the Noguchi Institute is gratefully acknowledged. T. Hashimoto is grateful for a Research Fellowship for Young Scientists from JSPS (213169).

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