DOI: 10.1002/adsc.201000434

Regioselective Preparation of Functionalized *exo*-Methylenecyclopentanes and *exo*-Methylenepyrrolidines *via* Silaborative Carbocyclization of 1,6-Enynes

Martin Gerdin,[a] Sailendra Kumar Nadakudity,[a] Christin Worch,[a] and Christina Moberg[a,*]

[a] KTH School of Chemical Science and Engineering, Organic Chemistry, SE-10044 Stockholm, Sweden
Fax: (+46)-8-791-2333; e-mail: kimo@kth.se

Received: June 3, 2010; Revised: August 26, 2010; Published online: October 12, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000434.

Abstract: Silaborative carbocyclization of 1,6-enynes catalyzed by Pd-PEPPSI-IPr {PEPPSI = pyridine-enhanced precatalyst preparation stabilization and initiation; IPr = *N*,*N*-bis[2,6-(diisopropyl)phenyl]imidazolium} employing either (dimethylphenylsilyl)pinacolborane or (chlorodimethylsilyl)pinacolborane provides access to densely functionalized five-membered rings as single diastereomers in excellent yields. The vinylboronate functions were employed in palladium-catalyzed Suzuki cross-coupling reactions with a range of aryl bromides, containing electron-withdrawing as well as electron-donating substituents, furnishing arylated *exo*-methylenecyclopentanes or *exo*-methylenepyrrolidines in good yields. Subsequent oxidation of the isopropoxydimethylsilyl function generated *via* addition of (chlorodimethylsilyl)-pinacolborane provided access to hydroxymethyl derivatives of the arylated compounds. Use of a chiral ester, bismenthyl (2-propenyl)(2-propynyl)malonate, afforded two diastereomeric products which could be separated, thereby giving access to the cyclized compounds as single isomers, with opposite absolute configurations at the newly formed stereocenter.

Keywords: cross-coupling; cyclization; enynes; oxidation; palladium; silylboranes

Introduction

A large variety of catalytic methods, using a wide range of metal catalysts, for the cyclization of 1,6-enynes have been reported in recent years.[1] The reactions provide efficient and convenient access to five-membered carbocycles and heterocycles. Of particular interest are methods leading to products containing reactive functional groups for further synthetic elaboration. Silacarbocyclizations,[2] boracarbocyclizations,[3] and stannacarbocyclizations,[4] including a few enantioselective processes,[2d,f,3a] are examples of transformations of this type.

When compounds containing interelement linkages,[5] such as Si–Sn,[6] B–Sn,[7] and B–Si[8] are added, cyclized products containing two reactive functional groups can be obtained. The carbocyclizations are usually catalyzed by group 10 metal complexes and proceed in competition with interelement addition to the triple bond.[9] Compounds with Si–Sn linkages react by insertion of the alkyne into the metal-silicon bond, resulting in the formation of vinylsilanes (Figure 1, **a**), whereas the other two types of interelement compounds react *via* insertion into the metal-boron bond, thereby producing vinylboronates (Figure 1, **b** and **c**, respectively).

The silastannylative carbocyclization of 1,6-enynes has been most thoroughly studied. A number of 1,6-enynes were successfully employed using either phosphine-free Pd complexes[6a] or Pd N-heterocyclic carbene complexes[6b,c] as catalysts, giving the products in good yields. Terminally substituted enynes were generally less reactive than unsubstituted substrates, the former resulting in moderate to poor yields. The only

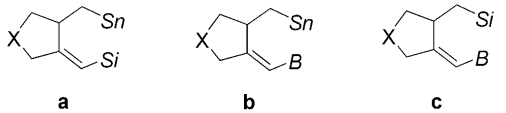
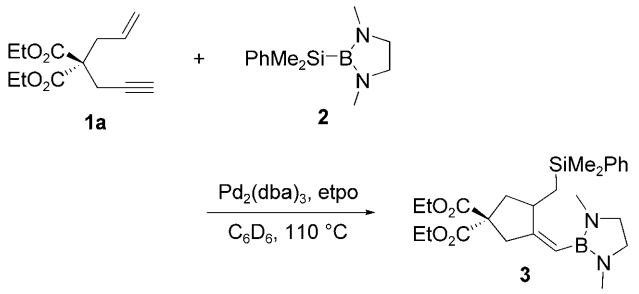


Figure 1. Products obtained by carbocyclization of 1,6-enynes with Si–Sn (**a**), B–Sn (**b**), and B–Si (**c**) bonds.



Scheme 1. Silaborative carbocyclization of enyne **1a** according to Tanaka.[8]

silaborative carbocyclization reported is that by Tanaka and co-workers who, as part of a study on silaborations of alkynes and diynes, reacted enyne **1a** with silylborane **2** using a $Pd_2(dba)_3$/$P(OCH_2)_3CEt$ (etpo) catalyst system (M:L ratio 1:2, C_6D_6, 110 °C, 2 h) to obtain cyclopentane derivative **3** in 84% yield along with a by-product (9%) believed to be obtained by silaboration of the triple bond (Scheme 1).[8] Although the product offers promising reactivities for further synthetic elaborations, its reactivity was not investigated. Due to the synthetic versatility of silyl[10] and boryl[11] functions generated *via* silaborations of unsaturated substrates,[12] we decided to extend our studies on silylboranes[13] to the silaborative carbocyclization of 1,6-enynes, and to explore the utility of the products formed.

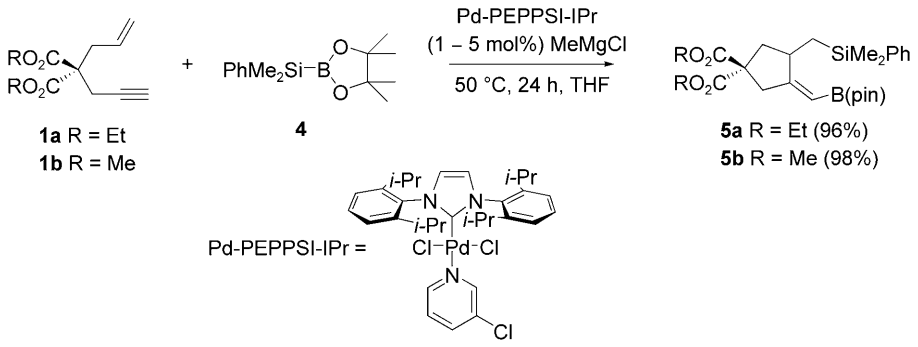
Results and Discussion

Palladium-Catalyzed Silaborations

We started our investigation by examining the reaction of enyne **1b**, derived from dimethyl malonate, with (dimethylphenylsilyl)pinacolborane (**4**) in the presence of Pd(0) catalysts. The choice of **4** rather than **2** was dictated by the facts that boronic esters are suitable partners for Suzuki cross-couplings, thus allowing further transformations of the initially formed products, and that **4** is commercially available.[14] For the initial experiments 1:2 mixtures of $Pd_2(dba)_3$ and various phosphorus ligands were attempted. The electronic and steric properties of the catalysts are crucial for the different steps in the catalytic cycle to proceed. However, neither phosphanes such as $PPhMe_2$ and PPh_3, nor phosphites [$P(OEt)_3$, $P(OPh)_3$] resulted in formation of the desired cyclized product in toluene at 110 °C, although the product from silaboration of the alkyne could be observed.

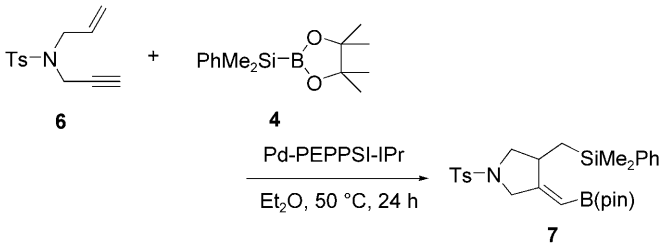
N-heterocyclic carbenes[15] have proven to serve as versatile ligands for a number of catalytic processes.[16] PEPPSI (pyridine-enhanced precatalyst preparation stabilization and initiation) catalysts,[17] which are commercial air- and water-stable palladium complexes, have proven to exhibit excellent reactivity in a large number of palladium-catalyzed cross-coupling reactions.[18] The commercial Pd(II) complexes are activated with base to generate catalytically active Pd(0) carbene species. Encouraged by the fact that N-heterocyclic carbenes catalyzed the silastannative carbocyclization of 1,6-enynes,[6b,c] in moderate to good yields, we decided to switch to dichloro-*N*,*N*-bis[2,6-(diisopropyl)phenyl]imidazolium(3-chloropyridine)-palladium, Pd-PEPPSI-IPr,[19] as catalyst. We were pleased to find that the desired product was obtained in 50% yield in diethyl ether as a 5:1 mixture of isomers,[20] with that having *Z* configuration of the olefinic bond (**5b**) as the major isomer. Although no by-products could be identified, the enyne was completely consumed during the reaction. As enyne decomposition seemed to be a major problem, the amount of enyne **1b**, which is readily available from inexpensive starting materials, was increased to 2 equivalents and the reaction temperature decreased to 50 °C. This led to the formation of the cyclized compound **5b** in 98% yield as a single diastereomer (Scheme 2), suggesting that substrate decomposition was caused by the catalyst. The ethyl ester **1a** reacted under the same conditions to provide **5a** (96% yield), also as a single diastereomer.

Silaborative carbocyclization of enyne **6** was also possible using Pd-PEPPSI-IPr as a catalyst. Pyrroli-



Scheme 2. Silaborative carbocyclization of enynes **1**.

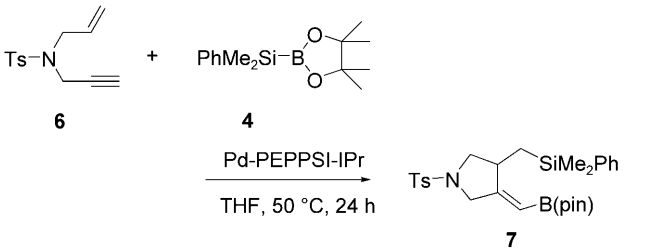
Table 1. Silaborative carbocyclization of enyne **6**.[a]



Entry	Temp. [°C]	Yield [%][b]	*dr*
1	110	31	2:1
2	80	42	5:1
3	50	49	>98:2
4	r.t.	25	>98:2

[a] Reactions performed on a 0.1-mmol scale in Et_2O using 10 mol% Pd-PEPPSI-IPr.
[b] Determined by ^1H NMR using 1-methoxynaphthalene as internal standard.

Table 2. Silaborative carbocyclization of enyne **6**.[a]



Entry	Catalyst (mol%)	Equiv. of **6**	Yield [%][b]
1	10	1	56
2	10	2	84
3	5	2	93
4	1	2	96

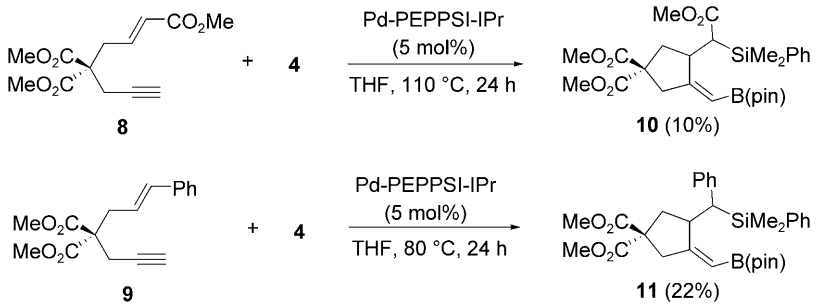
[a] Reactions performed on a 0.1-mmol scale in THF using Pd-PEPPSI-IPr catalysis for 24 h at 50 °C, yielding the product as a single detectable diastereomer (^1H NMR).
[b] Determined by ^1H NMR using 1-methoxynaphthalene as internal standard.

dine **7** was obtained in modest yield (25–39%) when 1:1 mixtures of enyne and silylborane were used (Table 1); at 110 °C merely a 31% yield of a 2:1 mixture of isomers was obtained (entry 1). The optimum reaction temperature was found to be 50 °C; at this temperature decomposition was reduced and the desired product was formed in 49% yield (entry 3). Gratifyingly, the selectivity of the reaction was also improved and the product was now obtained as a single detectable diastereomer (^1H NMR).

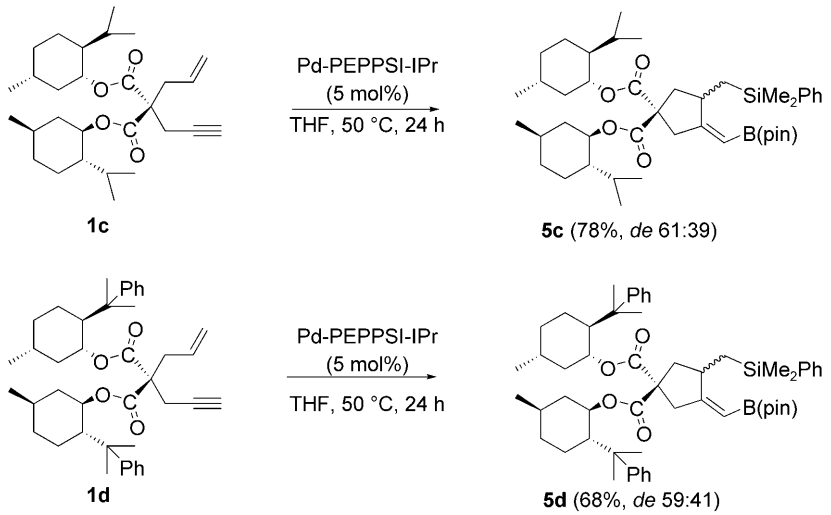
Slow addition of enyne **6** (over 15 h, using a syringe pump) to silylborane **4** did not lead to any improvement; after 18 h at 50 °C a disappointing 50% yield was recorded. Exchange of diethyl ether for THF improved the yield slightly, to 56% (Table 2, entry 1). Use of two equivalents of **6** resulted in a considerably higher yield, 84% (entry 2). The yield could be improved even further by reducing the amount of catalyst employed, underlining the importance of suppressing the decomposition pathways (entries 3 and 4).

A number of enynes bearing substituents at the terminal position of either the alkene[21] or alkyne[22] moiety were subjected to the same reaction conditions (50, 80 and 110 °C employing 5 mol% Pd-PEPPSI-IPr). In most cases no cyclized product was observed, although low yields of products were obtained from **8** and **9**, which provided cyclized compounds **10** (as two diasteromers in a 14.3:1 ratio) and **11** (as a 19:1 mixture of diastereomers) in 10 and 22% yield, respectively (Scheme 3).

Cyclizations of enynes **1c** and **d**, with ester groups derived from chiral alcohols, proceeded with low but significant selectivities, as determined by ^1H NMR spectroscopy (Scheme 4). Thus **5c** was obtained as a 61:39 ratio of diastereomers, in a combined yield of 78% after chromatography, and **5d** as a 59:41 mixture in 68% yield. Although poor diastereoselectivity was observed, the two diastereomers obtained by silaborative cyclization of bismenthyl (2-propenyl)(2-propynyl)malonate (**1c**) could be separated by column chromatography, thus providing the two compounds as single isomers (Figure 2).



Scheme 3. Cyclization of substituted enynes **8** and **9**.



Scheme 4. Chiral esters employed in silaborative carbocyclizations of enyne.

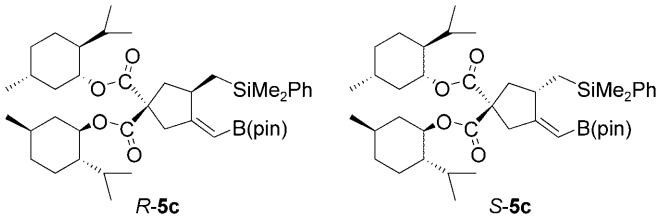


Figure 2. Diastereomers obtained from chiral enyne.

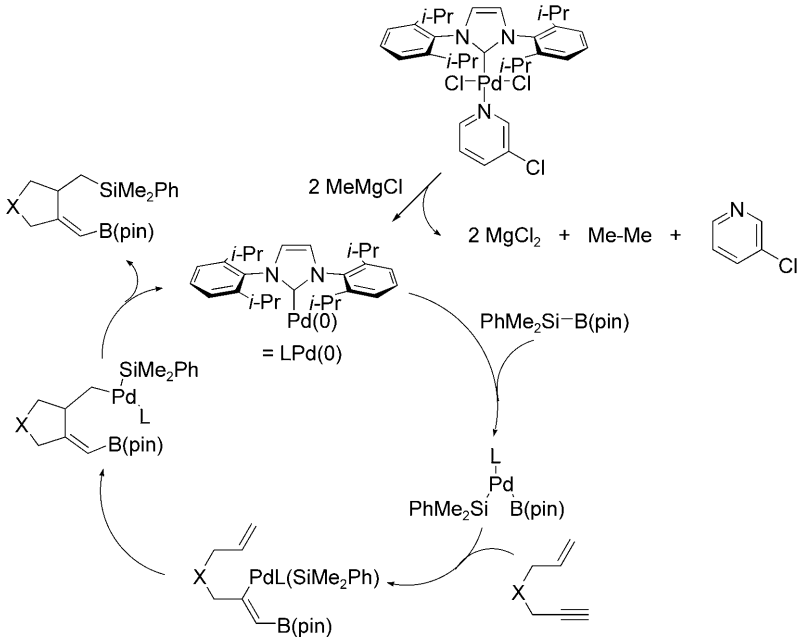
Mechanism

The mechanism of Pt-catalyzed silaborations of alkynes in the presence of phosphane ligands was investigated by Ozawa et al. by means of NMR spectroscopy.[23] The reaction was shown to follow the generally accepted catalytic cycle, proceeding *via* oxidative addition of the silylborane to a zerovalent metal complex, insertion of the acetylene into the Pt–B bond and, finally, reductive elimination. In reactions of 1,6-enynes, carbopalladation to form a five-membered ring probably precedes reductive elimination, although an alternative path proceeding *via* palladastannylation was suggested for silastannative carbocyclization of 1,6-enynes.[6c] The mechanism of interelement additions catalyzed by metal-carbene complexes has not been studied, but probably follows a similar pathway (Scheme 5). Pd-PEPPSI-IPr is activated by treatment with MeMgCl to form the active Pd(0) carbene complex, with dissociation of the labile 3-chloropyridine ligand.[18] Oxidative addition of the silylborane to this complex is facilitated by the good σ-donor ability of the carbene ligand. Insertion of the alkyne must proceed *via* a three-coordinated complex, in order to allow coordination of the triple bond to the metal center. In the case of phosphorus ligands, which usually lead to *SiB*ML_2 complexes, decoordination of one ligand is needed, whereas with the present 1:1 metal ligand ratio, the required three-coordinate complex is directly formed. Reductive elimination, finally, is facilitated by bulky ligands, such as PEPPSI-IPr.[18] The success of the carbene ligand is probably the result of these elementary catalytic steps being favored.

Palladium-Catalyzed Arylations

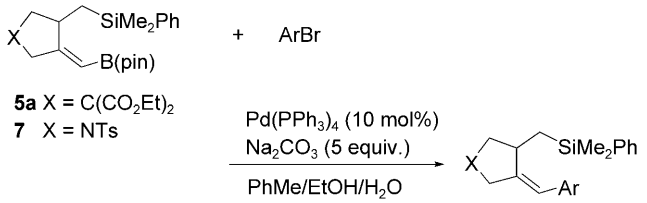
To explore the reactivity of the vinylboronates formed, the Suzuki cross-coupling reaction between pyrrolidine **7** and bromobenzene was investigated. After an initial screening of reaction conditions we found that the best result was obtained by using $Pd(PPh_3)_4$ as catalyst in a mixture of toluene, ethanol and water. Next, the substrate scope was examined using various aryl bromides and two types of vinylboronates. The results are summarized in Table 3.

The optimized conditions for the Suzuki cross-coupling of vinylpyrrolidine **7** and bromobenzene proved to be efficient for all other aryl bromides tested, and the corresponding arylated products were isolated in good yields. Neither electron-donating nor electron-withdrawing substituents on the aryl bromides seemed to have a significant influence on the outcome of the reaction (entries 2 and 5). Moreover, it was possible to couple even sterically demanding aryl bromides such as 2-bromomesitylene (entry 8) and 1-bromonaphthalene (entry 9) in good yields. Not only vinylpyrrolidine **7** but also vinylcyclopentane **5a** turned out to be a suitable substrate for the Suzuki cross-coupling (entries 10 and 11).



Scheme 5. Proposed mechanism for silaboration of 1,6-enynes.

Table 3. Suzuki cross-coupling of vinylboronates **5a** or **7** with aryl bromides.[a]



Entry	Substrate	Ar	Product	Yield [%][b]
1[c]	**7**	Ph	**12a**	87
2	**7**	4-$MeOC_6H_4$	**12b**	77
3	**7**	3-$MeOC_6H_4$	**12c**	78
4	**7**	2-$MeOC_6H_4$	**12d**	80
5	**7**	4-CNC_6H_4	**12e**	83
6	**7**	4-ClC_6H_4	**12f**	88
7	**7**	3-pyridyl	**12g**	77
8	**7**	2,4,6-$Me_3C_6H_2$	**12h**	77
9	**7**	1-naphthyl	**12i**	86
10	**5a**	4-$MeOC_6H_4$	**13a**	80
11	**5a**	4-CNC_6H_4	**13b**	85

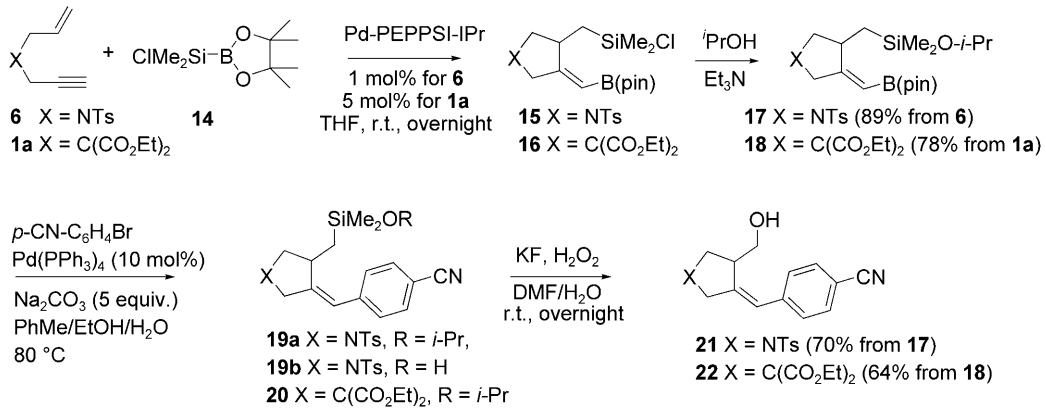
[a] All reactions were performed on a 0.20-mmol scale using substrate **7** or **5a** (1.0 equiv.), aryl bromide (1.2 equiv), Na_2CO_3 (5 equiv.), and $Pd(PPh_3)_4$ (10 mol%), in toluene/ethanol/water (3:1:1) (0.05 M with respect to the substrate **7** or **5a**), at 80 °C for 18 h.

[b] Isolated yield.

[c] Reaction was performed using 2.0 equiv. of bromobenzene.

Addition of (Chlorodimethylsilyl)pinacolborane – Oxidation of the Silyl Function

Next we moved to the functionalization of the silyl group. The dimethylphenylsilyl substituent proved to be inert towards the standard conditions used for oxidation.[24] Suginome and co-workers recently prepared a number of silylboranes which exhibit higher reactivity in silaborations and which result in products with more reactive silyl functions.[25] (Chlorodimethylsilyl)-pinacolborane (**14**) was prepared according to their procedure and reacted with enynes **1a** and **6** in the presence of Pd-PEPPSI-IPr to yield cyclized products **15** and **16**, respectively (Scheme 6). The reaction conditions were optimized using enyne **6**. The reaction proceeded smoothly in THF at room temperature overnight, but the yield was highly dependent on the amount of catalyst (Table 4). With 10 mol% catalyst and 1.5 equivalents of enyne, the cyclized product **15** was obtained as a single diastereomer in 75% yield (entry 1). This was somewhat improved, to 85%, when the catalyst was added slowly over 2 h (entry 2). Like in reactions using silylborane **4**, the yield was further improved by lowering the amount of the catalyst to 5 mol% (entry 3). Even in the presence of only one equivalent of enyne the reaction was successful. With 1–2 mol% catalyst a quantitative yield of **15** was observed (entries 5–6), whereas with 5 mol% of catalyst the yield was slightly lower (entry 4). With silylborane **14** decomposition of the substrate by the catalyst is evidently less pronounced than with **4**, probably as a result of the enhanced reactivity of **14** in the silaborative carbocyclization.



Scheme 6. Silaborative carbocyclizations followed by arylation and oxidation.

Table 4. Silaborative carbocyclization of **6** with silylborane **14**.

Entry	Catalyst (mol%)	Equiv. of **6**	Yield of **15** [%][a]	*dr*
1	10	1.5	75	>99:1
2	10[b]	1.5	85	>99:1
3	5[b]	1.5	96	>99:1
4	5	1	98	>99:1
5	2	1	>99	>99:1
6	1	1	>99	>99:1

[a] Reactions performed in THF using Pd-PEPPSI-IPr as catalyst overnight at room temperature; yields were determined by ^{1}H NMR using 1-methoxynaphthalene as internal standard.
[b] Slow addition of catalyst.

Cyclization of **1a** required a higher catalyst loading. Optimized conditions employed 5 mol% of the catalyst and 1 equivalent of **1a**. The products (**15** and **16**) were sensitive to moisture and therefore converted into isopropyl derivatives **17** and **18**, respectively, which were stable to chromatography and isolated in 89 and 78% yields (over two steps), respectively.

Suzuki cross-couplings of **17** and **18** with 4-bromobenzonitrile proceeded as expected. As a consequence of the basic conditions (Na_2CO_3) the silyl alcohol **19b** was obtained along with the expected **19a** from **17**. Formation of **19b** could be avoided by adding water and ethanol (used as co-solvents) when the temperature of the reaction mixture had reached 80 °C. By nOe studies it was concluded that the configuration of the double bond remained intact. In contrast to the situation with **17**, Suzuki coupling of **18** with the same bromide always resulted in a single product, **20**. Attempts to perform the palladium-catalyzed silaboration and the Suzuki coupling in one-pot, using the same catalyst (Pd-PEPPSI-IPr), were unsuccessful.

Compounds **19a** and **19b** were separated by flash chromatography and each compound treated with KF and H_2O_2 in DMF[26] in order to oxidize the silyl functional groups. Both reactions yielded the same pyrrolidine derivative **21**. Therefore, the mixture of **19a** and **b** was oxidized to yield pyrrolidine derivative **21** (70% yield from **17**, Scheme 5). This type of compound, with an *E*/*Z* ratio of 1:3, has previously been obtained in low yield *via* titanocene-mediated vinylation.[27] Treatment of **20** with KF and H_2O_2 in DMF provided alcohol **22** (64% from **18**).

Borylcarbocyclizations[3a] and silylcarbocyclizations[2g] have previously been shown to be synthetically versatile processes in that the products obtained can be further elaborated *via* Pd-catalyzed cross-coupling reactions. The silaborative carbocyclization presented here provides products with an additional functional group, thereby serving as more versatile starting materials.

Conclusions

A silaborative carbocyclization reaction using either (dimethylphenylsilyl)pinacolborane (**4**) or the more reactive (chlorodimethylsilyl)pinacolborane (**14**) has been developed, selectively furnishing functionalized five-membered derivatives in high yields. The reaction shows tolerance to substituents at the double or triple bond of the enyne. Cyclization of an enyne containing menthyl ester functions resulted in the formation of two diastereomers, which could be separated, thereby providing access to single isomers of the cyclized compounds.

A protocol for the Suzuki cross-coupling of the resulting vinylboronates formed was also developed. A wide range of aryl bromides, containing electron-donating as well as electron-withdrawing substituents, reacted to afford the corresponding arylated products in good yields and with retention of the double bond configuration. Subsequent oxidation of the silyl function resulted in formation of alcohol derivatives. The methodology presented here thus provides access to

stereo- and regiochemically defined *exo*-methylenecyclopentanes and *exo*-methlyenepyrrolidines containing two functional groups for further synthetic elaborations.

Experimental Section

General Considerations

All transition metal-catalyzed reactions were performed inside a nitrogen-filled glovebox using oven dried glassware. After the reaction flask had been sealed, heating was performed outside the glovebox. Toluene, THF, Et_2O, and CH_2Cl_2 were dried using a Glass-contour solvent dispensing system. Compounds **1a**,[28] **1b**,[29] **4**,[30] **6**,[31] **9**,[32] and **14**[25] were synthesized according to literature procedures. All other chemicals were of at least 97% purity and used as received. ^{1}H NMR spectra were recorded at 500 or 400 MHz and ^{13}C NMR spectra at 125 or 100 MHz. The ^{1}H and ^{13}C chemical shifts are reported relative to $CHCl_3$.

General Procedure for Silaborative Carbocyclization of Enynes using Silylborane 4

MeMgCl in THF (3 M, 13.3 μL, 0.04 mmol) was added to a THF solution (400 μL) of Pd-PEPPSI-IPr (13.6 mg, 0.02 mmol) at −35 °C inside a nitrogen-filled glovebox, and the resulting solution allowed to reach room temperature over 1 h. This solution (0.05 M in Pd, 10–100 μL) was added to a vial containing silylborane **4** (26.2 mg, 0.1 mmol), the enyne (1–2 equiv.), and 1-methoxynapthalene (15.8 mg, 0.1 mmol) in THF (300 μL). The vial was capped and heated outside the glovebox. The reaction was monitored by taking out 20 μL samples, evaporating the solvent and recording the ^{1}H NMR spectrum. NMR yields were calculated by comparing the integrals of the signals from the olefinic proton in the product and the methoxy group in 1-methoxynapthalene. Purification was performed by evaporating the solvents, adding the crude product onto a SiO_2 column and eluting with an appropriate eluent. *p*-Anisaldehyde solution was used to develop TLC plates.

(*Z*)-Diethyl 3-[(Dimethylphenylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methylene]cyclopentane-1,1-dicarboxylate (5a)

The reaction was performed using 1.5 equiv. of enyne **1** and 5 mol% Pd-PEPPSI-IPr catalyst at 50 °C for 24 h. After flash chromatography on SiO_2 the product was isolated as a colorless oil. The *E* configuration of the double bond was assigned by NOESY spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.34$ (s, 3H), 0.35 (s, 3H), 0.89 (dd, $J = 12.9$, 14.4 Hz, 1H), 1.18 (t, $J = 7$ Hz, 3H), 1.19 (t, $J = 7$ Hz, 6H), 1.21 (s, 6H), 1.22 (s, 6H), 1.40 (dd, $J = 14.4$, 2.2 Hz, 1H), 1.77 (dd, $J = 13.5$, 5.8 Hz, 1H), 2.59 (dd, $J = 13.5$, 8.3 Hz, 1H), 2.78 (d, $J = 16.5$ Hz, 1H), 3.08–3.18 (m, 1H), 3.25 (app. dt, $J = 16.5$, 2.0 Hz, 1H), 4.05–4.21 (m, 4H), 5.19 (s, 1H), 7.30–7.35 (m, 3H), 7.50–7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -1.88$, −1.60, 14.32, 14.33, 25.13, 25.28, 25.34, 38.8, 41.3, 44.2, 59.2, 61.7, 61.8, 83.2, 110.0, 128.0, 129.1, 133.9, 140.0, 171.9, 172.3, 173.7.

(*Z*)-Dimethyl 3-[(Dimethylphenylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methylene]cyclopentane-1,1-dicarboxylate (5b)

The reaction was performed using 2 equiv. of enyne **5** and 1 mol% Pd-PEPPSI-IPr catalyst at 50 °C for 24 h. After flash chromatography on SiO_2 (gradient of 5–20% Et_2O in hexane) the product was isolated as a colorless oil; yield: 98%. The *E* configuration of the double bond was assigned by NOESY spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.34$ (s, 3H), 0.35 (s, 3H), 0.87 (dd, $J = 14.3$, 12.8 Hz, 1H), 1.21 (s, 6H), 1.23 (s, 6H), 1.39 (dd, $J = 14.3$, 2.4 Hz, 1H), 1.83 (dd, $J = 13.5$, 5.7 Hz, 1H), 2.60 (ddd, $J = 13.5$, 8.3, 1.0 Hz, 1H), 2.80 (d, $J = 16.6$ Hz), 3.13 (m, 1H), 3.26 (app. dt, $J = 16.6$, 2.1 Hz, 1H), 3.67 (s, 3H), 3.68 (s, 3H), 5.18–5.21 (m, 1H), 7.31–7.36 (m, 3H), 7.51–7.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -1.88$, −1.58, 25.1, 25.3, 38.8, 41.3, 44.2, 53.07, 53.09, 59.0, 83.2, 110.0 (br), 130.0, 129.1, 133.9, 140.0, 172.4, 172.8, 173.4; anal calcd. for $C_{25}H_{37}BO_4Si$: C 63.55, H 7.89; found: C 63.48, H 7.73%.

(*E*)-3-[(Dimethylphenylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]-1-tosylpyrrolidine (7)

The reaction was performed using 2 equiv. of enyne **6** and 1 mol% Pd-PEPPSI-IPr catalyst at 50 °C for 24 h. After flash chromatography on SiO_2 (1:1 DCM/hexane) the product was isolated as a white solid; yield: 81%. The *E* configuration of the double bond was assigned by NOESY spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.32$ (s, 3H), 0.34 (s, 3H), 0.88–0.96 (m, 2H), 1.213 (s, 6H), 1.216 (s, 6H), 2.40 (s, 3H), 2.97 (dd, $J = 9.0$, 6.0 Hz, 1H), 3.08 (dd, $J = 9.6$, 1.8 Hz, 1H), 3.17–3.27 (m, 1H), 3.58 (dd, $J = 15.0$, 1.8 Hz, 1H), 4.03 (app. dt, $J = 15.0$, 1.7 Hz, 1H), 5.08–5.12 (m, 1H), 7.26–7.30 (m, 2H), 7.33–7.39 (m, 3H), 7.47–7.53 (m, 2H), 7.58–7.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -2.18$, −2.15, 21.5, 22.6, 24.7, 24.8, 39.2, 53.3, 54.0, 83.1, 109.0 (br), 127.80, 127.82, 129.0, 129.5, 132.6, 133.6, 138.8, 143.5, 167.6.

(*Z*)-Dimethyl 3-[(Dimethylphenylsilyl)methoxycarbonylmethyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclopentane-1,1-dicarboxylate (10)

The reaction was performed using 1.5 equiv. of enyne **8** and 5 mol% Pd-PEPPSI-IPr catalyst at 110 °C, 24 h. After flash chromatography on SiO_2 the product was isolated as a colorless oil contaminated by what seems to be by-products formed via alkyne silaboration (purity: ~80%, *dr* 14.3:1). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.43$ (s, 3H), 0.45 (s, 3H), 1.26 (s, 12H), 2.44 (ddd, $J = 12.5$, 8.8, 1.7 Hz, 1H), 2.64 (dd, $J = 12.5$, 10.0 Hz, 1H), 2.82 (d, $J = 15.9$ Hz, 1H), 2.9–3.0 (m, 1H), 3.33 (app. dt, $J = 15.9$, 2.6 Hz, 1H), 3.51 (s, 3H), 3.61 (s, 3H), 3.70 (s, 3H), 5.26 (s, 1H), 7.32–7.40 (m, 3H), 7.54–7.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -2.64$, −1.89, 25.1, 25.4, 37.0, 40.1, 40.5, 46.6, 51.0, 53.0, 53.2, 59.3, 83.4, 128.1, 129.7, 134.3, 134.4, 137.1, 171.1, 171.9, 172.4, 174.8.

(*Z*)-Dimethyl 3-[(Dimethylphenylsilyl)-phenylmethyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclopentane-1,1-dicarboxylate (11)

The reaction was performed using 1.5 equiv. of enyne **9** and 5 mol% Pd-PEPPSI-IPr catalyst at 80 °C for 24 h. After flash chromatography on SiO_2 (gradient of 5–20% Et_2O in hexane) the product could be isolated as a colorless oil in ~70% purity, *dr* 95:5. Major contaminant was what seem to be products of alkyne silaboration. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.37$ (s, 3H), 0.40 (s, 3H), 1.29 (s, 12H), 2.09 (app. dt, $J = 15.6$, 2.3 Hz, 1H), 2.34 (dd, $J = 13.8$, 7.2 Hz, 1H), 2.48 (d, $J = 15.6$ Hz, 1H), 2.68 (ddd, $J = 13.8$, 8.8, 1.2 Hz, 1H), 2.75–2.85 (m, 1H), 3.15 (d, $J = 5.1$ Hz, 1H), 3.64 (s, 3H), 3.65 (s, 3H), 5.21 (br s, 1H), 6.97–7.02 (m, 2H), 7.08–7.17 (m, 3H), 7.24–7.34 (m, 3H), 7.42–7.46 (m, 2H).

(*Z*)-3-[(Dimethylphenylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclopentane-1,1-dicarboxylic Acid Bis-[(−)-menthol] ester (5c)

The reaction was performed using 1.2 equiv. of enyne **1c** and 5 mol% Pd-PEPPSI-IPr catalyst at 50 °C for 24 h, yielding the cyclized product as two diastereomers (*dr* 61:39); yield: 95% (^{1}H NMR). After flash chromatography on SiO_2, using 5% Et_2O in hexane as eluent, a mixture of the two products were isolated as a colorless oil; yield: 78% (*dr* 61:39). The diastereomers were separated using a Biotage SP1 employing a gradient of 1–10% Et_2O in pentane as eluent.

Major isomer: $R_f = 0.32$ (10% Et_2O/pentane); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.34$ (s, 3H), 0.35 (s, 3H), 0.70 (app. t, $J = 7.0$ Hz, 6H), 0.78–0.90 (m, 18H), 0.9–1.1 (m, 2H), 1.21 (s, 6H), 1.22 (s, 6H), 1.30–1.53 (m, 4H), 1.64–1.71 (m, 4H), 1.78–1.87 (m, 3H), 1.88–1.95 (m, 2H), 2.51 (ddd, $J = 13.3$, 8.1, 1.4 Hz, 1H), 2.88–3.08 (m, 3H), 4.59–4.71 (m, 2H), 5.22 (s, 1H), 7.30–7.35 (m, 3H), 7.51–7.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -2.02$, −1.64, 16.2, 16.3, 21.22, 21.27, 22.35, 22.36, 23.35, 23.42, 25.1, 25.3, 25.6, 26.2, 31.7, 34.6, 38.3, 40.7, 40.9, 41.9, 44.7, 47.16, 47.22, 59.9, 75.69, 75.71, 83.1, 110.1 (br), 128.0, 129.1, 133.9, 140.1, 171.3, 171.6, 173.9; anal. calcd. for $C_{43}H_{69}BO_6Si$: C 71.64, H 9.65; found: C 71.55, H 9.79%

Minor isomer: $R_f = 0.28$ (10% Et_2O/pentane). ^{1}H NMR 500 MHz, ($CDCl_3$): $\delta = 0.326$ (s, 3H), 0.331 (s, 3H), 0.66 (d, $J = 6.9$ Hz, 3H), 0.70 (d, $J = 6.9$ Hz, 3H), 0.80–0.92 (m, 18H), 0.94–1.1 (m, 2H), 1.20 (s, 6H), 1.22 (s, 6H), 1.27–1.37 (m, 2H), 1.40–1.50 (m, 4H), 1.60–1.95 (m, 9H), 2.70 (ddd, $J = 12.9$, 8.2, 1.7 Hz, 1H), 2.74 (d, $J = 16.7$ Hz, 1H), 3.07–3.17 (m, 1H), 3.22 (app. dt, $J = 15.5$, 2.2 Hz, 1H), 4.60–4.72 (m, 2H), 5.17 (s, 1H), 7.31–7.35 (m, 3H), 7.51–7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -1.95$, −1.65, 16.3, 16.5, 21.12, 21.21, 22.36, 22.40, 23.34, 23.6, 25.1, 25.3, 26.1, 26.2, 26.4, 31.7, 34.6, 38.3, 40.9, 41.0, 42.0, 45.0, 47.3, 47.4, 60.1, 75.4, 75.5, 83.1, 128.0, 129.1, 133.9, 140.0, 171.0, 171.4, 173.4.

(*Z*)-3-[(Dimethylphenylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclopentane-1,1-dicarboxylic Acid Bis-[(−)-8-phenylmenthol] Ester (5d)

The reaction was performed using 1.2 equiv. of enyne **1d** and 5 mol% Pd-PEPPSI-IPr catalyst at 50 °C for 24 h, yielding the cyclized product as a mixture of two diastereomers (*dr* 59:41); yield: 98% (^{1}H NMR). After flash chromatography on SiO_2, using a gradient of Et_2O (5–10%) in hexane as eluent, the product was isolated as a white fluffy solid; yield: 68% (59:41 mixture of isomers). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.31$ (s, 3H, minor), 0.338 (s, 3H, minor), 0.344 (s, 3H, major), 0.35 (s, 3H, major), 0.62–0.78 (m, 2H), 0.80–1.02 (m, 12H), 1.18–1.63 (m, 32H), 1.75–2.05 (m, 5H), 2.41 (dd, $J = 13.0$, 7.8 Hz, 1H, major), 2.60–2.78 (m, 2H), 2.98–3.20 (m, 1H major, 2H minor), 4.79–4.96 (m, 2H), 5.19 (s, 1H, minor), 5.21 (s, 1H, major), 7.14–7.19 (m, 2H), 7.22–7.37 (m, 11H), 7.52–7.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -1.95$, −1.81, −1.45, −1.39, 22.17, 22.23, 23.7, 23.9, 24.0, 24.5, 25.17, 25.20, 25.22, 25.27, 25.7, 25.9, 27.67, 27.74, 30.5, 31.0, 31.2, 31.3, 31.6, 31.7, 34.79, 38.2, 38.6, 40.7, 40.8, 41.6, 41.7, 41.8, 42.0, 43.8, 44.8, 50.5, 50.6, 50.78, 50.80, 60.1, 60.2, 76.85, 76.89, 77.0, 83.1125.72, 125.75, 125.77, 126.02, 126.06, 126.2, 126.3, 128.03, 128.06, 128.39, 128.42, 128.45, 129.14, 129.18, 133.95, 133.99, 139.9, 140.0, 150.55, 150.67, 150.75, 150.79, 171.14, 171.18, 171.24, 173.3, 174.2.

General Procedure for Suzuki Cross-Coupling of Vinylboronates 7 and 5a

$Pd(PPh_3)_4$ (23.11 mg, 0.02 mmol), sodium carbonate (106 mg, 1.00 mmol), ethanol (0.8 mL), distilled water (0.8 mL) and aryl bromide (0.24 mmol) were added to a solution of vinylboronate **7** or **5a** (1.0 equiv., 0.20 mmol) in toluene (2.4 mL) in a Schlenk tube under a nitrogen atmosphere. The reaction mixture was heated for 18 h to 80 °C, and then taken up in dichloromethane (10 mL), and the organic layer was separated. The aqueous phase was extracted with dichloromethane (2×10 mL), and the combined organic layers dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The products were purified by column chromatography furnishing the corresponding pyrrolidines **12a–i** or cyclopentanes **13a** and **b**.

(*E*)-3-Benzylidene-4-[(dimethylphenylsilyl)methyl]-1-tosylpyrrolidine (12a)

Compound **12a** was isolated after flash chromatography on silica gel (pentane:Et_2O = 5:1, $R_f = 0.17$) as a yellow oil; yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.28$ (s, 3H), 0.32 (s, 3H), 0.80–0.95 (m, 2H), 2.42 (s, 3H), 3.07–3.15 (m, 3H), 3.81 (dd, $J = 13.7$, 1.7 Hz, 1H), 4.12 (d, $J = 13.7$ Hz, 1H), 6.15 (s, 1H), 6.99–7.04 (m, 2H), 7.14–7.18 (m, 3H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.37–7.42 (m, 3H), 7.42–7.46 (m, 2H), 7.69 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -2.6$, −2.5, 20.0, 21.5, 36.0, 52.8, 54.8, 121.2, 126.8, 127.8, 128.0, 128.1, 128.3, 129.3, 129.6, 133.0, 133.6, 136.2, 138.0, 143.5, 143.7.

(*E*)-3-[(Dimethylphenylsilyl)methyl]-4-(4-methoxybenzylidene)-1-tosylpyrrolidine (12b)

Compound **12b** was isolated after flash chromatography on silica gel (pentane:Et_2O = 4:1, $R_f = 0.15$) as a yellow oil; yield: 77%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.28$ (s, 3H), 0.34 (s, 3H), 0.80–0.95 (m, 2H), 2.42 (s, 3H), 3.05–3.14 (m, 3H), 3.75–3.80 (m, 4H), 4.10 (d, $J = 13.6$ Hz, 1H), 6.07 (s, 1H), 6.64–6.68 (m, 2H), 6.90–6.94 (m, 2H), 7.31 (d, $J =$ 8.0 Hz, 2H), 7.37–7.44 (m, 3H), 7.45–7.48 (m, 2H), 7.68 (d,

$J=8.2$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=-2.6$, -2.4, 19.9, 21.5, 35.9, 52.8, 54.9, 55.2, 113.7, 120.5, 127.7, 128.0, 128.8, 129.2, 129.3, 129.6, 133.0, 133.6, 138.1, 141.5, 143.5, 158.3.

(*E*)-3-[(Dimethylphenylsilyl)methyl]-4-(3-methoxybenzylidene)-1-tosylpyrrolidine (12c)

Compound **12c** was isolated after flash chromatography on silica gel (pentane:$Et_2O=4:1$, $R_f=0.15$) as a yellow oil; yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.28$ (s, 3H), 0.30 (s, 3H), 0.81–0.88 (m, 1H), 0.93 (d, $J=15.0$ Hz, 1H), 2.42 (s, 3H), 3.05–3.16 (m, 3H), 3.76 (s, 3H), 3.80 (dd, $J=13.8$, 1.1 Hz, 1H), 4.09 (d, $J=13.8$ Hz, 1H), 6.13 (s, 1H), 6.62 (d, $J=7.7$ Hz, 1H), 6.64–6.66 (m, 1H), 6.72–6.75 (m, 1H), 7.05–7.09 (m, 1H), 7.31 (d, $J=8.0$ Hz, 2H), 7.35–7.44 (m, 5H), 7.68 (d, $J=8.2$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=-2.6$, -2.5, 20.0, 21.5, 36.2, 52.8, 54.8, 55.1, 111.9, 114.4, 120.2, 121.1, 127.7, 127.9, 129.2, 129.3, 129.6, 132.9, 133.5, 137.6, 138.1, 143.6, 144.2, 159.6.

(*E*)-3-[(Dimethylphenylsilyl)methyl]-4-(2-methoxybenzylidene)-1-tosylpyrrolidine (12d)

Compound **12d** was isolated after flash chromatography on silica gel (pentane:$Et_2O=4:1$, $R_f=0.15$) as a yellow oil; yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.22$ (s, 3H), 0.25 (s, 3H), 0.70–0.77 (m, 1H), 0.87 (d, $J=15.0$ Hz, 1H), 2.42 (s, 3H), 2.97 (d, $J=9.7$ Hz, 1H), 3.03–3.09 (m, 1H), 3.16–3.21 (m, 1H), 3.77 (s, 3H), 3.89 (d, $J=13.7$ Hz, 1H), 4.07 (d, $J=13.6$ Hz, 1H), 6.39 (s, 1H), 6.70–6.75 (m, 1H), 6.82 (d, $J=8.2$ Hz, 1H), 6.95 (d, $J=7.5$ Hz, 1H), 7.16–7.21 (m, 1H), 7.31 (d, $J=7.9$ Hz, 2H), 7.33–7.41 (m, 5H), 7.66 (d, $J=7.9$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=-2.7$, -2.6, 19.9, 21.5, 36.0, 52.8, 54.9, 55.3, 110.4, 116.3, 120.2, 125.3, 127.8, 127.9, 128.2, 128.7, 129.1, 129.6, 133.1, 133.5, 138.1, 143.4, 143.6, 156.5.

(*E*)-4-{[(4-Dimethylphenylsilyl)methyl-1-tosylpyrrolidin-3-ylidene]methyl}benzonitrile (12e)

Compound **12e** was isolated after flash chromatography on silica gel (pentane:$Et_2O=2:1$, $R_f=0.14$) as a yellow oil; yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.27$ (s, 3H), 0.34 (s, 3H), 0.76–0.91 (m, 2H), 2.42 (s, 3H), 3.01–3.07 (m, 3H), 3.12–3.19 (m, 2H), 3.80 (dd, $J=14.4$, 1.6 Hz, 1H), 4.12–4.16 (m, 1H), 6.12 (s, 1H), 7.01 (d, $J=8.3$ Hz, 2H), 7.31–7.35 (m, 2H), 7.38–7.48 (m, 5H), 7.68–7.71 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta=-2.7$, -2.5, 20.2, 21.5, 36.2, 52.9, 54.7, 110.0, 118.7, 119.7, 127.8, 128.1, 128.4, 129.5, 129.7, 132.1, 132.8, 133.5, 137.6, 140.6, 143.8, 148.0.

(*E*)-3-(4-Chlorobenzylidene)-4-[(dimethylphenylsilyl)-methyl]-1-tosylpyrrolidine (12f)

Compound **12f** was isolated after flash chromatography on silica gel (pentane:$Et_2O=5:1$, $R_f=0.14$) as a yellow oil; yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.28$ (s, 3H), 0.33 (s, 3H), 0.83–0.86 (m, 2H), 2.42 (s, 3H), 3.01–3.07 (m, 1H), 3.10–3.16 (m, 2H), 3.78 (dd, $J=13.9$, 1.4 Hz, 1H), 4.08–4.12 (m, 1H), 6.08 (s, 1H), 6.90 (d, $J=8.5$ Hz, 2H), 7.08 (d, $J=8.5$ Hz, 2H), 7.32 (d, $J=8.0$ Hz, 2H), 7.38–7.45 (m, 5H), 7.69 (d, $J=8.2$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta=-2.7$, -2.5, 20.1, 21.5, 36.0, 52.8, 54.8, 120.0, 127.8, 128.0, 128.4, 129.3, 129.4, 129.6, 132.4, 132.9, 133.5, 134.6, 137.8, 143.6, 144.6.

(*E*)-3-{[4-[(Dimethylphenylsilyl)methyl]-1-tosylpyrrolidin-3-ylidene}methyl]pyridine (12g)

Compound **12g** was isolated after flash chromatography on silica gel (pentane:EtOAc=1:1, $R_f=0.26$) as a colorless oil; yield: 77%. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta=0.28$ (s, 3H), 0.31 (s, 3H), 0.79–0.93 (m, 2H), 2.42 (s, 3H), 3.00–3.08 (m, 1H), 3.09–3.17 (m, 2H), 3.81 (dd, $J=14.1$, 1.5 Hz, 1H), 4.12 (d, $J=14.1$ Hz, 1H), 6.11 (s, 1H), 6.99 (dd, $J=7.9$, 4.8 Hz ,1H), 7.19–7.23 (m, 1H), 7.32 (d, $J=8.1$ Hz, 2H), 7.35–7.45 (m, 5H), 7.68 (d, $J=8.2$ Hz, 2H), 8.34–8.36 (m, 1H), 8.37–8.40 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta=-2.7$, -2.6, 20.2, 21.5, 36.2, 52.8, 54.7, 117.5, 123.1, 127.8, 128.0, 129.4, 129.7, 131.9, 132.8, 133.5, 134.4, 137.7, 143.7, 146.7, 147.7, 149.6.

(*E*)-3-[(Dimethylphenylsilyl)methyl]-1-tosyl-4-(2,4,6-trimethylbenzylidene)pyrrolidine (12h)

Compound **12h** was isolated after flash chromatography on silica gel (pentane:$Et_2O=9:1$, $R_f=0.10$) as a yellow oil; yield: 77%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.01$ (s, 3H), 0.02 (s, 3H), 0.46–0.52 (m, 2H), 2.02 (br s, 6H), 2.29 (s, 3H), 2.41–2.49 (m, 4H), 2.79 (dd, $J=9.8$, 4.2 Hz, 1H), 3.23 (dd, $J=9.8$, 7.0 Hz, 1H), 3.91–4.01 (m, 2H), 6.13 (s, 1H), 6.82 (s, 2H), 7.09–7.12 (m, 2H), 7.24–7.28 (m, 2H), 7.31–7.35 (m, 3H), 7.68 (d, $J=8.1$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=-3.0$, -2.8, 18.9, 20.1, 20.9, 21.5, 36.9, 51.8, 54.9, 120.0, 127.7, 127.8, 128.0, 128.9, 129.6, 132.7, 132.8, 133.2, 135.3, 136.3, 138.0, 143.5, 144.2.

(*E*)-3-[(Dimethylphenylsilyl)methyl]-4-(naphthalen-1-ylmethylene)-1-tosylpyrrolidine (12i)

Compound **12i** was isolated after flash chromatography on silica gel (pentane:$Et_2O=5:1$, $R_f=0.13$) as a colorless oil; yield: 86%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.016$ (s, 3H), 0.020 (s, 3H), 0.59–0.69 (m, 2H), 2.45 (s, 3H), 2.88–2.98 (m, 2H), 3.21 (dd, $J=9.6$, 6.4 Hz, 1H), 4.06 (dd, $J=13.6$, 1.4 Hz, 1H), 4.14–4.18 (m, 1H), 6.72 (s, 1H), 7.12–7.16 (m, 3H), 7.24–7.37 (m, 6H), 7.45–7.52 (m, 2H), 7.72 (d, $J=8.1$ Hz, 2H), 7.75 (d, $J=8.2$ Hz, 1H), 7.82 (d, $J=8.2$ Hz, 1H), 7.84–7.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=-2.9$, -2.8, 20.3, 21.5, 36.2, 52.5, 54.9, 119.3, 124.4, 125.2, 125.7, 125.9, 126.0, 127.5, 127.76, 128.80, 128.4, 129.0, 129.7, 131.4, 133.0, 133.3, 133.5, 133.8, 137.9, 143.6, 145.9.

(*Z*)-Diethyl 3-[(Dimethylphenylsilyl)methyl]-4-(4-methoxybenzylidene)cyclopentane-1,1-dicarboxylate (13a)

Compound **13a** was isolated after flash chromatography on silica gel (pentane:$Et_2O=10:1$, $R_f=0.12$) as a colorless oil; yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.31$ (s, 3H), 0.36 (s, 3H), 0.81 (dd, $J=14.9$, 12.4 Hz, 1H), 1.15–1.27 (m, 7H), 1.87 (dd, $J=13.3$, 5.7 Hz, 1H), 2.68 (ddd, $J=13.3$, 8.1, 1.2 Hz, 1H), 2.88 (d, $J=15.6$ Hz, 1H), 3.13–3.22 (m, 1H), 3.25 (app. dt, $J=15.6$, 2.2 Hz, 1H), 3.79 (s, 3H), 4.08–4.26 (m, 4H), 6.16 (s, 1H), 6.67–6.72 (m, 2H), 6.98–7.03 (m, 2H),

7.35–7.40 (m, 3H), 7.47–7.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -2.4$, -2.2, 14.0, 21.7, 35.4, 42.1, 42.8, 55.2, 58.5, 61.4, 61.5, 113.5, 120.7, 127.8, 129.0, 129.4, 129.9, 133.6, 138.8, 146.6, 157.8, 171.6, 172.0; anal. calcd. for $C_{28}H_{36}O_5Si$: C 69.97, H 7.55; found: C 69.62, H 7.55%

(*Z*)-Diethyl 3-(4-Cyanobenzylidene)-4-[(dimethylphenylsilyl)methyl]cyclopentane-1,1-dicarboxylate (13b)

Compound **13b** was isolated after flash chromatography on silica gel (pentane:Et_2O = 8:1, R_f = 0.13) as a colorless oil; yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.29$ (s, 3H), 0.36 (s, 3H), 0.82 (dd, J = 14.9, 12.4 Hz, 1H), 1.02 (dd, J = 14.9, 1.8 Hz 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.93 (dd, J = 13.3, 5.6 Hz, 1H), 2.70 (ddd, J = 13.3, 8.1, 1.2 Hz, 1H), 2.92 (d, J = 16.1 Hz, 1H), 3.10–3.20 (m, 1H), 3.30 (app. dt, J = 6.1, 2.2 Hz, 1H), 4.10–4.28 (m, 4H), 6.21 (s, 1H), 7.09 (d, J = 8.3 Hz, 2H), 7.35–7.43 (m, 5H), 7.44–7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.5$, -2.3, 14.0, 22.2, 35.8, 41.9, 43.0, 58.3, 61.6, 61.7, 109.2, 119.1, 120.0, 128.0, 128.6, 129.3, 131.9, 133.6, 138.2, 141.7, 153.4, 171.4, 171.6.

General Procedure for Silaborative Carbocyclization of Enynes 6 and 1a using Chlorosilylborane 14

The reactions were run in 0.5 mmol scale as described for silaborations using **4** except that the reaction mixture was stirred at room temperature for 18 h. After the reaction was completed, propan-2-ol (38 μL, 0.5 mmol) and triethylamine (139 μL, 1.0 mmol) were added and the reaction mixture stirred for 1 h at room temperature. Then, the reaction mixture was filtered through a column filled with silica gel using diethyl ether as eluent to afford the crude product. Purification was performed by adding the crude product onto a SiO_2 column and eluting with an appropriate eluent. Phosphomolybdic acid (for reactions with **6**) and $KMnO_4$ (for reactions with **1a**) were used to develop TLC plates.

(*E*)-3-[(Chlorodimethylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]-1-tosylpyrrolidine (15)

A sample (20 μL) was taken from the reaction mixture prior to the addition of propan-2-ol. The solvent was removed under reduced pressure and the residue analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.45$ (s, 3H), 0.46 (s, 3H), 0.9–1.1 (m, 2H), 1.22 (s, 12H), 2.43 (s, 3H), 3.10 (dd, J = 9.6, 6.3 Hz, 1H), 3.28–3.32 (m, 1H), 3.43 (d, J = 9.6 Hz, 1H), 3.60 (d, J = 15.2 Hz, 1H), 4.09 (d, J = 15.2 Hz, 1H), 5.15 (s, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H).

(*E*)-3-[(Isopropoxydimethylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]-1-tosylpyrrolidine (17)

After flash chromatography on SiO_2 (20% ethyl acetate in hexane), the product was isolated as a highly viscous oil; overall yield: 217 mg (0.44 mmol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.09$ (s, 3H), 0.15 (s, 3H), 0.65 (d, J = 14 Hz, 1H), 0.85 (app. t, J = 14 Hz, 1H), 1.14 (d, J = 6.1 Hz, 3H), 1.17 (d, J = 6.1 Hz, 3H), 1.20 (s, 12H), 2.40 (s, 3H), 3.07 (dd, J = 9, 6.7 Hz, 1H), 3.18–3.23 (m, 1H), 3.48 (d, J = 9 Hz, 1H), 3.59 (d, J = 15.2, 1.4 Hz, 1H), 3.98 (sept, J = 6.1 Hz, 1H), 4.06 (d, J = 15.2 Hz, 1H), 5.09 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -0.57$, -0.22, 21.8, 24.1, 25.0, 25.2, 26.15, 26.19, 39.1, 53.6, 54.4, 65.3, 83.4, 128.3, 129.9, 133.1, 143.8, 168.3.

(*E*)-Diethyl 3-[(Chlorodimethylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methylene]cyclopentane-1,1-dicarboxylate (16)

The solvent was removed under reduced pressure and the residue analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.46$ (s, 3H), 0.48 (s, 3H), 0.99 (br t, J = 14 Hz, 1H), 1.18–1.29 (m, 18H), 1.46 (d, J = 14 Hz, 1H), 2.00 (dd, J = 13.5, 5.8 Hz, 1H), 2.71 (dd, J = 13.5, 8.5 Hz, 1H), 2.83 (d, J = 16.7 Hz, 1H), 3.15–3.22 (m, 1H), 3.25 (dd, J = 16.7, 1.8 Hz, 1H), 4.10–4.27 (m, 4H), 5.24 (br s, 1H).

(*E*)-Diethyl 3-[(Isopropoxydimethylsilyl)methyl]-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclopentane-1,1-dicarboxylate (18)

The reaction was performed with enyne **1a** using 5 mol% Pd-PEPPSI-IPr catalyst at room temperature for 18 h. After flash chromatography on SiO_2 (5% ethyl acetate in hexane), the product was isolated as a highly viscous oil; overall yield: 188 mg (0.39 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.15$ (s, 3H), 0.17 (s, 3H), 0.77 (dd, J = 14.3, 12.8 Hz, 1H), 1.14 (d, J = 6 Hz, 6H), 1.20–1.27 (m, 19H), 1.95 (dd, J = 13.6, 6.1 Hz, 1H), 2.72 (dd, J = 13.6, 8.3 Hz, 1H), 2.80 (d, J = 16.4 Hz, 1H), 3.07- 3.16 (m, 1H), 3.27 (app. dt, J = 16.4, 2.2 Hz, 1H), 4.00 (sept, J = 6 Hz, 1H), 4.00–4.23 (m, 4H), 5.20 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -0.29$, -0.06, 14.37, 14.41, 25.16, 25.24, 25.33, 26.20, 26.23, 26.29, 38.1, 41.3, 44.3, 59.3, 61.75, 61.82, 65.1, 83.1, 172.0, 172.4, 173.8.

General Procedure for Suzuki Cross-Coupling of Vinylboronates 17 and 18

The reactions were run as described for vinylboronates **7** and **5a** using $Pd(PPh_3)_4$ (23.11 mg, 0.02 mmol), sodium carbonate (106 mg, 1.00 mmol), ethanol (0.8 mL), distilled water (0.8 mL), 4-bromobenzonitrile (40 mg, 0.22 mmol) and vinylboronate **17** or **18** (0.20 mmol) in toluene (2.4 mL) at 80 °C. The crude products obtained (a mixture of **19a** and **b** or cyclopentane **20**) were used for the next step without further purification.

(*E*)-4-{[4-(Isopropoxydimethylsilyl)methyl-1-tosylpyrrolidin-3-ylidene]methyl}benzonitrile (19a)

A small portion of the crude reaction mixture was taken, and the product purified by flash chromatography (20–50% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.10$ (s, 3H), 0.11 (s, 3H), 0.60–0.75 (m, 2H), 1.15 (d, J = 6.0 Hz, 3H), 1.16 (d, J = 6.0 Hz, 3H), 2.43 (s, 3H), 3.18–3.23 (m, 2H), 3.39–3.44 (m, 1H), 3.82 (dd, J = 14.4, 1.7 Hz, 1H), 3.98 (sept, J = 6.0 Hz, 1H), 4.17 (d, J = 14.4 Hz, 1H), 6.17 (s,

1H), 7.33 (m, 4H), 7.57 (d, $J=8.3$ Hz, 2H), 7.74 (d, $J=8.3$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=-0.46$, -0.37, 21.3, 21.9, 26.2, 26.3, 36.2, 53.4, 55.2, 65.6, 110.5, 119.2, 119.9, 128.2, 129.1, 130.1, 132.5, 133.3, 141.2, 144.1, 148.8.

(*E*)-4-{[(4-(Hydroxydimethylsilyl)methyl-1-tosyl-pyrrolidin-3-ylidene]methyl}benzonitrile (19b)

The formation of this compound could be avoided by adding ethanol and water after heating the reaction mixture to 80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.14$ (s, 3H), 0.15 (s, 3H), 0.70 (d, $J=15.0$ Hz, 1H), 0.85 (dd, $J=15.0$, 11.3 Hz, 1H), 2.1 (br s, 1H), 2.43 (s, 3H), 3.13 (dd, $J=9.6$, 6.1 Hz, 1H), 3.27 (m, 1H), 3.48 (d, $J=9.6$ Hz, 1H), 3.76 (d, $J=14$ Hz, 1H), 4.22 (d, $J=14$ Hz, 1H), 6.19 (s, 1H), 7.30–7.35 (m, 4H), 7.57 (d, $J=8.2$ Hz, 2H), 7.73 (d, $J=8.2$ Hz, 2H).

(*E*)-Diethyl 3-(4-Cyanobenzylidene)-4-[(isopropoxy-dimethylsilyl)methyl]cyclopentane-1,1-dicarboxylate (20)

A small portion of the crude reaction mixture was taken, and the product purified by flash chromatography (20–50% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=$ 0.11 (s, 3H), 0.13 (s, 3H), 0.65 (dd, $J=15.0$, 12.3 Hz, 1H), 0.90 (dd, $J=15.0$, 1.6 Hz, 1H), 1.14 (app t, $J=6.1$ Hz, 6H), 1.23 (t, $J=7.1$ Hz, 3H), 1.27 (t, $J=7.1$ Hz, 3H), 2.03 (dd, $J=$ 13.6, 5.9 Hz, 1H), 2.83–2.73 (m, 1H), 2.95 (d, $J=16.0$ Hz, 1H), 3.25–3.39 (m, 2H), 3.95 (sept, $J=6.1$ Hz, 1H), 4.12–4.29 (m, 4H), 6.26 (s, 1H), 7.36 (d, $J=8.3$ Hz, 2H), 7.56 (d, $J=8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta=-0.33$, -0.15, 14.4, 22.9, 26.16, 26.24, 35.6, 42.2, 43.4, 58.6, 61.9, 62.0, 65.3, 109.7, 119.5, 120.3, 129.2, 132.3, 142.3, 153.9, 171.8, 172.0.

General Procedure for Oxidation of the Silyl Group

To a solution of crude products **19a**, **b** or **20** in DMF (2 mL) were successively added solid KF (0.8 mmol, 4 equiv.) and 50% H_2O_2 aqueous solution (2.4 mmol, 12 equiv.) at room temperature. The reaction mixture was stirred overrnight at room temperature, then diluted with H_2O and extracted with Et_2O. The extract was successively washed with 1 M $Na_2S_2O_3$ solution and H_2O and dried over $MgSO_4$. The solvent was removed by evaporation, followed by flash chromatography on silica gel to give alcohols **21** or **22.**

(*E*)-4-{[4-(Hydroxymethyl)-1-tosylpyrrolidin-3-ylidene]methyl}benzonitrile (21)

After flash chromatography on SiO_2, (50–100% ethyl acetate in hexane) the product was isolated as a highly viscous oil; yield: 48 mg (0.13 mmol, 65% based on **17**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.6$ (br, OH), 2.44 (s, 3H), 3.16 (dd, $J=9.7$, 6.2 Hz, 1H), 3.34–3.42 (m, 1H), 3.48 (app t, $J=$ 9.7 Hz, 1H), 3.58 (dd, $J=10.4$, 4.9 Hz, 1H), 3.70 (d, $J=$ 9.8 Hz, 1H), 3.78 (d, $J=14.4$ Hz, 1H), 4.13 (dd, $J=14.2$, 1.3 Hz, 1H), 6.42 (s, 1H), 7.32–7.39 (m, 4H), 7.73–7.75–7.7.78 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=21.80$, 29.92, 44.20, 51.39, 53.89, 61.77, 123.98, 128.10, 128.17, 128.30, 129.98, 132.25, 132.59, 139.75, 139.86, 168.96.

(*E*)-Diethyl 3-(4-Cyanobenzylidene)-4-(hydroxy-methyl)cyclopentane-1,1-dicarboxylate (22)

After flash chromatography on SiO_2 (20–50% ethyl acetate in hexane), the product was isolated as a highly viscous oil; yield: 43 mg (0.12 mmol, 60% based on **19**). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.25$ (t, $J=7.1$ Hz, 3H), 1.27 (t, $J=$ 7.1 Hz, 3H), 1.56 (s, 1H), 2.36 (dd, $J=13.7$, 4.9 Hz, 1H), 2.65 (dd, $J=13.7$, 7.5 Hz, 1H), 3.07 (A part of ABX, $J=$ 16.6 Hz, $J_X=0$ Hz, 1H), 3.21 (B part of ABX, $J=16.6$ Hz, $J_X=2$ Hz, 1H), 3.4–3.5 (m, 2H), 3.58–3.67 (m, 1H), 4.18–4.27 (m, 4H), 6.49 (s, 1H), 7.28 (d, $J=8.3$ Hz, 2H), 7.75 (d, $J=8.3$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=1.33$, 14.34, 37.52, 43.25, 43.88, 58.39, 62.01, 62.10, 63.68, 123.87, 127.94, 128.45, 131.50, 141.28, 144.87, 169.73, 171.94, 172.22 ppm.

Supporting Information

Experimental procedures for the preparation of compounds **1c**, **1d**, and **8** and ^{1}H and ^{13}C NMR spectra for all new compounds are presented in the Suppoprting Information. This material is also available free of charge from the corresponding author.

Acknowledgements

This work was supported by the Swedish Research Council, the Carl Trygger Foundation for Scientific Research, and the Deutscher Akademischer Austausch Dienst (DAAD). We are grateful to Sigma–Aldrich for a generous gift of Pd-PEPPSI-IPr. We would also like to thank Georgios Passas-Lagos for his efforts in the initial stages of this project.

References

[1] V. Michelet, P. Y. Toullec, J.-P. Genêt, *Angew. Chem.* **2008**, *120*, 4338–4386; *Angew. Chem. Int. Ed.* **2008**, *47*, 4268–4315.

[2] a) I. Ojima, R. J. Donovan, W. R. Shay, *J. Am. Chem. Soc.* **1992**, *114*, 6580–6582; b) I. Ojima, A. T. Vu, S.-Y. Lee, J. V. McCullagh, A. C Moralee, M. Fujiwara, T. H. Hoang, *J. Am. Chem. Soc.* **2002**, *124*, 9164–9174; c) R. A. Widenhoefer, *Acc. Chem. Res.* **2002**, *35*, 905–913; d) H. Chakrapani, C. Liu, R. Widenhoefer, *Org. Lett.* **2003**, *5*, 157–159; e) K. H. Park, S. Y. Kim, S. U. Son, Y. K. Chung, *Eur. J. Org. Chem.* **2003**, 4341–4345; f) B.-M. Fan, J.-H. Xie, S. Li, L.-X. Wang, Q.-L. Zhou, *Angew. Chem.* **2007**, *119*, 1297–1299; *Angew. Chem. Int. Ed.* **2007**, *46*, 1275–1277; g) S. E. Denmark, J. H.-C. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 3737–3744.

[3] a) R. E. Kinder, R. A. Widenhoefer, *Org. Lett.* **2006**, *8*, 1967–1969; b) J. Marco-Martínez, V. López-Carillo, E. Bunuel, R. Simancas, D. J. Cárdenas, *J. Am. Chem. Soc.* **2007**, *129*, 1874–1875.

[4] M. Lautens, J. Mancuso, *Org. Lett.* **2000**, *2*, 671–673.

[5] K. Tamao, S. Yamaguchi, *J. Organomet. Chem.* **2000**, *611*, 3–4.

[6] a) M. Mori, T. Hirose, H. Wakamatsu, N. Imakuni, Y. Sato. *Organometallics* **2001**, *20*, 1907–1909; b) Y. Sato, N. Imakuni, M. Mori, *Adv. Synth. Catal.* **2003**, *345*, 488–491; c) Y. Sato, N. Imakuni, T. Hirose, H. Wakamatsu, M. Mori, *J. Organomet. Chem.* **2003**, *687*, 392–402.
[7] S.-y. Onozawa, Y. Hatanaka, N. Choi, M. Tanaka, *Organometallics* **1997**, *16*, 5389–5391.
[8] S.-y. Onozawa, Y. Hatanaka, M. Tanaka, *Chem. Commun.* **1997**, 1229–1230.
[9] For reviews of interelement additions, see: a) M. Suginome, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221–3256; b) I. Beletskaya, C. Moberg, *Chem. Rev.* **2006**, *106*, 2320–2354.
[10] a) M. J. Curtis-Long, Y. Aye, *Chem. Eur. J.* **2009**, *15*, 5402–5416; b) S. E. Denmark, C. S. Regens, *Acc. Chem. Res.* **2008**, *41*, 1486–1499.
[11] H. Doucet, *Eur. J. Org. Chem.* **2008**, 2013–2030.
[12] a) Y. Ito, *J. Organomet. Chem.* **1999**, *576*, 300–304; b) M. Suginome, Y. Ito, *J. Organomet. Chem.* **2003**, *680*, 43–50; c) T. Ohmura, M. Suginome, *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29–49.
[13] a) M. Gerdin, C. Moberg, *Adv. Synth. Catal.* **2005**, *347*, 749–753; b) M. Gerdin, C. Moberg, *Org. Lett.* **2006**, *8*, 2929–2932; c) C. Lüken, C. Moberg, *Org. Lett.* **2008**, *10*, 2505–2508; d) G. Durieux, M. Gerdin, C. Moberg. A. Jutand, *Eur. J. Inorg. Chem.* **2008**, 4236–4241; e) M. Gerdin, M. Penhoat, R. Zalubovskis, C. Pétermann, C. Moberg, *J. Organomet. Chem.* **2008**, *693*, 3519–3526.
[14] Diaminosilylboranes such as **2** are less prone to undergo oxidative addition and insertion into alkyne bonds, at least in the presence of Pt(0), see ref.[23]
[15] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[16] a) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561–3598; b) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; c) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708–3742.
[17] M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2006**, *12*, 4749–4755.
[18] M. G. Organ, G. A. Chass, D.-C. Fang, A. C. Hopkinson, C. Valente, *Synthesis* **2008**, 2776–2797.
[19] M. G. Organ, M. Abdel-Hadi, S. Avola, N. Hadei, J. Nasielski, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2007**, *13*, 150–157.
[20] Under optimized conditions, minute amounts of the minor isomer were formed. The structure of this compound was not accurately analyzed, but it is beleived to be the *E*-isomer.
[21] *E*-CH_3, *E*-C_5H_6, *E*-*p*-$C_6H_4NO_2$, di-CH_3, *Z*-Cl, *E*-CO_2Me.
[22] Me.
[23] T. Sagawa, Y. Asano, F. Ozawa, *Organometallics* **2002**, *21*, 5879–5886.
[24] a) K. Tamao, N. Ishida, *J. Organomet. Chem.* **1984**, *269*, C37–39; b) I. Fleming, P. E. J. Sanderson, *Tetrahedron Lett.* **1987**, *28*, 4229–4232.
[25] T. Ohmura, K. Masuda, H. Furukawa, M. Suginome, *Organometallics* **2007**, *26*, 1291–1294.
[26] A. Ptaka, F. Katagiri, T. Kinoshita, Y. Odagaki, S. Oishi, H. Tamamura, N. Hamanaka, N. Fujii, *J. Org. Chem.* **2002**, *67*, 6152–6161.
[27] D. Leca, K. Song, M. Albert, M. Grangeio-Gonçalves, L. Fensterbank, E. Lacôte, M. Malacria, *Synthesis* **2005**, 1405–1420.
[28] T. Morimoto, K. Fuji, K. Tsutsumi, K. Kakiuchi, *J. Am. Chem. Soc.* **2002**, *124*, 3806–3807.
[29] K. Miura, H. Saito, N. Fujisawa, A. Hosomi, *J. Org. Chem.* **2000**, *65*, 8119–8122.
[30] M. Suginome, T. Matsuda, Y. Ito, *Organometallics* **2000**, *19*, 4647–4649.
[31] M. Patel, T. Livinghouse, B. L: Pagenkopf, *Org. Synth.* **2003**, *80*, 93–103.
[32] B. M. Trost, C. A. Merlic, *J. Am. Chem. Soc.* **1990**, *112*, 9590–9600.

