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Arynes and Their Precursors from Arylboronic Acids via Catalytic C–H Silylation

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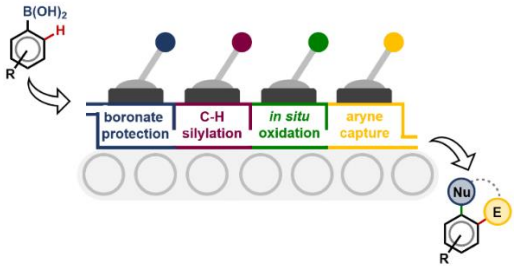
Arynes, Boronates, C-H Functionalization, Ruthenium, Silanes



ABSTRACT: A new, operationally simple approach is presented to access arynes and their fluoride-activated precursors based on Ru-catalyzed C-H silylation of arylboronates. Chromatographic purification may be deferred until after aryne capture, rendering the arylboronates *de facto* precursors. Access to various new arynes and their derivatives is demonstrated, including – for the first time – those based on a 2,3-carbazolyne and 2,3-fluorenyne core, which pave the way for novel derivatizations of motifs relevant to materials chemistry.

The trapping of aryne intermediates has evolved into an extraordinarily powerful arylation strategy.[1] It allows the regioselective introduction of C-, B-, pnictogen, chalcogen and halogen-based functionality to electrophilic[2] (hetero)arene units via various multi-component,[1e] cycloaddition,[3] insertion,[4] and rearrangement sequences[5] as well as transition metal-mediated/catalyzed processes.[6] Such versatility has led to the use of aryne trapping in the synthesis of natural products,[7] polycyclic aromatic hydrocarbons (PAHs),[3b,8] polymers[9] and organometallic complexes.[6,10] Arguably, aryne-based methodology has benefitted most profoundly from the development of fluoride-activated precursors that work mild conditions.[11] These incorporate a silane (or other fluorophile[12] *ortho* with respect to a nucleofuge.[12b,13] Thus, the highly reactive aryne triple bond may be generated and trapped under mild, tolerant conditions. With this advantage in hand, most of the focus has fallen on diversifying the transformations aryne triple bonds undergo. Typically, however, most new reactions are demonstrated on only a handful of simple, commercially available or easy-to-make precursors. Many even modestly more complex precursors require *de novo* synthesis, sometimes via laborious and/or low yielding routes or involve separate installation and removal of directing groups to facilitate intermediate *ortho*-lithiation.[14] Few *ortho*-bromophenols, the most common starting materials for precursor synthesis, are commercially available and their selective preparation is often inefficient.

In recent years, catalytic C-H functionalization has emerged as a powerful alternative to 'classical' reactivity,[15] allowing new transformations and the circumvention of tedious stoichiometric routes and harsh conditions.[15a]

Despite this, only a small handful of C-H functionalization routes to arynes or their precursors has been described (Figure 1). These include the Rh-catalyzed *ortho*-silylation of phenols,[16] Pd-catalyzed *ortho*-oxygenation using a silane-tethered directing group,[17] and the direct generation of arynes via C-H palladation-decarboxylation of benzoic acids.[18] Only the former benefits from an extended scope, although it also requires stoichiometric MeLi. Otherwise, the use of strong stoichiometric bases to remove a proton *ortho* to a good leaving group continues to underpin a substantial portion of modern aryne methodology.[19] Our interest in C-H functionalization and aryne chemistry[20] led us to envisage an alternative, operationally simple route to aryne precursors – *and even arynes themselves* – predicated on Ru-

catalyzed[21] catalytic C-H silylation[22] of arylboronates as the key step.

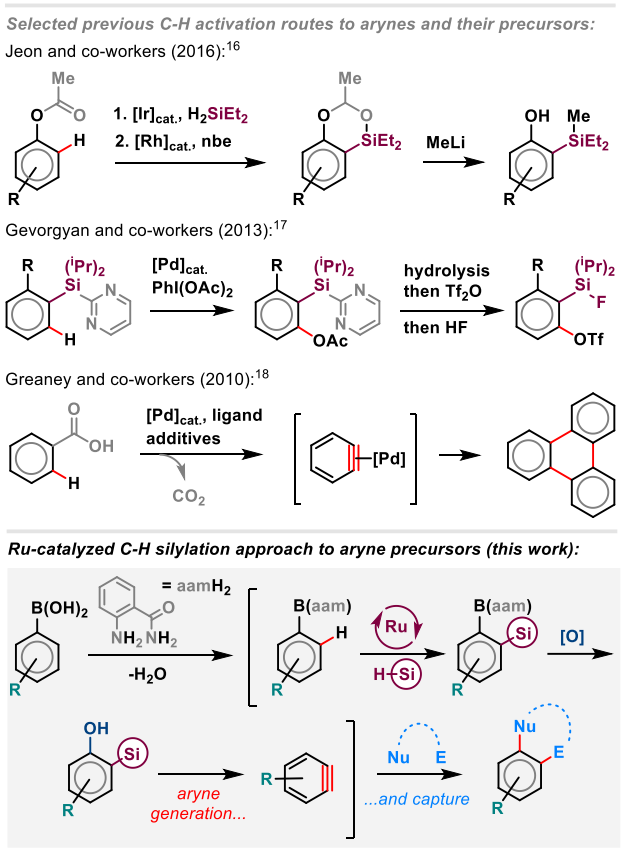
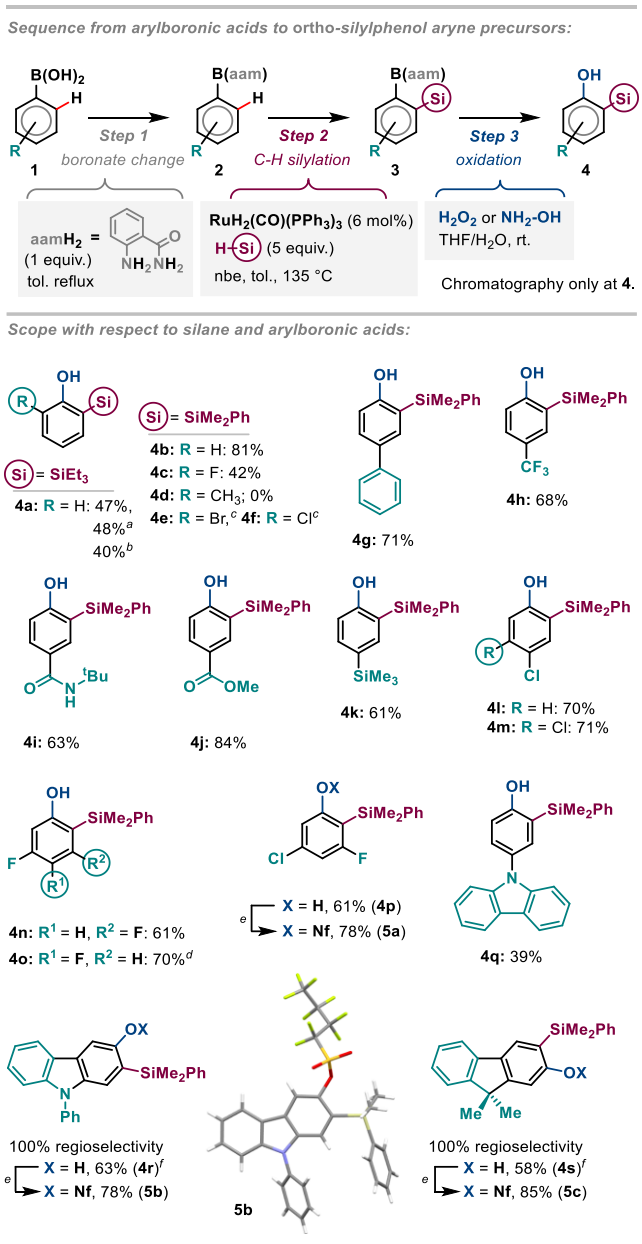


Figure 1: Past and present approaches to aryne precursors using C-H activation strategies.

Our route starts with arylboronic acids (**1**), many variants of which are commercially available or easily synthesized. The convenience of arylboronic acids is underscored by their near ubiquity in organic chemistry laboratories – a consequence of the C-B bond's considerable synthetic utility.[23] The key steps in our route (Scheme 1, top) are: *1)* the protection of **1** as anthranilamido boronates, ArB(aam),[24] **2**; *2)* their direct catalytic C-H silylation based on Suginome's approach to give intermediates **3**, and *3)* selective *in situ* oxidation[25] of the boronate to give *ortho*-silylphenols **4**. These may be stored indefinitely and used directly as aryne precursors via activation using 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonyl fluoride (NfF) to provide the leaving group.[13b] This obviates the need for much more expensive but less stable triflate derivatives.[26] As described below, we found that phenols **4** may, alternatively, be purified via a *single aqueous wash* to a degree sufficient for direct, efficient aryne generation and capture in a sequence that requires no chromatography until the aryne capture product is obtained (Scheme 2). Thus, boronic acids **1** can act as *de facto* aryne precursors.

Scheme 1 shows the results of our study on the scope of this approach to generate *ortho*-silyl phenols, **4**. At the outset, we confirmed the greater efficiency of Ru- over Ir-catalysis[27] and that of $HSiMe_2Ph$ compared to $HSiEt_3$[24e] (**4a** vs **4b**). Substrates bearing phenyl (**4g**), trifluoromethyl (**4h**), amido- (**4i**), ester (**4j**), silyl (**4k**), chloro- (**4l, 4m** and **4p**), fluoro- (**4n**, **4o** and **4p**) and amino- (**4q**) functionality were amenable to our general conditions. The average yield for our general conditions across these products was 65%, corresponding to 87% average yield per step for Scheme 1. The route was also compatible with carbazole- and fluorene-based substrates – obtained from commercially available boronic acids (products **4r** and **4s**, respectively); both of these units, as well as the aryl carbazole core of **4q**, play prominent roles in various organic electronic devices[28] and photocatalysts[29] for whose synthesis the huge potential of aryne chemistry has barely been explored. In Step 3 of the synthesis of **4r** and **4s**, H_2O_2 was replaced with the milder oxidant, $H_2N\text{-}OH\cdot H_2O$.[30]



Scheme 1: Scope with respect to arylboronic acids. General conditions in detail: Boronic acid (0.5-1.0 mmol). *Step 1:* anthranilamide (1 equiv.), toluene, Dean-Stark, reflux, overnight; *Step 2:* Direct addition of $RuH_2(CO)(PPh_3)_3$ (6 mol%), silane (5 equiv.), norbornene (5 equiv.) toluene, 135 °C, 20 h; *Step 3*:

Na_2CO_3, H_2O_2, EtOH, rt. [a][Ir(μ-OMe)COD]$_2$ (5 mol%) as catalyst, PPh_3 ligand (15 mol%). [b][$Ru_3(CO)_{12}$] (6 mol%) as catalyst, PPh_3 ligand (36 mol%). [c]Complex mixture. [d]3:1 mixture of regioisomers (major isomer shown). [e]Conditions: NfF (1.1 equiv), NaH (1.1 equiv), THF or MeCN, 0°C to rt., 16h. [f]Column chromatography after steps 2 and 3. Conditions for Step 3: NH_2-OH·HCl, NaOH, EtOH, rt.

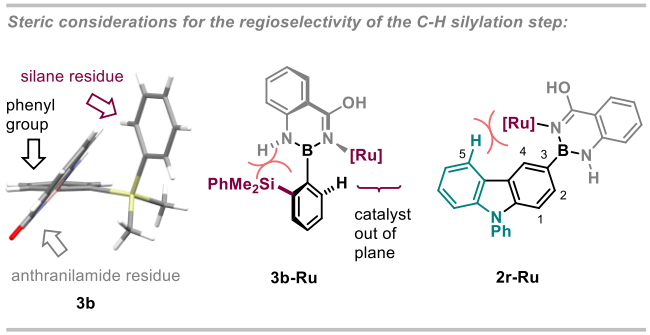
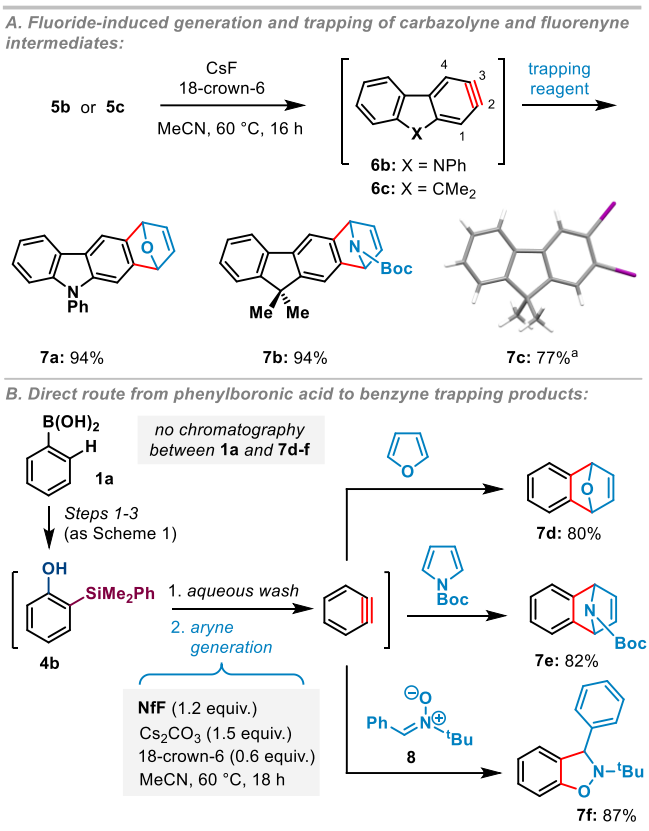


Figure 2: Steric influence over regioselectivity of C-H silylation.

We found that the steric profile of most substituents *ortho* to -B(aam) was sufficient to prevent C-H silylation (e.g. **4d** was not obtained). The crystal structure of **3b** (Figure 2) is illustrative: the -B(aam) group rests out of the plane with respect to its neighboring C-H bond due to steric repulsion between B(aam) and the silane residue, thereby hindering a second ruthenation event (e.g. in proposed intermediates of type **3b-Ru**[24c]). Meanwhile, *ortho*-bromo (**4e**) and -chloro (**f**) silyl phenols did not form; instead, only complex mixtures were obtained, presumably arising from cleavage of the C-halogen bond by Ru. Fluoride, however, proved small enough to give **4c** in 42% yield across all three steps (75% average yield per step). Installing the silane between the -B(aam) directing group and a *meta*-fluoro group met with further success: an overall yield of 61% (85% average per step) was obtained via the silylation en route to **4n** and **4p**. This is a pleasing outcome; the regioselectivity of aryne trapping reactions is most profoundly influenced by strongly electropositive[31] or electronegative groups[32] at the carbon adjacent to the aryne triple bond. Fluoride is able to induce the greatest levels of regioselectivity amongst all known substituents.[32b] Asymmetrically substituted boronates with two available C-H units *ortho* to -B(aam) underwent silylation exclusively at the least hindered site (**4m** and **4p**), except for **4o**, in which the less hindered position was favored in a 3:1 ratio.

We were also pleased to discover that the C-H silylation *en route* to **4r** proceeded with complete regioselectivity. We attribute this to the steric influence of the C5-H unit impeding C4-H silylation by Ru (e.g. in intermediates of type **2r-Ru**, Figure 2). This finding paves a new route to exclusively C2-silyl derivatives of the carbazole and various isosterically related motifs. By contrast, the synthesis of related compounds can require lithiation strategies that lead to mixtures of regioisomers. Compounds **4p**, **4r** and **4s** were converted in good yields to their corresponding nonaflates, **5a**, **5b** and **5c**. The structure of **5b** was confirmed using X-ray crystallography (Scheme 1, bottom).



Scheme 2: Generation and capture of arynes from (a) *ortho*-silyl aryl nonaflate or (b) an arylboronic acid as the *de facto* precursor. [a] 71 h reaction time.

To the best of our knowledge, fluoride-induced generation of 2,3-carbazolynes or any fluorenynes has not been previously reported. Arynes **6b** and **6c** were generated efficiently and converted to the corresponding products **7a-c** in good to excellent yields via [4+2] cycloaddition to furan, *N*-Boc-pyrrole and an insertion into I_2,[33] respectively (Scheme 2a). The identity of 2,3-diiodo-9,9-dimethyl-fluorene (**7c**) was confirmed crystallographically. These examples demonstrate a new route to functionalized carbazole and fluorene motifs that leverages the synthetic versatility of the aryne triple bond. Studies on extending this to the synthesis of more complex compounds of import to organic electronics applications are ongoing in our laboratory.

Finally, we carried out preliminary studies on the viability of generating aryne capture products from phenylboronic acid, **1a**, *without any chromatographic purification* of intermediates. Following steps 1-3 (as described above), the crude reaction mixture was subjected to a single aqueous wash and then directly to the conditions shown in Scheme 2b with furan, *N*-Boc-pyrrole or nitrone **8** as the trapping reagent. We were also pleased to find that the addition of exogeneous fluoride salts were not required to produce the aryne en route to the final products; fluoride released from attack on NfF by the phenolic residue appeared to suffice.[11d] Compounds **7d-f** were obtained in 80%, 82% and 87%, respectively. This corresponds to a mean

average yield of 95% per step across all reactions in Scheme 2b.

In summary, we have developed a new, expedient route to a variety of arynes, their fluoride-activated precursors and aryne derivatives. Whilst the procedure is relatively material-intensive compared to non-catalytic approaches (e.g. stoichiometric anthranilamide and high silane loadings are required) it brings several key benefits: operational simplicity, low requirements for chromatographic purification, high average yields per step, and the dual use of the B(aam) group as a masked phenol able to direct C-H silylation. Moreover, it enables the use of arylboronic acids as *de facto* aryne precursors; arylboronic acids are diverse and very common reagents in organic synthesis. Complete regioselectivity is obtained for both carbazole- and fluorene-based substrates, leading to previously un-reported aryne intermediates of high potential in the synthesis of motifs relevant to materials chemistry. We envisage that this approach may be utilized to exploit the unique nature of the aryne triple bond in more complex chemical environments.

EXPERIMENTAL SECTION

General information.

Unless otherwise stated, all reactions were performed under an atmosphere of Argon with magnetic stirring. Thin layer chromatography (TLC) was carried out using aluminum-backed plates coated with Kieselgel 60 (0.20 mm, UV 254) and visualized under ultraviolet light (λ = 254 nm) or with $KMnO_4$ staining solution. Purification by column chromatography was performed using Kiesel gel 60 H silica gel (particle size 0.063-0.100 mm). THF was freshly distilled from Na^0/benzophenone and stored over 4 Å molecular sieves under Argon. Toluene and 1,4-dioxane were predried over 4 Å molecular sieves and stored under Argon prior to use. All arylboronic acid starting materials were obtained commercially and used 'as is' without further purification. Unless otherwise stated, all the other reagents, transition metal salts, anthranilamide, silanes and norbornene were obtained commercially and used without further purification. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Varian Unity 400 MHz (^1H 399.5MHz, ^{13}C 100.6, ^{19}F 376 MHz) or Varian Mercury Plus 300 MHz (^1H 300.0 MHz, ^{13}C 75.5 MHz) spectrometers at ambient temperature. NMR data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Chemical shifts are reported in ppm and referenced indirectly to tetramethylsilane *via* the residual solvent signals. ^1H: $CDCl_3$ at 7.26, DMSO-d_6 at 2.50, C_6D_6 at 7.16 ppm; ^{13}C: $CDCl_3$ at 77.0, DMSO-d_6 at 39.5, C_6D_6 at 128.1 ppm. ^{19}F ($CFCl_3$) chemical shifts were calibrated to an external standard at 0.00 ppm. High resolution accurate-mass mass spectra were run on either a VG Autospec (EI at 70eV), Bruker micrOTOF Focus II (ESI) or Bruker ultrafleXtreme II (MALDI with colloidal graphite matrix).

Crystallography: Single crystal X-ray diffraction was performed on a Bruker APEX-II single-crystal X-ray diffractometer at 150 K using Mo-Kα radiation, and the structures were solved using direct methods (ShlexS-2014)[34] refined by full-matrix least-squares procedures using OLEX2.[35] Semi-empirical absorption corrections from equivalents (multi-scan) were carried out using SADABS. CCDC 1882782-1882784 contain the supplementary crystallographic data for compounds **3b, 5b** and **7c**.

Synthesis of *ortho*-silyl phenols

Procedure A (direct preparation):

A 25 mL round-bottomed flask equipped with magnetic stir bar was charged with a mixture of the appropriate arylboronic acid (0.50-1.00 mmol, 1.0 eq.), anthranilamide (1.0 eq.) and toluene (10 mL/mmol). The mixture was heated at reflux in a Dean-Stark apparatus overnight. The toluene was then removed under reduced pressure or by draining the Dean-Stark trap. The resulting crude Ar-B(aam) was transferred to a pre-dried 5 mL Young's tube equipped with a magnetic stir bar, to which were added $RuH_2(CO)(PPh_3)_3$ (6 mol%) and norbornene (5.0 eq.). The flask was then evacuated and backfilled three times with Ar. The indicated silane (5.0 eq.) and toluene (0.5 mL/mmol) were added via a septum. The mixture was heated at 135 °C for 20 h, cooled to rt, transferred to a 100 mL round-bottomed flask and the toluene was removed under reduced pressure. To this mixture, at rt and under air, were added Na_2CO_3 (1.0 eq.) and ethanol (40 mL/mmol), followed the dropwise addition of H_2O_2 (30% w/w, 10 mL/mmol). Reaction progress was monitored by TLC. After consumption of the *ortho*-silyl arylboronate, the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Unless otherwise indicated, the product was purified by column chromatography using pentane/EtOAc as the eluent.

Procedure B (sequential preparation):

Step 1: Protection of arylboronic acids

A 25 mL round-bottomed flask equipped with magnetic stirrer bar was charged with a mixture of arylboronic acid (1.0 eq.), anthranilamide (1.0 eq.) and toluene (10 mL/mmol) and heated at reflux in a Dean-Stark apparatus overnight. The Ar-B(aam) intermediate was obtained by removal of toluene, either under reduced pressure or by draining the Dean-Stark trap.

Step 2: Silylation

To a pre-dried 5 mL Young's tube equipped with a magnetic stir bar were added Ar-B(aam) (1.0 eq.), $RuH_2(CO)(PPh_3)_3$ (6 mol%) and norbornene (5.0 eq.). The tube was evacuated and backfilled with argon three times and then silane (5.0 eq.) and toluene (0.5 mL/mmol of substrate) were added. The reaction mixture was heated at 135 °C for 20 h. After cooling to rt, the *ortho*-silyl arylboronate was purified by flash column chromatography.

Step 3: Oxidation of aromatic boronates

A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with *ortho*-silyl arylboronate, NaOH (2.0 eq.), $NH_2OH{\cdot}HCl$ (1.5 eq.) and ethanol (20 mL/mmol boronate). The mixture was stirred at rt and monitored by TLC until completion. The crude reaction mixture was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under

reduced pressure. The product was purified by column chromatography using pentane/EtOAc as the eluent.

Analytical data for aryl anthranilamido boronate

*2-(4-(9H-carbazol-9-yl)phenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (**2a**).* Prepared using General Procedure B (step 1). Yield = 0.387 g (98%, based on 1.00 mmol of 4-(9*H*-carbazol-9-yl)phenyl)boronic acid), beige solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.84 (s, 1H), 9.47 (s, 1H), 8.34 (d, J = 7.9 Hz, 2H), 8.25 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.59 (dd, J = 7.6 Hz, 1H), 7.49 – 7.42 (m, 5H), 7.34 – 7.25 (m, 2H), 7.12 (dd, J = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): 166.8, 145.9, 140.4, 139.3, 135.7, 133.9, 128.4, 126.8, 126.2, 123.3, 121.4, 121.0, 120.7, 119.3, 118.7, 110.2. HRMS-ESI calcd for $C_{25}H_{18}BN_3O$ [M+H]$^+$: 388.1616, found 388.1612.

*2-(9,9-Dimethyl-9H-fluoren-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (**2b**).* Prepared using general procedure B (step 1). Yield = 0.661 g (93%, based on 2.10 mmol of (9,9-dimethyl-9*H*-fluoren-2-yl)boronic acid), colorless solid. R_f = 0.5 (petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.75 (s, 1H), 9.35 (s, 1H), 8.33 (s, 1H), 8.09 – 8.04 (m, 2H), 7.91 (d, J = 7.7 Hz, 1H), 7.89 – 7.87 (m, 1H), 7.61 – 7.54 (m, 2H), 7.47 (d, J = 7.7 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.14 – 7.10 (m, 1H), 1.50 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 166.4, 153.8, 152.7, 145.6, 140.8, 138.4, 133.4, 132.3, 131.0, 128.0, 127.8, 127.1, 122.8, 120.7, 120.6, 119.5, 118.8, 118.1, 46.5, 26.9. HRMS-ESI calcd for $C_{22}H_{20}BN_2O$ [M+H]$^+$: 339.1667, found 339.1668.

Analytical data for *ortho*-silyl aryl anthranilamido boronate intermediates

*2-(3-(Dimethyl(phenyl)silyl)-9,9-dimethyl-9H-fluoren-2-yl)-2,3dihydrobenzo[d][1,3,2]diazabo rinin-4(1H)-one (**3a**).* Prepared using general procedure B (step 2). Yield = 0.069 g, (77%, based on 0.25 mmol of **2b**), colorless solid. R_f = 0.5 (pentane/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 – 8.18 (m, 2H), 7.87 – 7.84 (m, 1H), 7.64 (s, 1H), 7.52 – 7.48 (m, 3H), 7.44 – 7.36 (m, 6H), 7.27 (s, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.19 (d, J = 7.9 Hz, 1H), 6.03 (s, 1H), 1.53 (s, 6H), 0.56 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.5, 154.1, 153.8, 143.5, 140.4, 139.9, 139.7, 138.7, 134.0, 133.7, 129.5, 128.9, 128.5, 127.9, 127.4, 127.1, 126.9, 122.7, 121.8, 120.3, 118.6, 117.6, 47.1, 27.0, -1.1. HRMS-ESI calcd for $C_{30}H_{30}BN_2OSi$ [M+H]$^+$: 473.2221, found 473.2212.

Analytical data for new *ortho*-silyl phenols

*2-(Triethylsilyl)phenol (**4a**).* Prepared according to general procedure A. Yield = 0.095 g (47%, based on 0.50 mmol of the corresponding boronic acid). Yellow oil. R_f = 0.4 (pentane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 7.3, 1.7 Hz, 1H), 7.24 (dd, J = 7.7, 1.7 Hz, 1H), 6.93 (ddd, J = 7.3, 7.3, 0.9 Hz, 1H), 6.68 (dd, J = 7.7, 0.9 Hz, 1H), 4.77 (br s, 1H), 0.98 (d, J = 7.7 Hz, 9H), 0.91 – 0.82 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7, 136.4, 130.6, 122.5, 120.5, 114.6, 7.8, 3.7. HRMS-MALDI calcd for $C_{12}H_{19}OSi$ [M-H]$^-$: 207.1211, found 207.1215. Alternative procedure using [Ir(OMe)(COD)]$_2$: To a pre-dried 5 mL Young's tube equipped with a magnetic stir bar were added Ar-B(aam) (0.25 mmol, 1.0 eq.), [Ir(OMe)(COD)] (5 mol%), PPh_3 (15 mol%) and norbornene (5.0 eq.). The tube was evacuated and backfilled with argon three times and then H-SiEt_3 (5.0 eq.) and toluene (2 mL) were added. The reaction mixture was heated at 135 °C for 20 h. After cooling to rt, the *ortho*-silyl arylboronate was subjected to oxidation conditions listed in procedure A and the resulting *ortho*-silyl phenol was purified by flash column chromatography to afford product **4a** in 48% yield. Alternative procedure using [$Ru_3(CO)_{12}$]: To a pre-dried 5 mL Young's tube equipped with a magnetic stir bar were added Ar-B(aam) (0.25 mmol, 1.0 eq.), [$Ru_3(CO)_{12}$] (6 mol%), PPh_3 (36 mol%) and norbornene (5.0 eq.). The tube was evacuated and backfilled with argon three times and then H-SiEt_3 (5.0 eq.) and toluene (2 mL) were added. The reaction mixture was heated at 135 °C for 20 h. After cooling to rt, the *ortho*-silyl arylboronate was subjected to oxidation conditions listed in procedure A and the resulting *ortho*-silyl phenol was purified by flash column chromatography to afford product **4a** in 40% yield.

*2-(Dimethyl(phenyl)silyl)phenol (**4b**).* Prepared according to general procedure A. Yield = 0.092 g (81%, based on 0.50 mmol of the corresponding boronic acid). Colorless oil. R_f = 0.4 (Pentane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.59 (m, 2H), 7.41 – 7.32 (m, 4H), 7.28 – 7.22 (m, 1H), 6.93 (ddd, J = 7.3, 0.6 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 4.77 (s, 1H), 0.59 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.4, 138.0, 136.0, 134.2, 131.2, 129.3, 128.0, 123.1, 120.6, 115.0, -2.3. HRMS-MALDI calcd for $C_{14}H_{15}OSi$ [M-H]$^-$: 227.0898, found 227.0894.

*2-(Dimethyl(phenyl)silyl)-6-fluorophenol (**4c**).* Prepared according to general procedure A. Yield = 0.052 g (42%, based on 0.50 mmol of the corresponding boronic acid). Colorless oil. R_f = 0.6 (pentane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.42 – 7.35 (m, 3H), 7.12 – 7.09 (m, 1H), 7.07 – 7.03 (m, 1H), 6.83 (ddd, J = 7.7, 7.7 4.6 Hz, 1H), 5.26 (s, 1H), 0.63 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.7 (d, J_{CF} = 239.6 Hz), 147.9 (d, J_{CF} = 12.5 Hz), 137.9, 134.2, 130.9 (d, J_{CF} = 4.0 Hz), 129.2, 127.8, 126.5, 120.1 (d, J_{CF} = 5.6 Hz), 116.6 (d, J_{CF} = 18.3 Hz), -2.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.58 - -142.61 (m). HRMS- MALDI calcd for $C_{14}H_{14}FOSi$ [M-H]$^-$: 245.0803, found 245.0799.

*3-(Dimethyl(phenyl)silyl)-[1,1'-biphenyl]-4-ol (**4g**).* Prepared according to general procedure A. Yield = 0.108 g (71%, based on 1.00 mmol of the corresponding boronic acid). Colorless solid. R_f = 0.5 (pentane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.63 (m, 2H), 7.57 (d, J = 2.3 Hz, 1H), 7.52 – 7.50 (m, 3H), 7.43 – 7.37 (m, 5H), 7.30 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 4.82 (s, 1H), 0.64 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.1, 141.1, 137.8, 134.6, 134.2, 133.7, 130.0, 129.5, 128.7, 128.1, 126.8, 126.6, 123.6, 115.4, -2.20. HRMS-MALDI calcd for $C_{20}H_{19}OSi$ [M-H]$^-$: 303.1211, found 303.1209.

*2-(Dimethyl(phenyl)silyl)-4-(trifluoromethyl)phenol (**4h**).* Prepared according to general procedure A. Yield = 0.101 g (68%, based on 1.00 mmol of the corresponding boronic acid). Colorless oil. R_f = 0.3 (pentane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.60 (m, 3H), 7.52 (dd, J = 8.4, 2.0

Hz, 1H), 7.46 – 7.38 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.14 (s, 1H), 0.63 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.9, 136.8, 134.2, 133.0 (q, J_{CF} = 3.7 Hz), 129.8, 128.6 (q, J_{CF} = 3.7 Hz), 128.2, 124.5 (d, J_{CF} = 285.4 Hz), 124.2, 123.0 (d, J_{CF} = 44.3 Hz), 115.1, -2.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.40. HRMS- MALDI calcd for $C_{15}H_{14}F_3OSi$ $[M-H]^-$: 295.0772, found 295.0771.

*N-(tert-Butyl)-3-(dimethyl(phenyl)silyl)-4-hydroxybenzamide (**4i**).* Prepared according to general procedure A. Yield = 0.103 g (63%, based on 1.00 mmol of the corresponding boronic acid). Colorless solid. R_f = 0.2 (pentane/EtOAc = 15:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.58 – 7.52 (m, 4H), 7.37 – 7.30 (m, 3H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.82 (s, 1H), 1.43 (s, 9H), 0.58 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.7, 164.5, 137.9, 134.8, 134.2, 130.2, 129.2, 127.8, 126.5, 123.6, 114.8, 51.6, 28.9, -2.5. HRMS-MALDI calcd for $C_{19}H_{24}NO_2Si$ $[M-H]^-$: 326.1582, found 326.1589.

*Methyl 3-(dimethyl(phenyl)silyl)-4-hydroxybenzoate (**4j**).* Prepared according to general procedure A. Yield = 0.120 g (84%, based on 0.500 mmol of the corresponding boronic acid). Grey solid. R_f = 0.2 (pentane/EtOAc = 15:1). ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 2.2 Hz, 1H), 7.95 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.42 – 7.35 (m, 3H), 6.72 (d, *J* = 8.5 Hz, 1H), 5.71 (s, 1H), 3.87 (s, 3H), 0.62 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.3, 164.7, 138.1, 137.3, 134.1, 133.3, 129.6, 128.1, 123.4, 122.3, 114.9, 51.9, -2.4. HRMS-MALDI calcd for $C_{16}H_{17}O_3Si$ $[M-H]^-$: 285.0952, found 285.0949.

*2-(Dimethyl(phenyl)silyl)-4-(trimethylsilyl)phenol (**4k**).* Prepared according to general procedure A. Yield = 0.092 g (61%, based on 0.50 mmol of the corresponding boronic acid). Yellow oil. R_f = 0.4 (pentane/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.59 (m, 2H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.44 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.41 – 7.33 (m, 3H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.90 (s, 1H), 0.61 (s, 6H), 0.22 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.3, 141.3, 138.1, 136.6, 134.2, 131.0, 129.4, 128.0, 122.4, 114.5, -0.9, -2.2. HRMS-MALDI calcd for $C_{17}H_{23}OSi_2$ $[M-H]^-$: 299.1293, found 299.1289.

*4-Chloro-2-(dimethyl(phenyl)silyl)phenol (**4l**).* Prepared according to general procedure A. Yield = 0.092 g (70%, based on 1.0 mmol of the corresponding boronic acid). Yellow oil. R_f = 0.3 (pentane/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.58 (m, 2H), 7.44 – 7.37 (m, 3H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 4.77 (s, 1H), 0.60 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.9, 137.1, 135.2, 134.2, 130.9, 129.7, 128.2, 125.9, 125.8, 116.6, -2.5. HRMS-MALDI calcd for $C_{14}H_{14}ClOSi$ $[M-H]^-$: 261.0508, found 261.0502.

*4,5-Dichloro-2-(dimethyl(phenyl)silyl)phenol (**4m**).* Prepared according to general procedure A. Yield = 0.106 g (71%, based on 0.500 mmol of the corresponding boronic acid). Brown oil. R_f = 0.4 (pentane/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.56 (m, 2H), 7.44 – 7.38 (m, 3H), 7.33 (s, 1H), 6.82 (s, 1H), 4.94 (s, 1H), 0.58 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.2, 136.7, 136.5, 134.2, 134.1, 129.9, 128.3, 124.7, 124.3, 117.2, -2.5. HRMS-MALDI calcd for $C_{14}H_{13}Cl_2OSi$ $[M-H]^-$: 295.0118, found 295.0114.

*2-(Dimethyl(phenyl)silyl)-3,5-difluorophenol (**4n**).* Prepared according to general procedure A. Yield = 0.081 g (61%, based on 0.55 mmol of the corresponding boronic acid). Yellow oil. R_f = 0.3 (pentane/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.67 (m, 2H), 7.50 – 7.43 (m, 3H), 6.37 (ddd, *J* = 9.3, 9.3 2.2 Hz, 1H), 6.23 (ddd, *J* = 10.2, 2.2, 1.3 Hz, 1H), 5.29 (s, 1H), 0.66 (s, 3H), 0.65 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.2 (dd, J_{CF} = 241.2, 15.1 Hz), 163.9 (dd, J_{CF} = 247.8, 17.0 Hz), 162.3 (dd, J_{CF} = 17.2, 13.9 Hz), 136.7, 134.4, 130.5, 128.8, 105.1 (dd, J_{CF} = 33.2, 3.5 Hz), 99.6 (dd, J_{CF} = 23.4, 3.8 Hz), 96.2 (dd, J_{CF} = 31.6, 24.7 Hz), -1.2 (two silyl methyl peaks appears). ^{19}F NMR (376 MHz, $CDCl_3$): δ -94.41-(-94.47) (m),-107.81-(-107.89) (m). HRMS-MALDI calcd for $C_{14}H_{13}F_2OSi$ $[M-H]^-$: 263.0709, found 263.0702.

*2-(Dimethyl(phenyl)silyl)-4,5-difluorophenol (**4o**).* Prepared according to general procedure A. Yield = 0.075 g (57%, based on 0.50 mmol of the corresponding boronic acid). Colorless oil. R_f = 0.4 (pentane/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.57 (m, 2H), 7.45 – 7.38 (m, 3H), 7.06 (dd, *J* = 10.2, 9.8 Hz, 1H), 6.54 (dd, *J* = 11.4, 6.0 Hz, 1H), 4.79 (s, 1H), 0.58 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.5 (dd, J_{CF} = 8.5, 2.2 Hz), 151.4 (dd, J_{CF} = 250.2, 14.2 Hz), 145.9 (dd, J_{CF} = 241.9, 11.7 Hz), 136.8, 134.1, 129.8, 128.3, 123.1 (dd, J_{CF} = 16.5, 1.8 Hz), 119.7 (dd, J_{CF} = 3.8, 2.0 Hz), 104.8 (d, J_{CF} = 18.9 Hz), -2.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -134.01 – -134.12 (m), -149.17 – -149.27 (m). HRMS-MALDI calcd for $C_{14}H_{14}F_2NaOSi$ $[M+Na]^+$: 287.0674, found 287.0670.

*2-(Dimethyl(phenyl)silyl)-3,4-difluorophenol (**4o´**).* Prepared according to general procedure A. Yield = 0.017 g (13%, based on 0.50 mmol of the corresponding boronic acid). Yellow oil. R_f = 0.3 (pentane/EtOAc = 20:1). 10% of regioisomer **4o** present. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.66 (m, 2H), 7.46 – 7.41 (m, 3H), 7.06 – 6.99 (m, 1H), 6.39 (ddd, *J* = 8.9, 3.3, 1.7 Hz, 1H), 4.86 (s, 1H), 0.68 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.9 (dd, J_{CF} = 12.0, 2.5 Hz), 154.2 (dd, J_{CF} = 241.5, 12.5 Hz), 144.9 (dd, J_{CF} = 241.6, 16.9 Hz), 136.6, 134.2, 130.3, 128.6, 119.0 (dd, J_{CF} = 18.7, 2.3 Hz), 112.0 (dd, J_{CF} = 28.1, 2.6 Hz), 111.2 (d, J_{CF} = 5.0, 3.4 Hz), -1.2 (two silyl methyl peaks appears). ^{19}F NMR (376 MHz, $CDCl_3$): δ -122.73 – -122.84 (m) -148.47 - -149.29 (m). HRMS-MALDI calcd for $C_{14}H_{14}F_2NaOSi$ $[M+Na]^+$: 287.0674, found 287.0670.

*5-Chloro-2-(dimethyl(phenyl)silyl)-3-fluorophenol (**4p**).* Prepared according to general procedure A. Yield = 0.086 g (61%, based on 0.50 mmol of the corresponding boronic acid). Colorless oil. R_f = 0.5 (pentane/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.60 (m, 2H), 7.50 – 7.37 (m, 3H), 6.65 (dd, *J* = 8.8, 1.7 Hz, 1H), 6.51 (d, *J* = 1.7 Hz, 1H), 5.18 (s, 1H), 0.65 (s, 3H), 0.64 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.8 (d, J_{CF} = 242.7 Hz), 161.7 (d, J_{CF} = 15.8 Hz), 137.3 (d, J_{CF} = 14.4 Hz), 136.6, 134.3, 130.4, 128.7, 112.3 (d, J_{CF} = 3.4 Hz), 108.5 (d, J_{CF} = 32.0 Hz), 108.2 (d, J_{CF} = 32.7 Hz), -1.2 (two silyl methyl peaks appear). ^{19}F NMR (376 MHz, $CDCl_3$): δ -95.78 – -95.80 (m). HRMS-MALDI calcd for $C_{14}H_{13}ClFOSi$ $[M-H]^-$: 279.0414, found 279.0418.

*4-(9H-Carbazol-9-yl)-2-(dimethyl(phenyl)silyl)phenol (**4q**).* Prepared according to general procedure A. Yield = 0.082 g (39% based on 0.33 mmol of anthranilamido boronate **2a**). Brown oil, R_f = 0.2 (pentane/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.8 Hz, 2H), 7.71 – 7.63 (m, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.38 (m, 5H), 7.37 – 7.22 (m, 5H), 6.91 (d, J = 8.4 Hz, 1H), 5.15 (s, 1H), 0.64 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.7, 141.3, 137.3, 134.7, 134.2, 130.3, 130.1, 129.7, 128.2, 125.8, 125.3, 123.1, 120.2, 119.6, 116.4, 109.7, -2.3. HRMS-ESI calcd for $C_{26}H_{23}NOSiNa$ $[M+Na]^+$: 416.1441, found 416.1433.

*2-(Dimethyl(phenyl)silyl)-9-phenyl-9H-carbazol-3-ol (**4r**).* Prepared using a modified version of procedure A. 9-phenyl-9*H*-carbazol-3-yl)boronic acid (1.00 mmol, 0.287 g) and anthranilamide (1.00 mmol, 0.136 g) was heated at reflux in toluene (15 mL) in a Dean-Stark apparatus overnight. Silylation was performed according to silylation conditions listed in method A to yield 2-(2-(dimethyl(phenyl)silyl)-9-phenyl-9*H*-carbazol-3-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one. The crude mixture was transferred to a 100 mL round-bottomed flask and concentrated under reduced pressure. The resulting mixture was suspended in ethanol/THF (5:2 volume ratio, 35 mL). $NH_2OH{\cdot}HCl$ (4.0 mmol, 0.278 g) and NaOH (5.0 mmol, 0.200 mmol) was added in one portion and the resulting mixture stirred at rt for 3 h. The reaction was quenched with H_2O, extracted with EtOAc, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Silica gel chromatography (pentane/EtOAc 25:1). Yield = 0.248 g (63%, based on 1.00 mmol of the corresponding boronic acid). Beige solid. R_f = 0.3 (pentane/EtOAc = 25:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.8 Hz, 1H), 7.63 – 7.53 (m, 6H), 7.45 – 7.35 (m, 8H), 7.26 – 7.19 (m, 1H), 4.68 (s, 1H), 0.61 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.4, 141.4, 138.3, 137.9, 135.9, 134.2, 129.7, 129.3, 127.9, 127.0, 126.7, 126.3, 125.7, 123.0, 122.8, 120.5, 119.5, 116.5, 109.9, 105.5, -2.1. HRMS-ESI calcd for $C_{26}H_{23}NOSiNa$ $[M+Na]^+$: 416.1441, found 416.1444.

*3-(Dimethyl(phenyl)silyl)-9,9-dimethyl-9H-fluoren-2-ol (**4s**).* Prepared according to general procedure B. Yield = 0.042 g (81%, based on 0.15 mmol of the corresponding boronic acid). Colorless solid. R_f = 0.2 (pentane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.67 – 7.65 (m, 2H), 7.62 – 7.60 (m, 1H), 7.42 – 7.37 (m, 4H), 7.29 (ddd, J = 7.4, 7.4, 1.3 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.77 (s, 1H), 4.84 (s, 1H), 1.45 (s, 6H), 0.65 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.5, 157.7, 152.9, 139.1, 138.1, 134.3, 132.1, 129.4, 128.1, 127.0, 126.9, 126.1, 122.4, 121.5, 119.0, 109.9, 46.7, 27.2, -2.1. HRMS-EI calcd for $C_{23}H_{24}OSi$ $[M]^+$: 344.1591, found 344.1599.

Sulfonylation procedure

Nonaflation of *ortho*-silyl ethers was performed according to a modified literature procedure.[13b] *Ortho*-silyl phenol (0.30 mmol, 1.0 eq.) and NaH (0.30 mmol, 1.0 eq.) was added to a 10 mL oven-dried round bottomed flask equipped with a stir bar. The flask was then evacuated and backfilled three times with argon. Dry THF or MeCN (3.0 mL, 0.1 M) was added and the mixture was stirred 1h in room temperature. The flask was cooled on ice-bath for 15 minutes followed by dropwise addition of perfluorobutanesulfonyl fluoride (NfF) (0.33 mmol, 1.1 eq.). After 30 min the ice-bath was removed and the reaction was stirred at rt for 16 h. The reaction was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 x 25mL). Organic phases were combined, dried over Na_2SO_4 and reduced under vacuum. The products were purified by column chromatography using EtOAc/pentane or Et_2O/pentane as the eluent.

Analytical data for aryne precursors

*5-Chloro-2-(dimethyl(phenyl)silyl)-3-fluorophenyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (**5a**).* Synthesized from *ortho*-silyl phenol **4p** according to the general sulfonylation procedure listed above. Yield = 0.131 g (78%, based on 0.300 mmol of **4p**). Colorless oil. R_f = 0.9 (pentane/EtOAc 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 2H), 7.40 – 7.33 (m, 3H), 7.21 – 7.18 (m, 1H), 7.07 (dd, J = 8.4, 1.7 Hz, 1H), 0.71 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1 (d, J_{CF} = 249.0 Hz), 154.4 (d, J_{CF} = 16.4 Hz), 137.5 (d, J_{CF} = 13.2 Hz), 136.3 (d, J_{CF} = 1.3 Hz), 133.6, 133.0, 129.6, 127.9, 127.7, 125.3, 117.6 (d, J_{CF} = 33.6 Hz), 117.1 (q, J_{CF} = 2.6 Hz), 116.0 (d, J_{CF} = 30.8 Hz), -0.82, -0,86. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.60 – -80.80 (m), -90.86 – -91.07 (m), -108.82 – -109.06 (m), -120.82 – -121.03 (m), -125.73 – -125.91 (m). HRMS-ESI calcd for $C_{18}H_{13}ClF_{10}O_3SSiNa$ $[M+Na]^+$: 584.9776, found 584.9772.

*2-(Dimethyl(phenyl)silyl)-9-phenyl-9H-carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (**5b**).* Synthesized from *ortho* silyl phenol **4r** according to the general sulfonylation procedure listed above. Yield = 0.164 g (78%, based on 0.300 mmol of **4r**). Colorless solid. R_f = 0.8 (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CDCl3): δ 8.15 (d, J = 7.9 Hz, 1H), 8.11 – 8.05 (m, 1H), 7.60 – 7.50 (m, 4H), 7.49 – 7.42 (m, 5H), 7.42 – 7.29 (m, 5H), 0.70 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.3, 141.8, 138.8, 136.9, 136.9, 134.1, 129.9, 129.3, 128.2, 127.8, 127.7, 127.4, 126.7, 125.2, 122.5, 120.9, 120.5, 117.7, 111.4 (t, J_{CF} = 2.6 Hz), 110.3, -2.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.54 – -80.69 (m), -109.66 – -109.84 (m), -120.84 – -121.04 (m), -125.63 – -125.88 (m). HRMS-ESI calcd for $C_{30}H_{22}F_9NO_3SSiNa$ $[M+Na]^+$: 698.0838, found 698.0846.

*3-(Dimethyl(phenyl)silyl)-9,9-dimethyl-9H-fluoren-2-yl1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (**5c**).* Synthesized from *ortho*-silyl phenol **4s** according to the general sulfonylation procedure listed above. Yield = 0.532 g (85%, based on 1.00 mmol of **4s**). Colorless solid. R_f = 0.4 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.61 – 7.57 (m, 3H), 7.44 – 7.38 (m, 4H), 7.36 (s, 1H), 7.33 – 7.40 (m, 2H), 1.49 (s, 6H), 0.71 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.5, 155.0, 153.8, 138.3, 137.4, 136.7, 134.2, 129.5, 129.2, 128.0, 127.9, 127.9, 127.2, 122.7, 120.2, 114.3 (t, J_{CF} = 2.5 Hz), 47.3, 26.8, -2.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.61 – -80.67 (m), -109.65 – -109.74 (m), -120.94 – -121.01 (m), -125.71 – -125.86 (m). HRMS-ESI calcd for $C_{27}H_{23}F_9O_3SSiNa$ $[M+Na]^+$: 649.0886, found 649.0891

Cycloadditions of arynes (*trapping procedure 1*)

A pre-dried microwave vial equipped with magnetic stir bar was charged with aryne precursor (1.0 eq.), *N*-Boc-pyrrole

or furan (3.0 eq.), CsF (3.0 eq.) and CH_3CN was added to obtain a 0.10 M solution with respect to the aryne precursor. This mixture was heated at 60 °C for 16 h. The resulting capture product was purified by column chromatography using pentane/EtOAc as the eluent.

*5-Phenyl-7,10-dihydro-5H-7,10-epoxybenzo[b]carbazole (**7a**).* Synthesized from aryne precursor **5b** according to trapping procedure 2 using furan as arynophile. Yield = 0.042 g (94%, based on 0.20 mmol of **5b**). Colorless solid. R_f = 0.2 (pentane/EtOAc = 25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 1H), 7.98 – 7.93 (m, 1H), 7.63 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.50 – 7.43 (m, 1H), 7.38 – 7.30 (m, 3H), 7.28 – 7.23 (m, 1H), 7.14 – 7.07 (m, 1H), 7.05 – 6.98 (m, 1H), 5.89 – 5.83 (m, 1H), 5.76 – 5.71 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 143.6, 142.4, 141.0, 140.0, 138.6, 137.6, 129.9, 127.6, 127.3, 124.9, 123.4, 119.9, 119.7, 119.5, 112.3, 109.9, 104.0, 82.6, 82.4. HRMS-ESI calcd for $C_{22}H_{16}NO$ $[M+H]^+$: 310.1226, found 310.1231.

*Tert-butyl 11,11-dimethyl-9,11-dihydro-6H-6,9-epiminobenzo[b]fluorene-12-carboxylate (**7b**).* Synthesized from aryne precursor **5c** using *N*-Boc-pyrrole as the arynophile. Yield = 0.055 g (94%, based on 0.10 mmol of **5c**). Colorless solid. R_f = 0.2 (pentane/EtOAc = 25:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.60 (m, 2H), 7.40 – 7.37 (m, 1H), 7.33 – 7.31 (m, 1H), 7.31 – 7.24 (m, 2H), 7.02 (m, 2H), 5.55 – 5.52 (m, 2H), 1.44 (s, 3H), 1.42 (s, 3H), 1.39 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 155.1, 154.0, 151.0, 147.8, 147.5, 143.0, 139.2, 136.0, 126.8, 126.6, 122.3, 119.4, 115.8, 113.1, 80.6 (2C), 66.5, 46.6, 28.2, 27.0, 26.7. HRMS-ESI calcd for $C_{24}H_{25}NO_2Na$ $[M+Na]^+$: 382.1777, found 382.1781.

Iodine insertion into aryne (*trapping procedure 2***)**

*2,3-Diiodo-9,9-dimethyl-9H-fluorene (**7c**).* A pre-dried microwave vial equipped with a magnetic stir bar was charged with aryne precursor **5c** (1.0 eq.), iodine (4.0 eq.), CsF (8.0 eq.) and CH_3CN was added to obtain a 0.10 M solution with respect to the aryne precursor. This mixture was heated at 60 °C for 71 h. The resulting product **7c** was purified by column chromatography using pentane as the eluent. Yield = 0.054 g, 77% (based on 0.10 mmol of **5c**). Colorless solid. R_f = 0.9 (pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.95 (s, 1H), 7.66 – 7.65 (m, 1H), 7.42 - 7.40 (m, 1H), 7.38 – 7.33 (m, 2H), 1.46 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 155.2, 153.2, 141.3, 136.9, 133.8, 130.7, 128.5, 127.3, 122.7, 120.4, 105.6, 105.5, 46.8, 26.8. HRMS-EI calcd for $C_{15}H_{12}I_2$ $[M]^+$: 445.9023, found 445.9041

Direct generation and cycloaddition of benzyne (*trapping procedure 3*)**.**

Ortho-silyl phenol (1.0 mmol, 1.0 eq.) was prepared according to a modified procedure A. After completion of the oxidation, without further purification of the ortho-silyl phenol by column chromatography, the crude mixture was extracted with CH_2Cl_2 (25 mL × 3). The combined layers were dried over $MgSO_4$ and concentrated under reduced pressure. To this mixture Cs_2CO_3 (1.5 mmol, 1.5 eq.), 18-crown-6 (0.6 mmol, 0.6 eq.), NfF (1.2 mmol, 1.2 eq.), arynophile (3.0 mmol, 3.0 eq.) and CH_3CN (10 mL, 0.10 M) were added. This mixture was heated at 60 °C for 18 h. The reaction mixture was extracted with CH_2Cl_2 (25 mL × 3). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The product was purified by column chromatography using pentane/EtOAc as the eluent. Yields are reported over 4 steps.

*1,4-Dihydro-1,4-epoxynaphthalene (**7d**).* Synthesized in a 4-step procedure from phenylboronic acid according to trapping procedure 1 using furan as arynophile. Yield = 0.100 g (70%, based on 1.00 mmol of phenylboronic acid). Colorless solid. R_f = 0.3 (pentane/EtOAc = 20:1). Spectral data agrees with previously reported values.[36]

*Tert-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (**7e**).* Synthesized in a 4-step procedure from phenylboronic acid according to trapping procedure 1 using *N*-Boc-pyrrole as arynophile. Yield = 0.126 g (52%, based on 1.00 mmol of phenylboronic acid). Colorless solid. R_f = 0.2 (pentane/EtOAc = 25:1). Spectral data is in accordance with previously reported values.[37]

2-(*Tert*-butyl)-3-phenyl-2,3-dihydrobenzo[d]isoxazole (**7f**). Synthesized in a 4-step procedure from phenylboronic acid according to trapping procedure 1 using *N*-*tert*-butyl-α-phenylnitrone as arynophile. Yield = 0.176 g (69%, based on 1.00 mmol of phenylboronic acid). Colorless solid. R_f = 0.5 (pentane/EtOAc = 20:1). Spectral data is in accordance with previously reported values.[38]

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website. This includes copies of NMR spectra for all new compounds (.pdf format) and crystallography data: (ORTEP plots in .pdf and original data in .cif format) for compounds **3b**, **5b** and **7c**.

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