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# Ir-Catalyzed, Silyl-Directed, *peri*-Borylation of C-H Bonds in Fused Polycyclic Arenes and Heteroarenes

Bo Su and John F. Hartwig\*

Dedication ((optional))

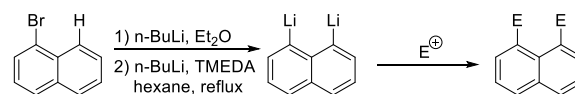
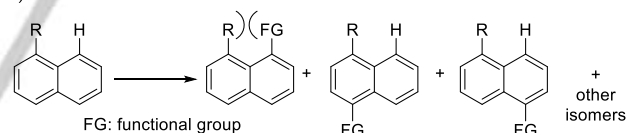
**Abstract:** *peri*-Disubstituted naphthalenes exhibit interesting physical properties and unique chemical reactivity, due to the parallel arrangement of the bonds to the two *peri*-disposed substituents. Regioselective installation of a functional group at the position *peri* to 1-substituted naphthalenes is challenging due to the steric interaction between the existing substituent and the position at which the second one would be installed. We report an iridium-catalyzed borylation of the C-H bond *peri* to a silyl group in naphthalenes and analogous polyaromatic hydrocarbons. The reaction occurs under mild conditions with wide functional group tolerance. The silyl group and the boryl group in the resulting products are precursors to a range of functional groups bound to the naphthalene ring through C-C, C-O, C-N, C-Br and C-Cl bonds.

*peri*-Substitution refers to the introduction of a substituent at the 8 position of 1-substituted naphthalene rings. Substituents located at mutually *peri*-positions are much closer to each other than those at mutually *ortho* positions. Due to the rigidity of the backbone of the naphthalene ring and the juxtaposition of two parallel chemical bonds at the *peri*-positions, sterically congested *peri*-disubstituted naphthalenes possess special features, including distortions of the backbone, extreme steric strain, abnormal molecular spectra, intramolecular hydrogen bonding, high proton affinity, and unique chemical reactivity.<sup>[1]</sup> These properties of *peri*-disubstituted naphthalenes and related fused arenes have led to applications of such structures in molecular and ion recognition,<sup>[2]</sup> ligand design<sup>[3]</sup> and catalysis.<sup>[2b]</sup> However, the synthesis of these *peri*-substituted compounds has been challenging,<sup>[4]</sup> due to the steric interaction between

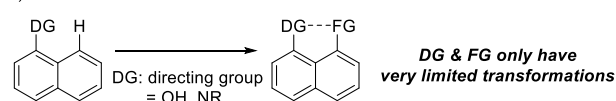
the existing substituent and the position at which the second one would be installed.

Several classical and catalytic methods to *peri*-substituted molecules have been studied, but each has severe limitations. Electrophilic aromatic substitution of 1-substituted naphthalenes is one approach to synthesize *peri*-disubstituted naphthalenes (Scheme 1a), but low yields of the 1,8-substituted products are obtained because of poor regioselectivity.<sup>[5]</sup> Addition of electrophiles to 1,8-dilithionaphthalenes generated by lithium-halogen exchange and subsequent deprotonation of 1-bromonaphthalenes is a second approach (Scheme 1a), but this method is limited to the formation of products containing identical *peri*-substituents and limited to reactants containing functional groups that tolerate organolithium reagents.<sup>[6]</sup>

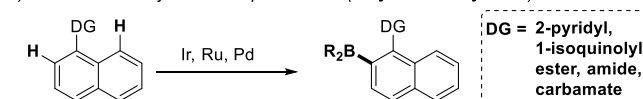
a) traditional methods:



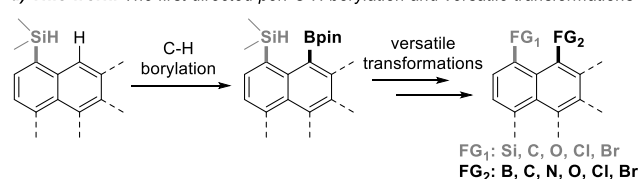
b) directed C-H functionalization:



c) directed C-H borylation of naphthalenes: (only *ortho*-borylation)



d) This work: The first directed *peri*-C-H borylation and versatile transformations



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**Scheme 1.** Functionalization at the *peri*-positions of naphthalene and related compounds

The functionalization of C-H bonds catalyzed by transition metal-complexes is a third approach.<sup>[7]</sup> In specific cases, this type of reaction can install a substituent *peri* to an OH or NH<sub>2</sub> group of naphthols and naphthylamines. However, the reactions of naphthols at the *peri* position have been limited to phenylation at high temperatures and a series of alkynylations,<sup>[7a, 7n]</sup> while the reactions of naphthylamines at the *peri* position have required picolinamide as the directing group and lead to the installation of a limited set of groups.<sup>[7b, 7d, 7g-i, 7k-m]</sup> In other cases, reactions of 1-naphthol and 1-aminonaphthalene derivatives have formed annulated products in which the directing groups (OH and NR) are linked to the newly installed functionalities (Scheme 1b).<sup>[7c-f, 7k, 7o, 8]</sup> In such structures, manipulations of the directing group and the newly introduced functional groups is difficult. Other directing groups (eg. carboxylic acid, amide, 2-pyridyl group etc.) have led to *ortho*-substituted products,<sup>[7n, 9]</sup> rather than *peri*-substituted products.

The borylation of aromatic C-H bonds catalyzed by transition-metal catalysts usually occurs under mild conditions with high functional group compatibility, and the C-B bond in the product undergoes a wide range of transformations.<sup>[10], [11]</sup> Due to steric hindrance between *peri*-positions, no undirected C-H borylation has occurred at the *peri*-positions of naphthalenes. All of the catalytic, directed borylation of C-H bonds in 1-substituted naphthalenes, including those containing 1-quinolyl-, 2-pyridyl, ester, amide or carbamate moieties, have occurred at the position *ortho*, not the *peri*, to the directing groups (Scheme 1c).<sup>[11e, 11h, 11j, 11k, 11n]</sup> Thus, a strategy to enable the installation of a series of substituents at mutually *peri* positions for the synthesis of a wide range of *peri*-substituted polycyclic aromatic hydrocarbons is needed.

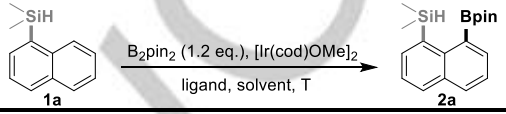
Our group has reported silyl-directed borylations of C-H bonds, in which the borylation occurred at *ortho*-position of aromatic C-H bonds or C(sp<sup>3</sup>)-H bonds.<sup>[12], [13]</sup> The silyl group adds transiently to the metal center and can be used after the borylation reaction to create a range of functional groups by transformations that are orthogonal in most cases to those of the transformations of C-B bonds, thus largely increasing the product diversity.<sup>[12]</sup>

We report the *peri* borylation of C-H bonds in 1-hydrosilyl naphthalenes and related polyaromatic hydrocarbons (Scheme 1d). This reaction occurs under mild conditions with high functional group compatibility. Reactions at the C-Si and C-B bonds in the *peri*-borylated arenes form final products containing a range of substituents bound to the arene unit by C-C, C-O, C-N, C-Cl and C-Br bonds.

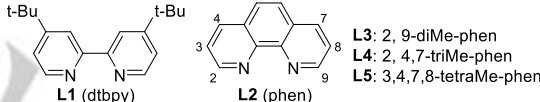
To identify conditions for the Ir-catalyzed, *peri* borylation of C-H bonds in 1-hydrosilyl naphthalenes, we conducted reactions of 1-dimethylhydrosilyl naphthalene **1a** with B<sub>2</sub>pin<sub>2</sub> catalyzed by iridium complexes derived from [Ir(cod)OMe]<sub>2</sub> and *N, N*-donor ligands **L1-L5** in THF at 80 °C (Table 1,

entries 1-5). Reactions with 3,4,7,8-tetramethyl phenanthroline **L5** formed product **2a** in higher yield (61%) than those with 4,4'-di-*tert*-butyl bipyridine **L1** and phenanthroline ligands **L2-L4** (up to 47%). Reactions conducted in alternative solvents and at higher temperatures did not occur in higher yield (Table 1, entries 6-12), but reactions with 1.5 equiv of B<sub>2</sub>pin<sub>2</sub> instead of 1.2 equiv occurred in a higher 68% yield. Ultimately, the product was obtained in a high 84% when the reaction was run with 1.5 equiv of B<sub>2</sub>pin<sub>2</sub> for a longer 24 h.

**Table 1:** Evaluation of the silyl-directed borylation of the *peri*-C-H bond.<sup>[a]</sup>



Entry	Ligand	Solvent	T	Yield <sup>b</sup>
1	<b>L1</b>	THF	80 °C	28%
2	<b>L2</b>	THF	80 °C	45%
3	<b>L3</b>	THF	80 °C	trace
4	<b>L4</b>	THF	80 °C	47%
5	<b>L5</b>	THF	80 °C	61%
6	<b>L5</b>	2-MeTHF	80 °C	27%
7	<b>L5</b>	Dioxane	80 °C	trace
8	<b>L5</b>	Dibutylether	80 °C	13%
9	<b>L5</b>	heptane	80 °C	49%
10	<b>L5</b>	dichloroethane	80 °C	trace
11	<b>L5</b>	THF	100 °C	56%
12	<b>L5</b>	THF	65 °C	50%
11 <sup>c</sup>	<b>L5</b>	THF	80 °C	68%
12 <sup>c,d</sup>	<b>L5</b>	THF	80 °C	84%



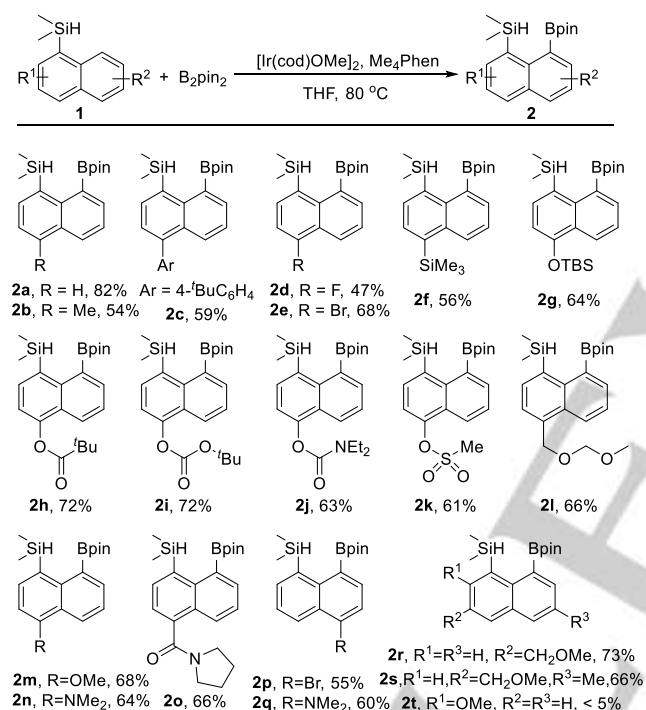
<sup>[a]</sup>The reaction was conducted with **1a** (0.20 mmol), [Ir(cod)OMe]<sub>2</sub> (2.0 mol %), ligand (4.5 mol %), and B<sub>2</sub>pin<sub>2</sub> (1.2 equiv) in the solvent (1.0 mL) for 12 h under N<sub>2</sub>. <sup>[b]</sup>The yield was determined by <sup>1</sup>H NMR spectrum using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>[c]</sup>The reaction was conducted with 1.5 equiv. of B<sub>2</sub>pin<sub>2</sub>. <sup>[d]</sup>The reaction was conducted for 24 h.

Having identified conditions for the silyl-directed, *peri*-borylation of compound **1a**, we assessed the scope of the reaction (Table 2). Reactions of 1-dimethylhydrosilylnaphthalenes containing a range of functional groups afforded the products from borylation of the *peri*-C-H bonds in moderate to good yields. To test the tolerance of this reaction for functional groups, the borylation was conducted with a series of 1-hydrosilyl-4-substituted naphthalenes. Unsubstituted **1a** and alkyl- or aryl-substituted **1b** and **1c** gave the products **2a-2c** in 54%-82% yields. Reactions of the naphthalenes containing fluoride or bromide (**2d** and **2e**), a trimethylsilyl group (**2f**), a silyl ether (**2g**), a pivalate ester (**2h**), a carbonate (**2i**), a carbamate (**2j**), a methyl sulfonate (**2k**) and even a labile ketal (**2l**) gave the *peri*-substituted product in 47-72% yields.

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Reactions of substrates containing varied electronic and steric properties of the arenes were also conducted. Substituents located *para* to the silyl group with varied electronic properties did not affect the yield (**2m-2o**). Moreover, reactions of 3-substituted, 5-substituted, and 6-substituted 1-silyl naphthalenes **1p-1s** underwent borylation at the *peri*-C-H bond smoothly to give products **2p-2s** in good yields. However, the reaction of 2-methoxy-substituted **1t** did not give any product from borylation, presumably because the steric demand of a 2-substituent causes the silyl group to adopt a conformation in which the Si-H bond is more hindered because it is oriented toward the 2-substituent, rather than the *peri*-C-H bond.

**Table 2:** Scope of the silyl-directed *peri*-C-H borylation of naphthalenes.<sup>[a]</sup>

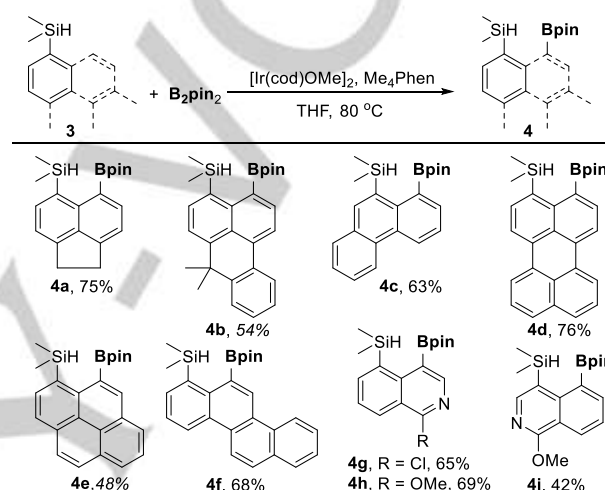


<sup>[a]</sup>The reaction was conducted under N<sub>2</sub> for 18-24 h and was monitored by GC/MS; the yields refer to isolated yields.

This silyl-directed *peri*-borylation of C-H bonds also occurred with polyaromatic hydrocarbons (PAHs) and benzo-fused heteroaromatic compounds (Table 3). These compounds are commonly used in material chemistry,<sup>[14]</sup> and selective functionalization of these compounds by alternative methods is challenging because they contain a large set of distinct aromatic C-H bonds.<sup>[15]</sup> However, the silyl-directed borylation occurred selectively at the C-H bonds located *peri* to the silyl group in 5-hydrosilyl acenaphthene **3a** and 4-hydrosilyl-7,7-dimethyl-7H-benzo[de]anthracene **3b** to form the corresponding products **4a** and **4b** in 75% and 54% yields. The reactions with additional PAHs, such as 1-hydrosilyl

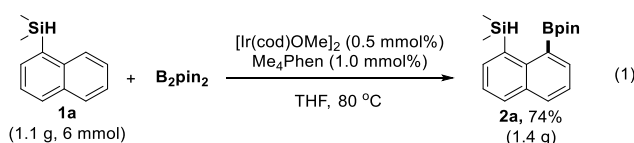
phenanthrene **3c**, 3-hydrosilyl perylene **3d**, 1-hydrosilyl pyrene **3e** and 1-hydrosilyl chrysene **3f** formed the corresponding *peri*-borylated products **4c-4f** in moderate to good yields. Moreover, reactions occurred with the heteroaromatic 1-substituted isoquinolines **3g-3h** to give the corresponding *peri*-substituted products **4g-4h**. For reasons we do not understand, no reaction occurred when 2-chloro-4-hydrosilyl quinoline and 1-phenylsulfonyl-3-hydrosilyl indole (structures not shown) were subjected to the reaction conditions.

**Table 3:** Scope of the silyl-directed *peri*-C-H borylation of isoquinolines and other polyaromatic hydrocarbons.<sup>[a]</sup>



<sup>[a]</sup>The reaction was conducted under N<sub>2</sub> for 18-24 h and was monitored by GC/MS; the yields refer to isolated yields.

This silyl-directed *peri*-selective C-H borylation occurred on a gram scale in yields similar to the reactions on smaller scale. The reaction of **1a** with 6.0 mmol of silylarene (1.1 g) (eq 1) formed the borylated product **2a** in 74% yield with only 0.50 mol % catalyst, instead of the 2.0 mol % catalyst used for reactions with 0.20 mmol of the silylarene.

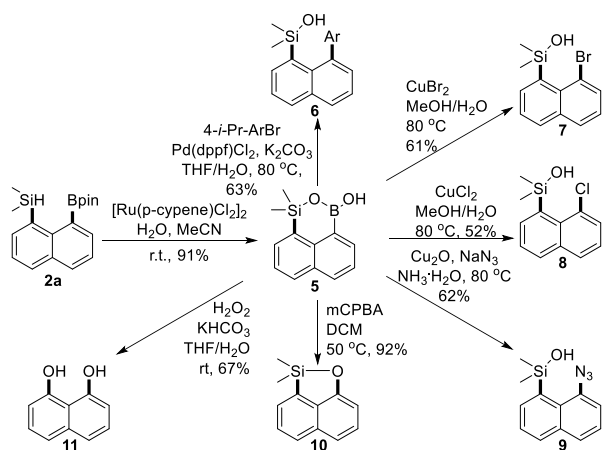


To illustrate the utility of this reaction, we investigated transformations of the boryl and the silyl groups in compound **2a**. Boronate **2a** was transformed to *peri* silyl boronic anhydride **5** in the presence of a ruthenium catalyst. Compound **5** was presumably formed via oxidation of the silane to the corresponding silanols, followed by displacement of the pinacol by intramolecular substitution and hydrolysis.<sup>[16]</sup> The C-B bond in **5** was converted to a C-C bond in a biaryl by a palladium-catalyzed Suzuki-coupling reaction.<sup>[17]</sup> The C-B bond in **5** also was transformed to a C-



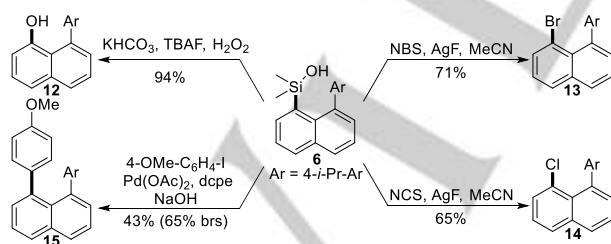
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halogen bond (C-Br and C-Cl) and C-N bond by copper-catalyzed and copper-mediated processes.<sup>[18]</sup> The C-B bond in **5** also was oxidized selectively to a C-O bond, while leaving the C-Si bond intact, with 1.5 equiv of *m*-CPBA as the oxidant to form the naphthalene-fused silole **10** after dehydration. Oxidation of both the C-B and C-Si bonds in **5** occurred to give naphthalene-1,8-diol when an excess of H<sub>2</sub>O<sub>2</sub> was used under basic conditions.



**Scheme 2.** Transformations of the C-B bond in the borylated product

To expand the diversity of the products derived from the *peri*-C-H borylation further, transformations of the C-Si bond in **6** were explored. The C-Si bond in compound **6** was oxidized to the C-O bond in naphthol **12** when treated with a combination of hydrogen peroxide, base and fluoride. Halogenation of the C-Si bond in **6** with NXS (X = Br and Cl) and AgF occurred smoothly to give products **13** and **14** in 71% and 65% yields respectively.<sup>[19]</sup> The C-Si bond also was converted to a C-C bond in the 1,8-diarylnaphthalene by palladium-catalyzed coupling.<sup>[20]</sup>



**Scheme 3.** Further transformations of the C-Si bond in the product

In summary, we have developed an iridium-catalyzed, *peri* borylation of naphthalene derivatives and analogous polyaromatic hydrocarbons directed by a hydrosilyl group under mild conditions with broad functional-group

tolerance. Both the boryl group and the silyl group at the *peri*-positions have been transformed to a wide range of groups, such as aryl groups, hydroxyl groups, an azido group and halogens. This reaction greatly expands the diversity of readily accessible *peri*-disubstituted naphthalenes and related polyaromatic hydrocarbons, and further studies will be conducted to expand the scope of *peri*-selective reactions of fused heteroarenes.

## Acknowledgements ((optional))

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**Keywords:** C-H activation • *peri* selective • *peri*-disubstituted • borylation • naphthalene •

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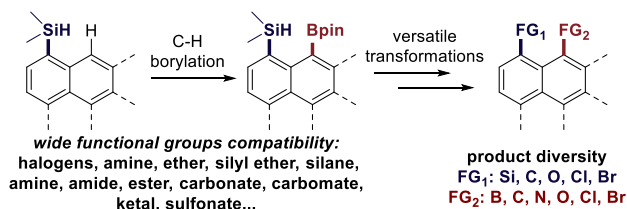
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## COMMUNICATION

Layout 2:

## COMMUNICATION



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**Ir-Catalyzed, Silyl-Directed, peri-Borylation of C-H Bonds in Fused Polycyclic Arenes and Heteroarenes**

**Peri-Functionalization via C-H Borylation:** An iridium-catalyzed, hydrosilyl directed, *peri*-C-H borylation of naphthalenes and analogous polyaromatic hydrocarbons has been developed. The reaction occurs under mild conditions with broad functional-group tolerance. Both the boryl group and the silyl group at the *peri*-positions can be transformed to a wide range of groups, such as aryl groups, hydroxyl groups, an azido group and halogens. This reaction greatly expands the diversity of readily accessible *peri*-disubstituted naphthalenes and related polyaromatic hydrocarbons.