JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Benzannulation of Heterocyclic Frameworks by 1,1-Carboboration Pathways

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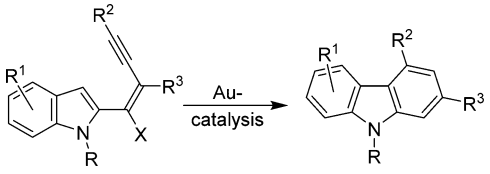
Supporting Information

ABSTRACT: A small series of S- and N-heterocyclic 1,2-bis(trimethylsilylethynyl)arenes (**2**, **9**, and **12**) react with the strongly electrophilic borane $B(C_6F_5)_3$ in consecutive 1,1-carboboration sequences to benzannulated heterocyclic systems. With this approach, highly substituted carbazole (**6**), benzothiophene (**10**), and quinoline (**14**) derivatives can be synthesized. While benzannulation occurs in all three cases, the reactions are quite different in detail. Finally, one-pot deborylation reactions lead to hydroxy-hetarenes, as demonstrated for the hydroxy-carbazole **7** and the hydroxy-benzothiophene **11**.

INTRODUCTION

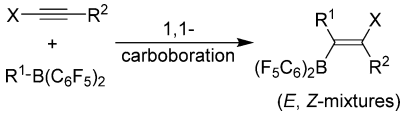
Benzannulated heterocycles are most frequently synthesized by schemes that involve the construction of the heterocyclic ring system as the essential step by making use of functional groups already present at the benzenoid carbocycle. Typical classical examples that are making use of this conventional strategy include Fischer indole synthesis,[1] the Skraup quinoline synthesis,[2] the Bischler-type synthesis of isochinoline systems,[3] and many, many more.[4] There is some minor current development toward developing single synthetic schemes that are directed toward preparing benzannulated heterocycles in the opposite way, namely, by starting from a suitably substituted heterocycle and constructing the annulated phenylene moiety subsequently. Scheme 1 shows a recent example of this strategy, which is making use of contemporary gold catalysis to construct one annulated benzene ring of substituted carbazole systems.[5]

Scheme 1. Gold-Catalyzed Carbazole Formation



We have now utilized the unique features of the 1,1-carboboration reaction[6−10] to construct the attached benzoid carbocycles of related benzannulated heterocycles. The 1,1-carboboration reaction is conceptionally related to the reverse Fritsch−Buttenberg−Wiechell rearrangement.[11] It features electrophilic attack of a borane to an acetylene, which initiates 1,2-migration of a substituent along the alkyne framework coupled with 1,2-migration of a substituent from boron to the initially attacked acetylene carbon atom (see Scheme 2). The 1,1-carboboration reaction, especially in its contemporary variants using the strongly electrophilic R-$B(C_6F_5)_2$ boranes,[8−10] represents a very suitable method for the synthesis of specifically substituted alkenyl boranes.[12]

Scheme 2. 1,1-Carboboration Reaction of Acetylene Derivatives



Variants of the 1,1-carboboration reaction have been used to prepare various heterocyclic ring systems, including siloles,[13,14] phospholes,[15] and even boroles.[16,17]

We had used the 1,1-carboboration reaction quite successfully for naphthalene syntheses by means of annulation reactions starting from *o*-bis(alkynyl)benzenes.[18] The resulting boryl-substituted naphthalene derivatives were subsequently employed in deborylation reactions, e.g., Suzuki−Miyaura cross-coupling (see Scheme 3 for a typical example). We have now used this advanced variant of the 1,1-carboboration reaction to construct annulated six-membered rings of a small series of benzannulated heterocyclic ring systems starting from the respective vicinally bis-alkynyl substituted hetarenes. We will illustrate this procedure for examples of carbazole, benzothiophene, and quinoline preparations.

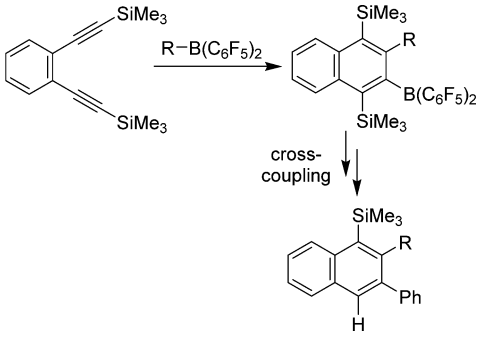
RESULTS AND DISCUSSION

The 1,1-Carboboration Route to Carbazoles. We used a *N*-methylindole derivative for the 1,1-carboboration−benzannulation reaction to the respective carbazole derivative. For that purpose, the dibromoindole **1**[19a] was Negishi-coupled[20] with the *in situ* generated zinc trimethylsilylacetylene reagent to give the vicinal bis(trimethylsilylethynyl)indole **2** (see Scheme 4).

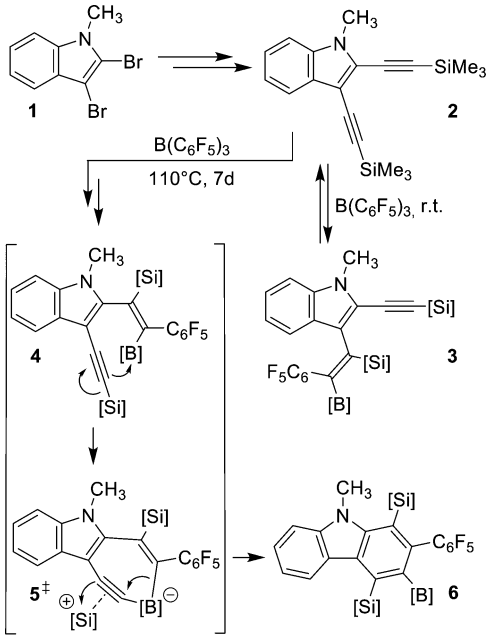
Received: December 5, 2014
Published: January 12, 2015

DOI: 10.1021/jo502753s
J. Org. Chem. 2015, 80, 2240−2248

Scheme 3. Preparation of Deborylated Naphthalene Derivatives



Scheme 4. Reaction Pathway to the Borylated Carbazole 6



Compound **2** was then reacted with one molar equivalent of $B(C_6F_5)_3$[21] at ambient temperature. This gave a single product, which was identified as the 1,1-carboboration product **3** of one of the trimethylsilylethynyl functional groups. We obtained single crystals of compound **3** that allowed for its characterization by a X-ray crystal structure analysis (see Figure 1). Compound **3** shows one unchanged $-C\equiv C\text{-}SiMes_3$ group that is attached at carbon atom C2 of the indole framework. The 1,1-carboboration reaction has taken place selectively at the other alkynyl moiety, giving an *E*-configurated tetrasubstituted alkenylborane. Both the C_6F_5 substituent and the $B(C_6F_5)_2$ group are found bonded to the same carbon atom (C12). The trimethylsilyl group is found 1,2-migrated at the carbon atom C11.

The solution NMR data of compound **3** were obtained from an *in situ* experiment without isolating the compound. It shows the ^{1}H NMR resonances of two different trimethylsilyl substituents at δ 0.33 and 0.05 (^{29}Si NMR: δ −1.1, −16.9) and a ^{11}B NMR resonance at ca. δ 64, which is typical for a Lewis acidic planar tricoordinate R-$B(C_6F_5)_2$ situation.[22] The ^{13}C NMR features of the newly formed alkenylborane occur at δ 165.4 (=C[Si]) and δ 145.3 (=C[B]), respectively. The

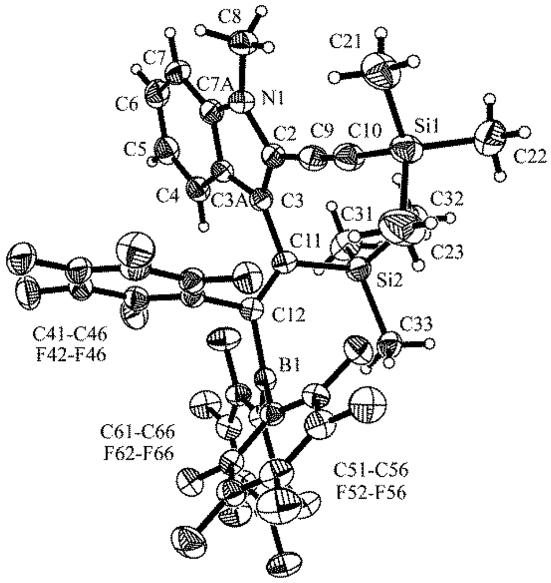


Figure 1. Molecular structure of the 1,1-carboboration product **3** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C2−C3: 1.392(4), C3−C3A: 1.434(4), N1−C8: 1.463(4), C9−C10: 1.201(4), C11−C12: 1.348(4), C12−B1: 1.582(4), C2−C9−C10: 176.9(3), C3−C11−C12: 119.5(2), N1−C2−C9: 120.0(3), $\Sigma B1^{CCC}$ = 359.1.

unchanged $-C\equiv C\text{-}SiMe_3$ shows the corresponding ^{13}C NMR signals at δ 104.8 ($\equiv$C[Si], $^1J_{SiC}$ = 81.1 Hz) and δ 95.5, respectively, and there are two sets of *o*, *p*, *m* ^{19}F NMR resonances of the C_6F_5 group and the $B(C_6F_5)_2$ substituent in a 1:2 intensity ratio. The 1,1-carboboration product **3** has the wrong stereochemistry at the alkenylborane group to allow for a direct ring closure by a subsequent 1,1-alkenylboration reaction. However, there is evidence that many carboboration reactions are reversible.[7] Consequently, heating the bis(alkynyl)indole starting material **2** with $B(C_6F_5)_3$ (1 equiv) in toluene solution for 7 days at 110 °C eventually gave the carbazole product **6** under conditions of thermodynamic control. The product was isolated, and its composition was determined by X-ray diffraction (see Figure 2 and Scheme 4).

The structural characterization has revealed that the arene annulation has been completed to give the carbazole ring system. The newly formed phenylene ring system has the pair of $SiMe_3$ groups attached at its proximal carbon atoms C1 and C4. The single C_6F_5 substituent is found at the carbon atom C2, and the $B(C_6F_5)_2$ moiety is found attached at the adjacent carbon atom C3. In solution, compound **6** shows the ^{1}H/^{13}C NMR signals of the original "left" carbazole phenylene moiety and, in addition, the ^{13}C NMR signals of the newly formed "right" per-substituted phenylene ring. There are the NMR signals of two chemically different $SiMe_3$ groups and two sets of *o*, *p*, *m*-^{19}F NMR resonances of the C_6F_5 subsituent and the $B(C_6F_5)_2$ group in a 1:2 ratio. Compound **6** shows a ^{11}B NMR signals at ca. δ 61, typical as it is expected for the planar tricoordinate Lewis acid function (for details, see the Experimental Section and the Supporting Information).

It can be seen from the reaction scheme (see Scheme 4) that the kinetic 1,1-carboboration product **3** cannot directly be converted to the observed carboboration product **6**. The pathway to **6** requires a mono-1,1-carboboration product to be formed as an intermediate, that has (a) a *Z*-configurated alkenylborane moiety adjacent to an alkynyl group and (b) the

DOI: 10.1021/jo502753s
J. Org. Chem. 2015, 80, 2240−2248

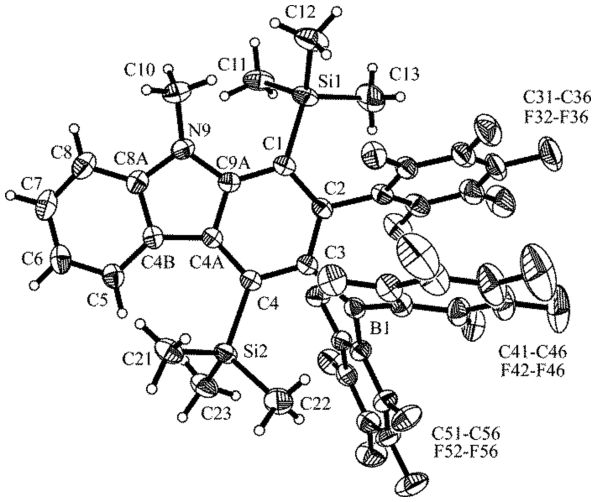
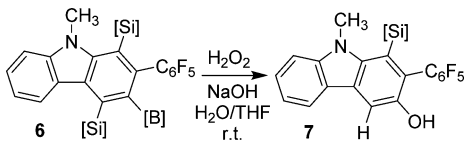


Figure 2. Molecular structure of the carbazole product **6** (thermal ellipsoids are shown with 30% probability; one of two molecules found in the asymmetric unit is shown). Selected bond lengths (Å) and angles (deg): C1−C2: 1.407(4), C1−C9A: 1.408(4), C2−C3: 1.426(4), C3−C4: 1.421(4), N9−C10: 1.463(4), C3−B1: 1.564(4), C4A−C4−C3: 116.9(2), N9−C9A−C1: 127.4(2), $\Sigma B1^{CCC}$ = 359.8.

alkynyl group adjacent to nitrogen converted to the reactive alkenylborane. Only then will the subsequent 1,1-alkenylboration step result in the formation of the observed $B(C_6F_5)_2$ substituted carbazole derivative **6** (see Scheme 4 and Figure 2). Therefore, it must be assumed that the initial 1,1-carboboration reaction giving the product **3** is reversible and that eventually thermodynamic control of the **2** + $B(C_6F_5)_3$ reaction will generate compound **4** as a reactive intermediate. This then would rapidly undergo ring closure under the applied reaction conditions to eventually form the specifically substituted carbazole product **6** by the sequence of consecutive 1,1-carboboration steps (see Scheme 4).

The borylated carbazole product **6** (generated *in situ* from compound **2** + $B(C_6F_5)_3$) was subsequently treated with H_2O_2/NaOH. This resulted in the oxidative removal of the boryl group as expected, but at the same time, the adjacent $SiMe_3$ group was cleaved off (see Scheme 5). We isolated the respective hydroxycarbazole product **7** in ca. 50% yield. The compound was characterized by C, H, N elemental analysis, by spectroscopy, and by X-ray diffraction.

Scheme 5. Deborylation of the Carbazole Derivative 6



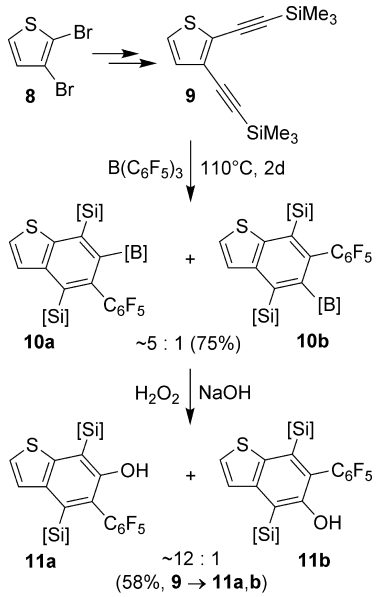
[Si]: $SiMe_3$; [B]: $B(C_6F_5)_2$

The X-ray crystal structure analysis has confirmed the successful oxidative cleavage of the boryl group (see the Experimental Section and the Supporting Information). The "right" carbazole phenylene moiety now has retained the $SiMe_3$ substituent at carbon atom C1, proximal to the NMe unit, and it still features the C_6F_5 group at the adjacent carbon atom (C2). The newly introduced OH functional group is found at carbon atom C3, and carbon atom C4 has lost its trimethylsilyl substituent in proto-desilylation during this process. In the ^1H NMR spectrum of compound **7**, we see a sharp OH resonance at δ 8.35, four resonances of the hydrogen atoms at the "left" unsubstituted phenylene ring, and a sharp signal for the newly introduced single H at the distal position of the "right" substituted phenylene ring at δ 7.57. In addition, we have monitored the $^1H/^{13}C/^{29}Si$ signals of the remaining $SiMe_3$ substituent and the $^{13}C/^{19}F$ NMR signals of the adjacent C_6F_5 substituent.

Benzothiophenes by 1,1-Carboboration. We also used the sequential ring closure reaction of pairs of *o*-trimethylsilylacetylenes for the preparation of substituted benzothiophenes. For that purpose, we prepared the starting material **9** by Pd-catalyzed coupling of 2,3-dibromothiophene (**8**) with $ZnCl_2$/LiC≡C-$SiMe_3$. Compound **9** was isolated in 84% yield (for details, see the Experimental Section and the Supporting Information).[19b,20]

The bis-alkynyl thiophene starting material **9** was reacted with a stoichiometric quantity of $B(C_6F_5)_3$ in toluene solution for 2 days at 110 °C. This resulted in a clean conversion to the respective substituted benzothiophene product **10** (see Scheme 6). It was obtained as a mixture of two regioisomers **10a**:**10b** in

Scheme 6. Formation of the Benzothiophene Derivatives 11



[Si]: $SiMe_3$; [B]: $B(C_6F_5)_2$

a ratio of ca. 5:1 in 75% yield. An *in situ* experiment with direct NMR monitoring without workup showed that these two isomers were formed in the reaction under these conditions in the same ratio of 5:1. Both of the isomers show characteristic NMR data [e.g., ^{11}B NMR: δ 63 (for both isomers), ^{29}Si: δ −2.5, −4.4 (**10a**), δ −2.2, −4.0 (**10b**); for additional NMR data, see the Experimental Section and the Supporting Information].

We treated the **10a**/**10b** mixture of isomers (generated *in situ* from **9** + $B(C_6F_5)_3$) with H_2O_2/NaOH and obtained a 58% yield of a ca. 12:1 mixture of the respective hydroxybenzothiophene regioisomers **11a,b** after workup involving chromatography and crystallization. In this case, both $SiMe_3$ groups were retained. The major isomer **11a** was characterized by X-ray diffraction (see the Experimental Section and the Supporting Information). In the crystal compound, **11a** features the bicyclic aromatic benzothiophene framework.

DOI: 10.1021/jo502753s
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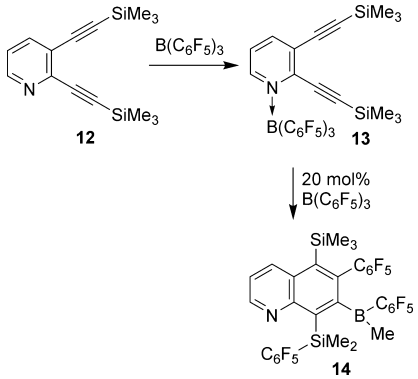
Both the $SiMe_3$ substituents are still attached at the annulated benzene ring. Carbon atom C6 now has the newly introduced OH group attached to it, and the C_6F_5 substituent is bonded at the adjacent carbon atom C5 (see Scheme 6). The major isomer **11a** shows its thiophene ^1H NMR signals at δ 7.43 and 7.59 ($^3J_{HH}$ = 5.8 Hz). It shows the ^1H NMR signals of the pair of $SiMe_3$ substituents at δ 0.54 and 0.15 (corresponding ^{29}Si NMR resonances: δ −3.0 and −3.7), and we have monitored the sharp OH ^1H NMR resonance of compound **11a** at δ 4.93. For additional details and the NMR data of the minor isomer **11b**, see the Experimental Section and the Supporting Information.

Synthesis of a Quinoline Derivative by the 1,1-Carboboration Sequence. Bis(trimethylsilylethynyl)pyridine **12** was synthesized by the standard route that was already used for the other vicinal bis-alkynyl compounds used in this study.[19c,20] Treatment of compound **12** with $B(C_6F_5)_3$ at room temperature first gave the Lewis acid/Lewis base adduct **13**.[23] It was isolated in 84% yield and fully characterized including a X-ray crystal structure analysis (for details, see the Experimental Section and the Supporting Information).

Then compound **12** was treated with 1.2 equiv of $B(C_6F_5)_3$ and kept in toluene at 110 °C for 2 days. Workup gave the product **14** in 50% yield as a yellow solid (see Scheme 7). It was characterized by C, H, N elemental analysis and by X-ray diffraction.

Scheme 7. Preparation of the Quinolone Derivative 14



The X-ray crystal structure analysis of compound **14** (see Figure 3) revealed that the pair of trimethylsilylacetylene units had been converted to the annulated benzene ring of the resulting quinoline product. During this process, both the silyl groups had undergone 1,2-migration along their alkynyl frameworks and ended up at the quinoline carbon atoms C5 and C8, respectively. The single C_6F_5 substituent is bonded at C6 and the boryl group at C7. There is a special feature to be mentioned: the boryl group in product **14** bears only one C_6F_5 substituent but also one methyl group. This has originated from the adjacent silyl substituent at C8. Consequently, this silyl group bears only two remaining methyl substituents and one newly attached C_6F_5 group. We had previously seen such methyl/C_6F_5 exchange reactions between silyl and boryl moieties occasionally in other systems as well.[24,25]

In solution, compound **14** shows two ^{29}Si NMR signals at δ −4.8 ($SiMe_3$) and −11.7 [$SiMe_2(C_6F_5)$]. The ^1H NMR spectrum shows the $SiMe_3$ resonance at δ −0.20. The $SiMe_2(C_6F_5)$ substituent shows ^1H NMR signals of a pair of diastereotopic methyl substituents (δ 0.90 and 0.52), and we see the remaining B-CH_3 resonance at δ 1.52. The system shows restricted rotation of the C-C_6F_5 substituent and the B-C_6F_5 substituent, each shows a total of five ^{19}F resonances. The Si-C_6F_5 group is freely rotating on the NMR time scale and only shows three ^{19}F NMR signals. The ^{11}B NMR shift of compound **14** is at δ 74, indicating planar tricoordinate boron (for additional details, see the Experimental Section and the Supporting Information).

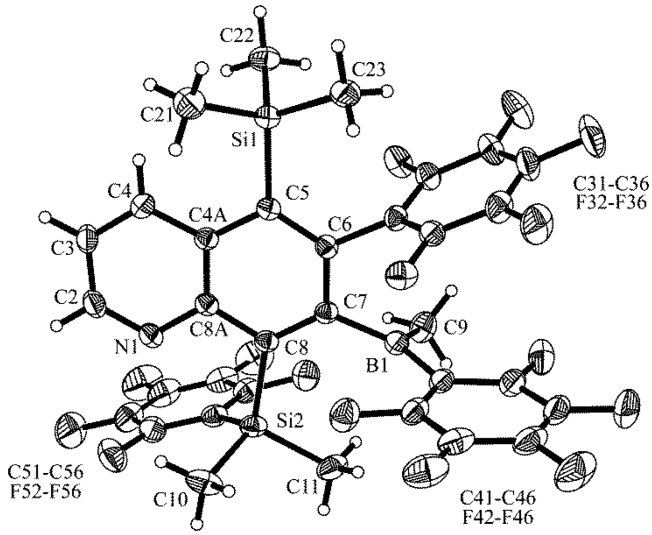


Figure 3. A view of the molecular structure of the quinoline derivative **14** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): N1−C8A: 1.364(4), N1−C2: 1.308(4), C8−C7: 1.383(4), C7−C6: 1.442(4), C5−C6: 1.386(4), B1−C9: 1.563(5), B1−C7: 1.590(5), B1−C41: 1.580(5), Si1−C21: 1.870(4), Si2−C10: 1.860(4), Si2−C51: 1.909(3), C2−N1−C8A: 118.1(3), C8A−C8−Si2: 114.5(2), C4A−C5−Si1: 119.3(2), $\Sigma B1^{CCC}$ = 359.6.

CONCLUSIONS

Benzannulated heterocycles are mostly synthesized by reaction sequences concentrating on the formation of the heterocyclic component. Schemes that are designed building of the aromatic ring are much less frequently encountered. This study has shown that the 1,1-carboboration reaction is a very well suited synthetic tool to develop this latter approach. We could show that the "advanced" version of the 1,1-carboboration reaction using strongly Lewis acidic R-$B(C_6F_5)_2$ type reagents in conjunction with silyl substituents serving as suitable migrating groups at the acetylenic functions makes sequences of reactions available that lead to the straightforward formation of the annulated six-membered rings, which was investigated for a small series of examples here.

The products of our 1,1-carboboration sequence are borylated benzannulated heterocyclic systems. We have shown here that these can be converted to −OH groups in the typical oxidative degradation of borane compounds. We had previously shown that some related arene-$B(C_6F_5)_2$ systems were undergoing Suzuki−Miyaura cross-coupling reactions easily.[9,18] We assume that our sequence will possibly also allow alkyl-$B(C_6F_5)_2$[9] or even alkenyl-$B(C_6F_5)_2$ reagents[26] to be used, and we expect that other more suitable substituted silyl groups will be tolerated as migrating groups and thereby open further pathways of a possible functionalization, e.g., Hiyama coupling[27] and related reactions.

DOI: 10.1021/jo502753s
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EXPERIMENTAL SECTION

General Information. All reactions were carried out under an argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. Assignments of the NMR resonances are supported by 2D experiments. ((Trimethylsilyl)ethynyl)lithium,[28] 2,3-bis((trimethylsilyl)ethynyl)pyridine (**12**),[19c] 2,3-bis(trimethylsilylethynyl)thiophene (**9**),[20,29] and 2,3-dibromo-1-methylindole (**1**)[19a] were prepared according to modified literature procedures. $B(C_6F_5)_3$ was obtained from Boulder Scientific Company.

Synthesis of 1-Methyl-2,3-bis((trimethylsilyl)ethynyl)indole (2). $ZnCl_2$ (707 mg, 5.19 mmol, 3 equiv) and ((trimethylsilyl)-ethynyl)lithium (541 mg, 5.19 mmol, 3 equiv) were dissolved separately in THF (∼5 mL each). The solutions were combined at room temperature and stirred for 30 min at this temperature. Simultaneously, XPhos (80.9 mg, 10 mol %) and $Pd(dba)_2$ (49.7 mg, 5 mol %) were added to a solution of 2,3-dibromo-1-methylindole (**1**, 500 mg, 1.73 mmol, 1 equiv) in toluene (∼10 mL). Both solutions were combined, and the resulting reaction solution was heated to 70 °C for 3 days. Then it was cooled down to room temperature and 1 M HCl (∼30 mL) was added. The phases were separated, and the organic phase was extracted with Et_2O (3 × ∼20 mL). The combined organic phases were washed with brine (∼20 mL) and H_2O (∼20 mL) and dried with $MgSO_4$, and then all volatiles were removed *in vacuo*. The obtained crude product was purified by flash chromatography (SiO_2, *n*-pentane: dichloromethane = 4:1) to give compound **2** as a red-brown oil (468 mg, 1.4 mmol, 84%). Anal. Calcd for $C_{19}H_{25}NSi_2$: C, 70.52 H, 7.79 N, 4.33. Found: C, 71.03 H, 7.78 N, 4.24. IR[ATR]: $\tilde{\nu}$ [cm^{-1}] = 2959 (m), 2899 (w), 2361 (w), 2314 (w), 2145 (s), 1465 (m), 1403 (w), 1367 (m), 1329 (w), 1247 (s), 1205 (w), 1153 (w), 1117 (w), 1036 (w), 927 (m), 837 (s), 785 (s), 740 (s), 725 (s), 689 (m), 658 (m), 632 (m). ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.65 (m, 1H, 4-H), 7.31 (m, 1H, 6-H), 7.29 (m, 1H, 7-H), 7.19 (m, 1H, 5-H), 3.79 (s, 3H, NCH_3), 0.34 (s, $^2J_{SiH}$ = 7.1 Hz, 9H, $^2SiCH_3$), 0.31 (s, $^2J_{SiH}$ = 7.2 Hz, 9H, $^3SiCH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 136.7 (C7a), 128.1 (C3a), 126.7 (C2), 124.6 (C6), 121.4 (C5), 120.5 (C4), 110.2 (C7), 106.3 (^{2}≡CSi), 103.7 (C3), 99.6 (^{3}≡CSi), 98.2, 94.6 (≡C), 31.4 (NCH_3), 0.4 ($^1J_{SiC}$ = 56.5 Hz, $^3SiCH_3$), −0.1 ($^1J_{SiC}$ = 56.2 Hz, $^2SiCH_3$). ^{29}Si{DEPT} NMR (119 MHz, CD_2Cl_2, 299 K): δ = −16.3 (^{2}Si), −18.1 (^{3}Si). $^1H\{^1H\}$ TOCSY (600 MHz, CD_2Cl_2, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 7.65/7.31, 7.29, 7.19 (4-H/6-H, 7-H, 5-H). $^1H\{^1H\}$ NOE (600 MHz, CD_2Cl_2, 299 K) [selected experiment]: $\delta^1H_{irr}/\delta^1H_{res}$ = 3.79/7.29, 0.34 (NCH_3/7-H, $^2SiCH_3$). ^{1}H,^{13}C GHSQC (600 MHz/151 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{13}C$ = 7.65/120.5 (C4), 7.31/124.6 (C6), 7.29/110.2 (C7), 7.19/121.4 (C5), 3.79/31.4 (NCH_3), 0.34/−0.1 ($^2SiCH_3$), 0.31/0.4 ($^3SiCH_3$). ^{1}H,^{13}C GHMBC (600 MHz/151 MHz CD_2Cl_2, 299 K) [selected traces]: $\delta^1H/\delta^{13}C$ = 7.65/136.7, 124.6, 103.7 (4-H/C7a, C6, C3), 7.29/128.1, 121.4 (7-H/C3a, C5), 3.79/136.7, 126.7 (NCH_3/C7a, C2), 0.34/106.3, −0.1 ($^2SiCH_3$/^{2}≡CSi, $^2SiCH_3$), 0.31/99.6, 0.4 ($^3SiCH_3$/^{3}≡CSi, $^3SiCH_3$). ^{1}H,^{29}Si GHMQC (600 MHz/119 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{29}Si$ = 0.34/−16.3 ($^2SiCH_3$), 0.31/−18.1 ($^3SiCH_3$).

Generation of Compound 3. *Characterization of Compound 3 (NMR).* 2,3-Bis(trimethylsilyl)ethynyl)-1-methylindole (**2**, 33.3 mg, 0.1 mmol, 1 equiv) in CD_2Cl_2 (∼1 mL) was added to $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol, 1 equiv). The resulting dark-red/black reaction solution was flame-sealed in an NMR tube and immediately investigated by NMR experiments, which revealed complete conversion to the mono-1,1-carboboration product **3**. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.47 (br d, $^3J_{HH}$ = 8.1 Hz, 1H, 4-H), 7.20 (m, 1H, 6-H), 7.16 (m, 1H, 7-H), 7.06 (m, 1H, 5-H), 3.69 (s, 3H, NCH_3), 0.33 (s, $^2J_{SiH}$ = 7.0 Hz, 9H, ≡$SiCH_3$), 0.05 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $^=$$SiCH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 165.4 (=CSi), 145.3 (br, =CB)^t, 137.0 (C7a), 126.0 (C3a), 123.7 (C6), 122.8 (C3), 121.2 (br, C4), 120.1 (C5), 118.9 (C2), 109.6 (C7), 104.8 ($^1J_{SiC}$ = 81.1 Hz, ≡CSi), 95.5 (≡C), 30.9 (NCH_3), 1.4 ($^1J_{SiC}$ = 52.0 Hz, $^=$$SiCH_3$), −0.4 ($^1J_{SiC}$ = 57.5 Hz, $^=$$SiCH_3$), [$C_6F_5$ not listed; ^{t} tentatively assigned]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = 63.8 ($\nu_{1/2}$ ∼ 2000 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −125.6 (m, 4F, *o*-BC_6F_5), −134.8, −135.8 (each br, each 1F, *o*-C_6F_5), −145.9 (tm, $^3J_{FF}$ = 20.3 Hz, 2F, *p*-BC_6F_5), −156.1 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-C_6F_5), −161.2 (m, 4F, *m*-BC_6F_5), −163.5, −163.7 (each br, each 1F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}(BC_6F_5)$ = 15.3]. ^{29}Si{DEPT} NMR (119 MHz, CD_2Cl_2, 299 K): δ = −1.1 ($\nu_{1/2}$ ∼ 2 Hz, $^=$Si), −16.9 ($\nu_{1/2}$ ∼ 2 Hz, ≡Si). $^1H\{^1H\}$ TOCSY (600 MHz, CD_2Cl_2, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 7.47/7.20, 7.16, 7.06 (4-H/6-H, 7-H, 5-H). $^1H\{^1H\}$ NOE (600 MHz, CD_2Cl_2, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 7.47/7.06, 0.05 (4-H/5-H, $^=$$SiCH_3$), 3.69/7.16 ($NCH_3$/7-H). ^{1}H,^{13}C GHSQC (600 MHz/151 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{13}C$ = 7.47/121.2 (C4), 7.20/123.7 (C6), 7.16/109.6 (C7), 7.06/120.1 (C5), 3.69/30.9 (NCH_3), 0.33/−0.4 ($^=$$SiCH_3$), 0.05/1.4 ($^=$$SiCH_3$). ^{1}H,^{13}C GHMBC (600 MHz/151 MHz, CD_2Cl_2, 299 K) [selected traces]: $\delta^1H/\delta^{13}C$ = 7.47/137.0, 123.7, 122.8 (4-H/C7a, C6, C3), 7.16/126.0, 120.1 (7-H/C3a, C5), 3.69/137.0, 118.9 (NCH_3/C1, C8), 0.33/104.8, −0.4 ($^=$$SiCH_3$/≡CSi, $^=$$SiCH_3$), 0.05/165.4, 1.4 ($^=$$SiCH_3$/=CSi, $^=$$SiCH_3$). ^{1}H,^{29}Si GHMQC (600 MHz/119 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{29}Si$ = 0.33/−1.1 ($^=$$SiCH_3$/$^=$Si), 0.05/−16.9 ($^=$$SiCH_3$/≡Si).

X-ray Crystal Structure Analysis of Compound 3. After addition of $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol, 1 equiv) to a solution of 2,3-bis(trimethylsilyl)ethynyl)-1-methylindole (**2**, 33.3 mg, 0.1 mmol, 1 equiv), the solution turned dark-red/black immediately, and besides that, crystallization of compound **3** was observed in the sample. Single crystals suitable for the X-ray crystal structure analysis were directly obtained from this NMR sample after 1 day at room temperature. Formula $C_{37}H_{25}BF_{15}NSi_2$, M = 835.57, colorless crystal, 0.20 × 0.05 × 0.03 mm, a = 10.4022(6) Å, b = 13.0301(8) Å, c = 14.7160(8) Å, α = 109.281(4), β = 95.936(5), γ = 93.636(5)°, V = 1862.5(2) Å^3, ρ_{calc} = 1.490 g cm^{-3}, μ = 1.822 mm^{-1}, empirical absorption correction (0.712 ≤ T ≤ 0.947), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 40 525 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 6146 independent (R_{int} = 0.077) and 4410 observed reflections [$I > 2\sigma(I)$], 512 refined parameters, R = 0.047, wR^2 = 0.120, max. (min.) residual electron density 0.19 (−0.27) e·Å^{-3}; hydrogen atoms were calculated and refined as riding atoms.

Preparation of Compound 6. A solution of compound **2** (129 mg, 0.4 mmol, 1 equiv) in toluene (∼2 mL) was combined with a solution of $B(C_6F_5)_3$ (205 mg, 0.4 mmol, 1 equiv) in toluene (∼2 mL) at room temperature. The resulting dark-red/black solution was heated at 110 °C for 7 days. Then all volatiles were removed *in vacuo* at room temperature, and the obtained residue was dissolved in *n*-pentane (∼5 mL). Immediately after the addition of the solvent, it was removed again *in vacuo* (this procedure was repeated one more time to remove toluene). Then *n*-pentane (∼30 mL) was added to the residue. The resulting suspension was filtered through Celite, the solvent of the filtrate was removed *in vacuo*, and the obtained residue was washed with *n*-pentane (3 × ∼3 mL). Drying of the residue *in vacuo* gave compound **6** (170 mg, 0.2 mmol, 51%) as a yellow-green solid. Anal. Calcd for $C_{37}H_{25}BF_{15}NSi_2$: C, 53.19; H, 3.02; N, 1.68. Found: C, 53.20; H, 2.78; N, 1.65. Further workup of the washing solution gave another crop of products (Total yield: 218 mg, 0.26 mmol, 65%).

Characterization of Compound 6 (NMR). Compound **2** (33.3 mg, 0.1 mmol, 1 equiv) was dissolved in tol-d_8 (∼1 mL), and $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol, 1 equiv) was added. The resulting dark-red/black solution was heated at 110 °C for 7 days, then cooled down to room temperature, and investigated by NMR spectroscopy. ^{1}H NMR (600 MHz, tol-d_8, 299 K): δ = 8.19 (dm, $^3J_{HH}$ = 8.1 Hz, 1H, 5-H), 7.32 (m, 1H, 7-H), 7.13 (m, 1H, 6-H), 7.00 (dm, $^3J_{HH}$ = 8.2 Hz, 1H, 8-H), 3.09 (s, 3H, NCH_3), 0.25 (s, 9H, $^4SiCH_3$), −0.09 (s, 9H, $^1SiCH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, tol-d_8, 299 K): δ = 150.2 (C9a), 145.6 (C8a), 142.9 (br, C3)^t, 140.4 (C4), 131.4 (C4a), 129.3 (C2)^t 127.1 (C7), 126.0 (C5), 123.9 (C4b), 123.8 (br, C1), 119.9 (C6), 110.7 (C8), 36.2 (NCH_3), 3.0 (br, $^4SiCH_3$), 2.4 ($^1J_{SiC}$ = 53.4 Hz, $^1SiCH_3$), [C_6F_5 not listed; ^{t} tentative assignment]. $^{11}B\{^1H\}$ NMR (192 MHz, tol-d_8, 299 K): δ = 60.6 ($\nu_{1/2}$ ∼ 2500 Hz). ^{19}F NMR (564 MHz, tol-d_8, 299 K): δ = −122.2, −125.7 (each 2F, *o*), −141.7, −146.8 (each 1F, *p*), −161.5 (4F, *m*) (each br, BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 19.9, 14.8], −136.2 (m, 2F, *o*), −153.8 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*), −162.7 (br, 2F, *m*) (C_6F_5)[$\Delta\delta^{19}F_{m,p}$

DOI: 10.1021/jo502753s
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= 8.9]. ^{29}Si{DEPT} NMR (119 MHz, tol-d_8, 299 K): δ = −4.4 ($\nu_{1/2}$ ∼ 2 Hz, ^{4}Si), −6.2 ($\nu_{1/2}$ ∼ 2 Hz, ^{1}Si). ^{1}H{^{1}H} TOCSY (600 MHz, tol-d_8, 299 K) [selected experiment]: $\delta^1H_{irr}/\delta^1H_{res}$ = 8.19/7.32, 7.13, 7.00 (5-H/7-H, 6-H, 8-H). ^{1}H{^{1}H} NOE (600 MHz, tol-d_8, 299 K) [selected experiment]: $\delta^1H_{irr}/\delta^1H_{res}$ = 3.09/7.00, −0.10 (NCH_3/8-H, $^1SiCH_3$). ^{1}H,^{13}C GHSQC (600 MHz/151 MHz, tol-d_8, 299 K): $\delta^1H/\delta^{13}C$ = 8.19/126.0 (C5), 7.32/127.1 (C7), 7.13/119.9 (C6), 7.00/110.7 (C8), 3.09/36.2 (NCH_3), 0.25/3.0 ($^4SiCH_3$), −0.09/2.4 ($^1SiCH_3$). ^{1}H,^{13}C GHMBC (600 MHz/151 MHz, tol-d_8, 299 K) [selected traces]: $\delta^1H/\delta^{13}C$ = 8.19/145.6, 131.4, 127.1 (5-H/C8a, C4a, C7), 7.00/123.9, 119.9 (8-H/C4b, C6), 3.09/150.2, 145.6 (NCH_3/C9a, C8a), 0.25/140.4, 3.0 ($^4SiCH_3$/C4, $^4SiCH_3$), −0.09/123.8, 2.4 ($^1SiCH_3$/C1, $^1SiCH_3$). ^{1}H,^{29}Si GHMQC (600 MHz/119 MHz, tol-d_8, 299 K): $\delta^1H/\delta^{29}Si$ = 0.25/−4.4 ($^4SiCH_3$), −0.09/−6.2 ($^1SiCH_3$). ^{19}F,^{19}F GCOSY (470 MHz/470 MHz, tol-d_8, 299 K) [selected trace]: $\delta^{19}F/\delta^{19}F$ = −162.7/−136.2, −153.9 (m-C_6F_5/o-C_6F_5, p-C_6F_5). ^{1}H,^{19}F HOESY (600 MHz/564 MHz, tol-d_8, 299 K) [selected traces]: $\delta^1H/\delta^{19}F$ = 0.25/−161.5 ($^4SiCH_3$/m-BC_6F_5), −0.09/−136.2, −162.7 ($^1SiCH_3$/o-C_6F_5, m-C_6F_5). ^{19}F,^{1}H HOESY (564 MHz/600 MHz, tol-d_8, 299 K) [selected traces]: $\delta^{19}F/\delta^1H$ = −136.2/−0.09 (o-C_6F_5/$^1SiCH_3$), −161.5/0.25 (m-BC_6F_5/$^4SiCH_3$).

X-ray Crystal Structure Analysis of Compound ***6***. A solution of compound **2** (64.5 mg, 0.2 mmol, 1 equiv) in toluene (∼2 mL) was combined with a solution of $B(C_6F_5)_3$ (102 mg, 0.2 mmol, 1 equiv) in toluene (∼2 mL) at room temperature. The resulting dark-red/black solution was heated at 110 °C for 7 days. Then all volatiles were removed *in vacuo* at room temperature and the obtained residue was dissolved in *n*-pentane (∼5 mL). Immediately after the addition of the solvent, it was removed again *in vacuo* (this procedure was repeated one more time to remove toluene). The residue was taken up in CH_2Cl_2 layered with *n*-pentane and stored at −40 °C for several days, which gave crystals of compound **6** suitable for the X-ray crystal structure analysis. Formula $C_{37}H_{25}BF_{15}NSi_2$, M = 835.57, yellow crystal, 0.30 × 0.07 × 0.03 mm, a = 19.0787(6) Å, b = 12.0494(2) Å, c = 34.2690(12) Å, β = 111.900(2)°, V = 7309.5(4) Å^3, ρ_{calc} = 1.519 g cm^{-3}, μ = 1.856 mm^{-1}, empirical absorption correction (0.605 ≤ T ≤ 0.946), Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 78 186 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 12 742 independent (R_{int} = 0.066) and 9507 observed reflections [$I > 2\sigma(I)$], 1023 refined parameters, R = 0.053, wR^2 = 0.143, max. (min.) residual electron density 0.43 (−0.26) e·Å^{-3}; hydrogen atoms were calculated and refined as riding atoms.

Preparation of Compound 7. A solution of compound **2** (129 mg, 0.4 mmol, 1 equiv) in toluene (∼2 mL) and a solution of $B(C_6F_5)_3$ (205 mg, 0.4 mmol, 1 equiv) in toluene (∼2 mL) were combined at room temperature and then stirred at 110 °C for 7 days. After cooling to room temperature, the solvent was removed *in vacuo* and *n*-pentane (∼5 mL) was added and directly removed again *in vacuo*. Then THF (∼4 mL) was added to the obtained residue, and subsequently NaOH (0.2 mL, 3 M) and H_2O_2 (30%, 0.14 mL) were added. The resulting mixture was stirred for 2 h at room temperature; then H_2O (∼10 mL), Na_2SO_3 (10%, ∼50 mL), and Et_2O (∼50 mL) were added. The phases were separated and the aqueous phase was extracted with Et_2O (∼20 mL) two more times. The combined organic phases were washed with brine (∼50 mL) and H_2O (∼50 mL) and dried with $MgSO_4$, and the solvent was removed *in vacuo*. The obtained residue was purified by flash chromatography (SiO_2, *n*-pentane:dichloromethane = 1:1), and the crude product was washed with *n*-pentane (3 × ∼2 mL) to give compound **7** (91 mg, 0.21 mmol, 52%) as a colorless solid. Single crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a solution of **7** in dichloromethane at room temperature. Anal. Calcd for $C_{22}H_{18}F_5NOSi$: C, 60.68; H, 4.17; N, 3.22. Found: C, 60.12; H, 4.14; N, 2.94. ^{1}H NMR (600 MHz, TDF, 299 K): δ = 8.35 (s, 1H, OH), 7.97 (dm, $^3J_{HH}$ = 7.8 Hz, 1H, 5-H), 7.57 (s, 1H, 4-H), 7.42 (m, 2H, 7-H, 8-H), 7.15 (m, 1H, 6-H), 3.84 (s, 3H, NCH_3), 0.21 (s, $^2J_{SiH}$ = 6.3 Hz, 9H, $SiCH_3$). ^{13}C{^{1}H} NMR (151 MHz, TDF, 299 K): δ = 149.9 (C3), 146.6 (C8a), 146.2 (dm, $^1J_{FC}$ ∼ 240 Hz, C_6F_5), 145.0 (C9a), 141.6 (dm, $^1J_{FC}$ ∼ 250 Hz, C_6F_5), 138.6 (dm, $^1J_{FC}$ ∼ 250 Hz, C_6F_5), 127.6 (C4a), 127.3 (C7), 124.5 (C4b), 124.2 ($^1J_{SiC}$ = 62.6 Hz, C1), 120.6 (C5), 120.3 (C6), 119.4 (C2), 117.2 (m, i-C_6F_5), 111.3 (C8), 107.9 (C4), 37.2 (NCH_3), 2.3 ($^1J_{SiC}$ = 53.5 Hz, $SiCH_3$). ^{19}F NMR (564 MHz, TDF, 299 K): δ = −139.5 (m, 2F, o-C_6F_5), −158.8 (t, $^3J_{FF}$ = 20.8 Hz, m-C_6F_5), −166.2 (m, 2F, o-C_6F_5). ^{29}Si{DEPT} NMR (119 MHz, TDF, 299 K): δ = −5.9 ($\nu_{1/2}$ ∼ 2 Hz). ^{1}H{^{1}H} TOCSY (600 MHz, TDF, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 7.97/7.42, 7.15 (5-H/(7-H, 8-H), 6-H). ^{1}H{^{1}H} NOE (600 MHz, TDF, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 8.35/7.57 (OH/4-H), 7.57/8.35, 7.97 (4-H/OH, 5-H), 3.84/7.42, 0.21 (NCH_3/8-H, $SiCH_3$). ^{1}H,^{13}C GHSQC (600 MHz/151 MHz, TDF, 299 K): $\delta^1H/\delta^{13}C$ = 7.97/120.6 (C5), 7.57/107.9 (C4), 7.42/127.3 (C7), 7.42/111.3 (C8), 7.15/120.3 (C6), 3.82 (NCH_3), 0.21/2.3 ($SiCH_3$). ^{1}H,^{13}C GHMBC (600 MHz/151 MHz, TDF, 299 K): $\delta^1H/\delta^{13}C$ = 8.35/149.9, 119.4, 107.9 (OH/C3, C2, C4), 7.97/146.6, 127.6, 127.3 (5-H/C8a, C4a, C7), 7.57/149.9, 145.0, 124.5, 119.4 (4-H/C3, C9a, C4b, C2), 7.42/146.6, 120.6 (7-H/C8a, C5), 7.42/124.5, 120.3 (8-H/C4b, C6), 7.15/111.3 (6-H/C8), 3.84/146.6, 145.0 (NCH_3/ C8a, C9a), 0.21/124.2, 2.3 ($SiCH_3$/ C1, $SiCH_3$).

X-ray Crystal Structure Analysis of Compound 7. Formula $C_{22}H_{18}F_5NOSi$, M = 435.46, colourless crystal, 0.35 × 0.20 × 0.12 mm, a = 13.0052(2), b = 7.3635(1), c = 20.9912(4) Å, β = 101.869(1)°, V = 1967.2(1) Å3, ρ_{calc} = 1.470 gcm^{-3}, μ = 0.180 mm^{-1}, empirical absorption correction (0.939 ≤ T ≤ 0.978), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 14 562 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.67 Å^{-1}, 4746 independent (R_{int} = 0.032) and 4129 observed reflections [$I>2\sigma(I)$], 279 refined parameters, R = 0.044, wR^2 = 0.122, max. (min.) residual electron density 0.27 (−0.26) e.Å^{-3}, the hydrogen at O1 atom was refined freely; others were calculated and refined as riding atoms.

Preparation of Compounds 10a,b. A solution of 2,3-bis-(trimethylsilylethynyl)thiophene (**9**, 55.3 mg, 0.2 mmol, 1 equiv) in toluene (∼2 mL) and a solution of $B(C_6F_5)_3$ (102 mg, 0.2 mmol) in toluene (∼2 mL) were combined at room temperature and then heated at 110 °C for 2 days. After the reaction mixture was cooled to room temperature, all volatiles were removed *in vacuo* and *n*-pentane (∼5 mL) was added and directly removed *in vacuo* (this procedure was repeated one more time). The resulting yellow solid was washed with *n*-pentane (3 × 2 mL), dried *in vacuo*, and identified as a mixture of the regioisomers **10a,b** (85 mg, 0.11 mmol, 55%, **10a**:**10b** ∼ 5:1, ^{1}H). Workup of the washing solution gave some additional product (total yield: 119 mg, 0.15 mmol, 75%, **10a**:**10b** ∼ 5:1). Anal. Calcd for $C_{32}H_{20}BF_{15}SSi_2$: C, 48.74; H, 2.56. Found: C, 48.69; H, 2.63.

Characterization of Compounds ***10a,b*** *(NMR).* 2,3-Bis(trimethylsilylethynyl)thiophene (**9**, 27.7 mg, 0.1 mmol, 1 equiv) was dissolved in tol-d_8 (∼1 mL), and $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol, 1 equiv) was added. The solution was transferred into a NMR tube and flame-sealed *in vacuo*. The resulting solution was heated to 110 °C for 2 days and then investigated by NMR spectroscopy. The NMR experiments revealed a ratio of **10a**:**10b** ∼ 5:1. **10a**: ^{1}H NMR (600 MHz, tol-d_8, 299 K): δ = 7.40 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 3-H), 7.02 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 2-H), 0.20 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $^7SiCH_3$), −0.12 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $^4SiCH_3$). ^{13}C{^{1}H} NMR (151 MHz, tol-d_8, 299 K): δ = 147.8, 144.2 (C3a, C7a), 138.0 (C7), 137.3 (C4), 127.8 (C2), 125.2 (C3), 1.4 ($^1J_{SiC}$ = 52.4 Hz, $^7SiCH_3$), 1.0 ($^1J_{SiC}$ = 52.9 Hz, $^4SiCH_3$), [C_6F_5 not listed, C5, C6 not observed]. ^{11}B{^{1}H} NMR (192 MHz, tol-d_8, 299 K): δ = 63.0 ($\nu_{1/2}$ ∼2000 Hz). ^{19}F NMR (470 MHz, tol-d_8, 273 K): δ = −119.6 (o), −124.3 (o'), −139.1 (p), −160.6 (m), −161.3 (m')(each m, each 1F, BC_6F_5[a])[$\Delta\delta^{19}F_{m,p}$ = 21.5, $\Delta\delta^{19}F_{m',p}$ = 22.2], −123.7 (o), −128.8 (o'), −145.6 (p), −159.6 (m), −162.7 (m')(each m, each 1F, BC_6F_5[b])[$\Delta\delta^{19}F_{m,p}$ = 14.0, $\Delta\delta^{19}F_{m',p}$ = 17.0], −136.1 (o), −138.9 (o'), −154.0 (p), −161.3 (m'), −164.2 (m)(each m, each 1F, C_6F_5). ^{29}Si{DEPT} NMR (119 MHz, tol-d_8, 299 K): δ = −2.5 ($\nu_{1/2}$ ∼ 2 Hz, ^{7}Si), −4.4 ($\nu_{1/2}$ ∼ 2 Hz ^{4}Si). ^{1}H{^{1}H} NOE (500 MHz, tol-d_8, 273 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 7.37/6.97, −0.13 (3-H/2-H, $^4SiCH_3$), −0.13/7.38 ($^4SiCH_3$/3-H). ^{1}H,^{13}C GHSQC (500 MHz/126 MHz, tol-d_8, 273 K): $\delta^1H/\delta^{13}C$ = 7.37/125.1 (C3), 6.97/127.8 (C2), 0.20/1.4 ($^7SiCH_3$), −0.13/1.0 ($^4SiCH_3$). ^{1}H,^{13}C GHMBC (500 MHz/126 MHz, tol-d_8, 273 K): $\delta^1H/\delta^{13}C$ = 7.37/147.6, 144.1,

DOI: 10.1021/jo502753s
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127.8 (3-H/(C3a, C7a), C2), 6.97/147.6, 144.1, 125.1 (2-H/(C3a, C7a), C3), 0.21/137.8, 1.4 ($^7SiCH_3$/ C7, $^7SiCH_3$), −0.13/137.1, 1.0 ($^4SiCH_3$/C4, $^4SiCH_3$). ^{19}F,^{19}F GCOSY (470 MHz/470 MHz, tol-d_8, 273 K) [selected traces]: $\delta^{19}F/\delta^{19}F$ = −159.6/−123.7, −145.6 (*m*-$BC_6F_5^b$/*o*-$BC_6F_5^b$, *p*-$BC_6F_5^b$), −160.6/−119.6, −139.1 (*m*-$BC_6F_5^a$/*o*-$BC_6F_5^a$, *p*-$BC_6F_5^a$), −161.3/−124.3, −139.1 (*m*′-$BC_6F_5^a$/*o*-$BC_6F_5^a$, *p*-$BC_6F_5^a$), −161.3/−138.9, −154.0 (*m*′-C_6F_5/*o*′-C_6F_5, *p*-C_6F_5), −162.7/−128.8, −145.6 (*m*′-$BC_6F_5^b$/*o*′-$BC_6F_5^b$, *p*-$BC_6F_5^b$), −164.2/−136.1, −154.0 (*m*-C_6F_5/*o*-C_6F_5, *p*-C_6F_5). ^1H,^{19}F HOESY (600 MHz/564 MHz, [tol-d_8, 273 K) [selected traces]: $\delta^1H/\delta^{19}F$ = 0.21/−123.7, −124.3 ($^7SiCH_3$/*o*-$BC_6F_5^b$, *o*′-$BC_6F_5^b$), −0.13/−136.1, −138.9 ($^4SiCH_3$/ *o*-C_6F_5, *o*′-C_6F_5). ^{19}F,^1H HOESY (564 MHz/600 MHz, tol-d_8, 273 K) [selected traces]: $\delta^{19}F/\delta^1H$ = −123.7/0.21 (*o*-$BC_6F_5^b$/$^7SiCH_3$), −124.3/0.21 (*o*′-$BC_6F_5^a$/$^7SiCH_3$), −136.1/−0.13 (*o*-C_6F_5/$^4SiCH_3$), −138.9/−0.12 (*o*′-C_6F_5/$^4SiCH_3$). **10b**: ^1H NMR (600 MHz, tol-d_8, 299 K): δ = 7.40 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 3-H), 7.02 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 2-H), 0.07 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $^4SiCH_3$), 0.01 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $^7SiCH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, tol-d_8, 299 K): δ = 147.7, 144.1 (C3a, C7a), 139.4 (C4), 136.0 (C7), 127.7 (C2), 124.8 (C3), 2.3 ($^1J_{SiC}$ = 52.6 Hz, $^4SiCH_3$), 0.7 ($^1J_{SiC}$ = 53.2 Hz, $^7SiCH_3$), [C_6F_5not listed, C5, C6 not observed]. $^{11}B\{^1H\}$ NMR (192 MHz, tol-d_8, 299 K): δ = 63.0 ($\nu_{1/2}$ ∼2000 Hz). ^{19}F NMR (470 MHz, tol-d_8, 273 K): δ = −119.4 (*o*), −124.3 (*o*′), −139.1 (*p*), −160.7 (*m*), −161.1 (*m*′) (each 1F, each m, $BC_6F_5^a$)[$\Delta\delta^{19}F_{m,p}$ = 21.6, $\Delta\delta^{19}F_{m',p}$ = 22.0], −123.8 (m, *o*), −128.8 (m, *o*′), −145.7 (t, $^3J_{FF}$ = 20.9 Hz, *p*), −159.6 (m, *m*), −162.7 (m, *m*′) (each 1F, $BC_6F_5^b$)[$\Delta\delta^{19}F_{m,p}$ = 13.9, $\Delta\delta^{19}F_{m',p}$ = 17.0], −135.3 (m, *o*), −138.3 (m, *o*′), −153.7 (t, $^3J_{FF}$ = 20.9 Hz, *p*), −161.1 (m, *m*′), −164.0 (m, *m*)(each 1F, C_6F_5). $^{29}Si\{DEPT\}$ NMR (119 MHz, tol-d_8, 299 K): δ = −2.2 ($\nu_{1/2}$ ∼ 2 Hz, ^7Si), −4.0 ($\nu_{1/2}$ ∼ 2 Hz, ^4Si). $^1H\{^1H\}$ NOE (500 MHz, tol-d_8, 273 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 7.38/6.97, 0.07 (3-H/2-H, $^4SiCH_3$), 0.07/7.38 ($^4SiCH_3$/3-H). ^1H,^{13}C GHSQC (500 MHz/126 MHz, tol-d_8, 273 K): $\delta^1H/\delta^{13}C$ = 7.38/125.0 (C3), 6.97/127.7 (C2), 0.07/2.0 ($^4SiCH_3$), 0.01/0.5 ($^7SiCH_3$).

Preparation of Compounds 11a,b. A solution of compound **9** (111 mg, 0.4 mmol, 1 equiv) in toluene (∼2 mL) and a solution of $B(C_6F_5)_3$ (205 mg, 0.4 mmol, 1 equiv) in toluene (∼2 mL) were combined at room temperature and then stirred at 110 °C for 2 days. After cooling to room temperature, all volatiles were removed *in vacuo*. Then *n*-pentane (∼5 mL) was added to the residue and directly removed again *in vacuo*. Subsequently THF (∼4 mL) was added to the obtained residue; then 3 M NaOH (0.2 mL) and H_2O_2 (30%, 0.14 mL) were added and the resulting mixture was stirred for 2 h at room temperature; then H_2O (∼10 mL), Na_2SO_3 (10%, ∼50 mL), and Et_2O (∼50 mL) were added. The phases were separated and the aqueous phase was extracted with Et_2O (∼20 mL) two more times. The combined organic phases were washed with brine (∼50 mL) and H_2O (∼50 mL) and dried with $MgSO_4$, and the solvent was removed *in vacuo*. The residue was purified by flash chromatography (SiO_2, *n*-pentane:dichloromethane = 8:1) to give compounds **11a,b** (107 mg, 0.23 mmol, 58%) as a slightly yellow oil, which crystallized at −40 °C to a slightly yellow solid. Single crystals of **11a** suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a solution of **11a,b** (12:1, from ^1H NMR integration) in *n*-pentane at 8 °C. Anal. Calcd for $C_{20}H_{21}F_5SOSi_2$: C, 52.15 H, 4.60. Found: C, 53.38 H, 4.88. ***11a***: ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.59 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 3-H), 7.43 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 2-H), 4.93 (s, 1H, OH), 0.54 (s, $^2J_{SiH}$ = 6.8 Hz, 9H, $^7SiCH_3$), 0.15 (s, $^2J_{SiH}$ = 6.3 Hz, 9H, $^4SiCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 154.6 (C6), 148.6, 138.2 (C3a, C7a), 145.6 (dm, $^1J_{FC}$ ∼ 240 Hz, C_6F_5), 141.7 (dm, $^1J_{FC}$ ∼ 250 Hz, C_6F_5), 138.9 (C4), 138.4 (dm, $^1J_{FC}$ ∼ 250 Hz, *m*-C_6F_5), 124.9 (C3), 124.5 (C2), 118.8 ($^1J_{SiC}$ = 60.3 Hz, C7), 116.9 (m, C5), 113.8 (m, *i*-C_6F_5), 1.1 ($^1J_{SiC}$ = 53.1 Hz, $^4SiCH_3$), 0.9 ($^1J_{SiC}$ = 53.1 Hz, $^7SiCH_3$). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −139.1 (m, 2F, *o*-C_6F_5), −154.6 (tm, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), −162.6 (m, 2F, *m*-C_6F_5). $^{29}Si\{DEPT\}$ NMR (99 MHz, CD_2Cl_2, 299 K): δ = −3.0 ($\nu_{1/2}$ ∼ 2 Hz, ^7Si), −3.7 ($\nu_{1/2}$ ∼ 2 Hz, ^4Si). $^1H\{^1H\}$ NOE (500 MHz, CD_2Cl_2, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 7.59/7.43, 0.15 (3-H/2-H, $^4SiCH_3$), 4.93/0.54 (OH/$^7SiCH_3$). ^1H,^{13}C GHSQC (500 MHz/126 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{13}C$ = 7.59/124.9 (C3), 7.43/124.5 (C2), 0.54/0.9 ($^7SiCH_3$), 0.15/1.1 ($^4SiCH_3$). ^1H,^{13}C GHMBC (500 MHz/126 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{13}C$ = 7.59/[148.6, 138.2], 124.5 (3-H/[C3a, C7a], C2), 7.43/[148.6, 138.2], 124.9 (2-H/[C3a, C7a], C3), 4.93/154.6, 118.8, 116.9 (OH/C6, C7, C5), 0.54/118.8, 0.9 ($^7SiCH_3$/C7, $^7SiCH_3$), 0.15/138.9, 1.1 ($^4SiCH_3$/C4, $^4SiCH_3$). ^1H,^{29}Si GHMQC (500 MHz/99 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{29}Si$ = 0.54/−3.0 ($^7SiCH_3$/^7Si), 0.15/−3.7 ($^4SiCH_3$/^4Si). **11b**: ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.63 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 2-H), 7.56 (d, $^3J_{HH}$ = 5.8 Hz, 1H, 3-H), 5.10 (s, 1H, OH), 0.52 (s, 9H, $^4SiCH_3$), 0.21 (s, 9H, $^7SiCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 155.5 (C5), 145.5, 139.2 (C3a, C7a), 137.6 (C7), 128.5 (C2), 124.4 (C3), 118.8 (C4), 117.0 (C6), 1.6 ($^4SiCH_3$), 0.6 ($^7SiCH_3$). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −139.1 (m, 2F, *o*-C_6F_5), −155.0 (tm, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-C_6F_5), −163.0 (m, 2F, *m*-C_6F_5). $^{29}Si\{DEPT\}$ NMR (99 MHz, CD_2Cl_2, 299 K): δ = −1.9 ($\nu_{1/2}$ ∼ 2 Hz, ^7Si), −5.8 ($\nu_{1/2}$ ∼ 2 Hz, ^4Si). $^1H\{^1H\}$ NOE (500 MHz, CD_2Cl_2, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 5.10/0.52 (OH/$^4SiCH_3$), 0.52/7.56, 5.10 ($^4SiCH_3$/3-H, OH). ^1H,^{13}C GHSQC (500 MHz/126 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{13}C$ = 7.63/128.5 (C2), 7.56/124.4 (C3), 0.52/1.6 ($^4SiCH_3$), 0.21/0.6 ($^7SiCH_3$). ^1H,^{13}C GHMBC (500 MHz/126 MHz, CD_2Cl_2, 299 K) [selected traces]: $\delta^1H/\delta^{13}C$ = 7.56/[145.5, 139.2], 128.5 (3-H/[C3a, C7a], C2), 5.10/155.5, 118.8, 117.0 (OH/C5, C4, C6), 0.52/118.8, 1.6 ($^4SiCH_3$/C4, $^4SiCH_3$), 0.21/137.6, 0.6 ($^7SiCH_3$/C7, $^7SiCH_3$). ^1H,^{29}Si GHMQC (500 MHz/99 MHz, CD_2Cl_2, 299 K): $\delta^1H/\delta^{29}Si$ = 0.52/−5.8 ($^4SiCH_3$/^4Si), 0.21/−1.9 ($^7SiCH_3$/^7Si).

*X-Ray Crystal Structure Analysis of Compound **11a**.* Formula $C_{20}H_{21}F_5OSSi_2$, M = 460.61, colorless crystal, 0.15 × 0.07 × 0.03 mm, a = 24.4029(8) Å, b = 6.2523(2) Å, c = 29.3312(10) Å, β = 102.229(2)°, V = 4373.6(2) Å^3, ρ_{calc} = 1.399 g cm^{-3}, μ = 2.838 mm^{-1}, empirical absorption correction (0.675 ≤ T ≤ 0.919), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 16 944 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 3832 independent (R_{int} = 0.039) and 3403 observed reflections [$I > 2\sigma(I)$], 272 refined parameters, R = 0.045, wR^2 = 0.132, max. (min.) residual electron density 0.52 (−0.41) e·Å^{-3}; the hydrogen at O1 atom was refined freely, but with distance O−H restraints (DFIX); others were calculated and refined as riding atoms.

Preparation of Compounds 13. A solution of 2,3-bis((trimethylsilyl)ethynyl)pyridine (**12**, 109 mg, 0.4 mmol, 1 equiv) in toluene (∼5 mL) and a solution of $B(C_6F_5)_3$ (205 mg, 0.4 mmol, 1 equiv) in toluene (∼5 mL) were combined at room temperature and then stirred for 30 min. Subsequently the solvent was removed *in vacuo* and *n*-pentane (∼5 mL) was added and immediately removed *in vauco* (this procedure was repeated two times to remove toluene). The obtained colorless solid was dried *in vacuo* to give compound **13** (262 mg, 0.3 mmol, 84%). Single crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of compound **13** at −40 °C. Anal. Calcd for $C_{33}H_{21}BF_{15}NSi_2$: C, 50.59; H, 2.70; N, 1.79. Found: C, 50.62; H, 2.69; N, 1.58.

*X-ray Crystal Structure Analysis of Compound **13**.* Formula $C_{33}H_{21}BF_{15}NSi_2$, M = 783.50, yellow crystal, 0.28 × 0.20 × 0.10 mm, a = 23.8836(7) Å, b = 10.9631(3) Å, c = 29.7545(6) Å, β = 108.263(2)°, V = 7898.4(3) Å^3, ρ_{calc} = 1.407 g cm^{-3}, μ = 1.796 mm^{-1}, empirical absorption correction (0.633 ≤ T ≤ 0.840), Z = 8, monoclinic, space group $P2/c$ (No. 13), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 56 829 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 12 835 independent (R_{int} = 0.066) and 9737 observed reflections [$I > 2\sigma(I)$], 950 refined parameters, R = 0.068, wR^2 = 0.212, max. (min.) residual electron density 0.63 (−0.51) e·Å^{-3}; hydrogen atoms were calculated and refined as riding atoms.

*Characterization of Compounds **13** (NMR).* $B(C_6F_5)_3$ (**9**, 51.2 mg, 0.1 mmol, 1 equiv) was added to a solution of 2,3-bis((trimethylsilyl)ethynyl)pyridine (**12**, 27.2 mg, 0.1 mmol, 1 equiv) in tol-d_8 (∼1 mL). The resulting colorless solution was flame-sealed in a NMR tube and immediately characterized by NMR experiments. ^1H NMR (500 MHz, tol-d_8, 299 K): δ = 8.14 (m, 1H, 6-H), 7.01 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, 4-H), 6.11 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.3 Hz, 1H,

DOI: 10.1021/jo502753s
J. Org. Chem. 2015, 80, 2240−2248

5-H), 0.08 (s, $^2J_{SiH}$ = 7.0 Hz, 9H, $^3SiCH_3$), −0.01 (s, $^2J_{SiH}$ = 7.2 Hz, 9H, $^2SiCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, tol-d_8, 299 K): δ = 146.7 (m, C6), 145.1 (C4), 142.9 (d, J = 3.5 Hz, C2), 128.4 (C3), 122.4 (C5), 120.1 (d, J = 2.8 Hz, $^1J_{SiC}$ = 73.4 Hz, $^2\equiv$CSi), 106.6 ($^3\equiv$CSi, $^1J_{SiC}$ = 77.6 Hz), 98.9 ($^3\equiv$C, $^2J_{SiC}$ = 14.8 Hz), 96.0 (m, $^2\equiv$C), −0.5 ($^1J_{SiC}$ = 56.4 Hz, $^3SiCH_3$), −1.3 ($^1J_{SiC}$ = 57.0 Hz, $^2SiCH_3$), [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (160 MHz, tol-d_8, 299 K): δ = −2.5 ($\nu_{1/2}$ ∼350 Hz). ^{19}F NMR (470 MHz, tol-d_8, 299 K): δ = −126.9 (m, o), −131.8 (m, o'), −154.6 (t, $^3J_{FF}$ = 20.7 Hz, p), −161.3 (m, m'), −162.9 (m, m) (each 1F, BC_6F_5[a])[$\Delta\delta^{19}F_{m,p}$ = 8.3, $\Delta\delta^{19}F_{m',p}$ = 6.7], −128.3 (m, o), −133.6 (m, o'), −155.6 (t, $^3J_{FF}$ = 20.6 Hz, p), −163.2 (m, m), −164.9 (m, m') (each 1F, BC_6F_5[b])[$\Delta\delta^{19}F_{m,p}$ = 7.6, $\Delta\delta^{19}F_{m',p}$ = 9.3], −129.2 (m, o), −133.3 (m, o'), −159.1 (t, $^3J_{FF}$ = 15.9 Hz, p), −164.8 (m, m), −165.7 (m, m') (each 1F, BC_6F_5[c])[$\Delta\delta^{19}F_{m,p}$ = 5.7, $\Delta\delta^{19}F_{m',p}$ = 6.6]. $^{29}Si\{DEPT\}$ NMR (99 MHz, tol-d_8, 299 K): δ = −14.1 ($\nu_{1/2}$ ∼ 2 Hz, ^{2}Si), −16.2 ($\nu_{1/2}$ ∼ 2 Hz, ^{3}Si). $^1H\{^1H\}$ TOCSY (500 MHz, tol-d_8, 299 K) [selected experiment]: $\delta^1H_{irr}/\delta^1H_{res}$ = 8.14/7.01, 6.11 (6-H/4-H, 5-H). $^1H\{^1H\}$ NOE (500 MHz, tol-d_8, 299 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 8.14/6.11 (6-H/5-H), 7.01/6.11, 0.08 (4-H/5-H, $^3SiCH_3$), 6.11/8.14, 7.01 (5-H/6-H, 4-H), −0.01/0.08 ($^2SiCH_3/^3SiCH_3$). $^1H,^{13}C$ GHSQC (500 MHz/126 MHz, tol-d_8, 299 K): $\delta^1H/\delta^{13}C$ = 8.14/146.7 (C6), 7.01/145.1 (C4), 6.11/122.4 (C5), 0.08/−0.5 ($^3SiCH_3$), −0.01/−1.3 ($^2SiCH_3$). $^1H,^{13}C$ GHMBC (500 MHz/126 MHz, tol-d_8, 299 K): $\delta^1H/\delta^{13}C$ = 8.14/145.1, 142.9, 122.4 (6-H/C4, C2, C5), 7.01/146.7, 142.9, 98.9 (4-H/C6, C2, $^3\equiv$C), 6.11/146.7, 128.4 (5-H/C6, C3), 0.08/106.6, −0.5 ($^3SiCH_3/^3\equiv$CSi, $^3SiCH_3$), −0.01/120.1, −1.3 ($^2SiCH_3/^2\equiv$CSi, $^2SiCH_3$). $^1H,^{29}Si$ GHMQC (500 MHz/99 MHz, tol-d_8, 299 K): $\delta^1H/\delta^{29}Si$ = 0.08/−16.2 ($^3SiCH_3/^{C3}Si$), −0.01/−14.1 ($^{C2}SiCH_3/^{C2}Si$). $^{19}F,^{19}F$ GCOSY (470 MHz/470 MHz, tol-d_8, 299 K) [selected traces]: $\delta^{19}F/\delta^{19}F$ = −161.3/−131.8, −154.6 (m'-BC_6F_5[a]/o'-BC_6F_5[a], p-BC_6F_5[a]), −162.9/−126.9, −154.6 (m-BC_6F_5[a]/o-BC_6F_5[a], p-BC_6F_5[a]), −163.2/−128.3, −155.6 (m-BC_6F_5[b]/o-BC_6F_5[b], p-BC_6F_5[b]), −164.8/−129.2, −159.1 (m-BC_6F_5[c]/o-BC_6F_5[c], p-BC_6F_5[c]), −164.9/−133.6, −155.6 (m'-BC_6F_5[b]/o'-BC_6F_5[b], p-BC_6F_5[b]), −165.7/−133.3, −159.1 (m'-BC_6F_5[c]/o'-BC_6F_5[c], p-BC_6F_5[c]). $^1H,^{19}F$ HOESY (600 MHz/564 MHz, tol-d_8, 299 K) [selected trace]: $\delta^1H/\delta^{19}F$ = 8.14/−126.9, −133.3, −133.6 (6-H/o-BC_6F_5[a], o'-BC_6F_5[c], o'-BC_6F_5[b]). $^{19}F,^1H$ HOESY (564 MHz/600 MHz, tol-d_8, 299 K) [selected trace]: $\delta^{19}F/\delta^1H$ = −126.9/8.14 (o-BC_6F_5[a]/6-H).

Preparation of Compound 14. A solution of 2,3-bis(trimethylsilyl)ethynyl)pyridine (**12**, 103 mg, 0.38 mmol, 1 equiv) in toluene (∼2 mL) and a solution of $B(C_6F_5)_3$ (234 mg, 0.46 mmol, 1.2 equiv) in toluene (∼2 mL) were combined at room temperature and stirred at 110 °C for 2 days. Then all volatiles were removed *in vacuo* at room temperature and *n*-pentane (∼5 mL) was added and immediately removed again *in vacuo*. This procedure was repeated one more time to remove remaining toluene. Then *n*-pentane (∼10 mL) was added and the suspension was sonicated for 10 min. The supernatant was taken off, reduced to a volume of ∼4 mL, and stored at −40 °C for 2 h, which led to the precipitation of a colorless solid. The supernatant was taken off again, the solvent removed *in vacuo*, and the resulting slightly yellow solid was dried *in vacuo* to give compound **14** (150 mg, 0.19 mmol, 50%). Anal. Calcd for $C_{33}H_{21}BF_{15}NSi_2$: C, 50.59; H, 2.70; N, 1.79. Found: C, 50.70; H, 2.74; N, 1.40. ^1H NMR (500 MHz, tol-d_8, 253 K): δ = 8.34 (dd, $^3J_{HH}$ = 4.3 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 2-H), 8.10 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 4-H), 6.62 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 4.3 Hz, 1H, 3-H), 1.52 (br d, J = 3.2 Hz, 3H, BCH_3), 0.90, 0.52 (each s, each 3H, $^8SiCH_3$), −0.20 (s, 9H, $^5SiCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, tol-d_8, 253 K): δ = 156.7 (C7), 151.6 (C8a), 148.6 (C2), 141.8 (C5), 140.9 (C8), 136.3 (C4), 130.3 (C4a), 120.7 (C3), 117.5 (tm, $^2J_{FC}$ = 20.7 Hz, i-C_6F_5), 113.9 (tm, $^2J_{FC}$ = 22.7 Hz, i-C_6F_5B), 112.9 (tm, $^2J_{FC}$ = 31.7 Hz, i-C_6F_5Si), 18.5 (br, BCH_3), 2.0, 1.9 (each m, $^8SiCH_3$), 1.5 ($^5SiCH_3$), n.o. (C6), [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (160 MHz, tol-d_8, 253 K): δ = 74 ($\nu_{1/2}$ ∼4500 Hz). ^{19}F NMR (470 MHz, tol-d_8, 253 K): δ = −123.0 (br, o'), −128.2 (br m, o), −145.0 (tm, $^3J_{FF}$ = 21.3 Hz, p), −160.8 (m, m'), −161.1 (m, m) (each 1F, BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 16.2, $\Delta\delta^{19}F_{m',p}$ = 15.8], −136.1 (o'), −136.9 (o), −152.6 (t, $^3J_{FF}$ = 21.1 Hz, p), −160.7 (m'), −163.1 (m) (each 1F, C_6F_5), −127.5 (2F, o), −153.6 (t, $^3J_{FF}$ = 20.8 Hz, 1F, p), −162.2 (2F, m) (each m, C_6F_5Si)[$\Delta\delta^{19}F_{m,p}$ = 8.6]. $^{29}Si\{DEPT\}$ NMR (99 MHz, tol-d_8, 253 K): δ = −4.8 ($\nu_{1/2}$ ∼ 2 Hz, ^{5}Si), −11.7 ($\nu_{1/2}$ ∼ 12 Hz, ^{8}Si). $^1H\{^1H\}$ TOCSY (500 MHz, tol-d_8, 253 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 8.34/8.10, 6.62 (2-H/4-H, 3-H), 0.90/0.52 ($^8SiCH_3$). $^1H\{^1H\}$ NOE (500 MHz, tol-d_8, 253 K) [selected experiments]: $\delta^1H_{irr}/\delta^1H_{res}$ = 8.10/6.62, −0.20 (4-H/3-H, $^5SiCH_3$), 1.52/0.90, 0.52 ($BCH_3/^8SiCH_3$, $^8SiCH_3$), 0.52/1.52, 0.90 ($^8SiCH_3/BCH_3$, $^8SiCH_3$), −0.20/8.10 ($^5SiCH_3$/ 4-H). $^1H,^{13}C$ GHSQC (500 MHz/126 MHz, tol-d_8, 253 K): $\delta^1H/\delta^{13}C$ = 8.34/148.6 (C2), 8.10/136.3 (C4), 6.62/120.7 (C3), 1.52/18.5 (BCH_3), 0.90/2.0 ($^8SiCH_3$), 0.52/1.9 ($^8SiCH_3$), −0.20/1.5 ($^5SiCH_3$). $^1H,^{13}C$ GHMBC (500 MHz/126 MHz, tol-d_8, 253 K) [selected traces]: $\delta^1H/\delta^{13}C$ = 8.34/151.6 136.3, 120.7 (2-H/C8a, C4, C3), 8.10/151.6, 148.6, 141.8, 130.3 (4-H/C8a, C2, C5, C4a), 1.52/156.7, 113.9 (BCH_3/ C7, i-BC_6F_5), 0.90/140.9, 112.9, 1.9 ($^8SiCH_3$/C8, i-SiC_6F_5, $^8SiCH_3$), 0.52/140.9, 112.9, 2.0 ($^8SiCH_3$/C8, i-SiC_6F_5, $^8SiCH_3$), −0.20/141.8, 1.5 ($^5SiCH_3$/C5, $^5SiCH_3$). $^1H,^{29}Si$ GHMQC (500 MHz/99 MHz, tol-d_8, 253 K): $\delta^1H/\delta^{29}Si$ = 0.90/−11.7 ($^8SiCH_3/^8Si$), 0.52/−11.7 ($^8SiCH_3/^8Si$), −0.20/−4.8 ($^5SiCH_3/^5Si$). $^{19}F,^{19}F$ GCOSY (470 MHz/470 MHz, tol-d_8, 253 K) [selected traces]: $\delta^{19}F/\delta^{19}F$ = −160.7/−136.1, −152.6 (m'-C_6F_5/o'-C_6F_5, p-C_6F_5), −160.8/−123.0, −145.0 (m'-BC_6F_5/o'-BC_6F_5, p-BC_6F_5), −161.1/−128.2, −145.0 (m-BC_6F_5/o-BC_6F_5, p-BC_6F_5), −162.2/−127.5, −153.6 (m-SiC_6F_5/o-SiC_6F_5, p-SiC_6F_5), −163.1/−136.9, −152.6 (m-C_6F_5/o-C_6F_5, p-C_6F_5).

X-ray Crystal Structure Analysis of Compound 14. A solution of 2,3-bis(trimethylsilyl)ethynyl)pyridine (**12**, 54.2 mg, 0.2 mmol, 1 equiv) in toluene (∼2 mL) and a solution of $B(C_6F_5)_3$ (205 mg, 0.4 mmol, 1.2 equiv) in toluene (∼2 mL) were combined at room temperature and stirred at 110 °C for 2 days. Then all volatiles were removed *in vacuo* at room temperature and *n*-pentane (∼5 mL) was added and immediately removed again *in vacuo*. This procedure was repeated one more time to remove remaining toluene. The residue was identified as a 1:1 mixture of compound **14** and $B(C_6F_5)_3$. A solution of this mixture in benzene at room temperature gave crystals, which were suitable for the X-ray crystal structure analysis. Formula $C_{33}H_{21}BF_{15}NSi_2$, M = 783.50, colorless crystal, 0.14 × 0.10 × 0.05 mm, a = 14.2884(2) Å, b = 10.0454(2) Å, c = 23.2090(5) Å, β = 94.795(1)°, V = 3319.6(1) Å^3, ρ_{calc} = 1.568 g cm^{-3}, μ = 0.218 mm^{-1}, empirical absorption correction (0.970 ≤ T ≤ 0.989), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 19 031 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 8059 independent (R_{int} = 0.052) and 5491 observed reflections [$I > 2\sigma(I)$], 475 refined parameters, R = 0.072, wR^2 = 0.155, max. (min.) residual electron density 0.35 (−0.29) e·Å^{-3}; hydrogen atoms were calculated and refined as riding atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Contains a detailed description of experiments, characterization of all new compounds, and crystal-structure data (CIF) available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from SusChemSys, the European Research Council, and the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged. The project "Sustainable Chemical Synthesis (SusChemSys)" is co-financed by the European Regional Development Fund (ERDF) and the state of North Rhine-Westphalia, Germany, under the Operational Pro-

DOI: 10.1021/jo502753s
J. Org. Chem. 2015, 80, 2240−2248

gramme "Regional Competitiveness and Employment" 2007–2013.

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DOI: 10.1021/jo502753s
J. Org. Chem. 2015, 80, 2240–2248