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Synthesis of 9,9′-Spirobifluorenes and 4,5-Diaza-9,9′-spirobifluorenes and Their Application as Affinity Materials for Quartz Crystal Microbalances

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In memory of Fritz Vögtle

Two different classes of aza analogues of 9,9′-spirobifluorenes have been synthesized. These were obtained by either furnishing the spirobifluorene with additional pyridyl moieties or by installing the aza function directly into the spirobifluorene core. These structurally rigid compounds were then evaluated as affinity materials for quartz crystal microbalances and proved to be highly potent for the detection of volatile organic compounds.

Introduction

Structural rigidity of concave host structures exhibiting multiple binding sites has proven to be very advantageous to generate highly potent affinity materials for the detection of various analytes by quartz crystal microbalance (QCM)-based sensors.[1] For practical reasons, however, the affinity material should provide some additional properties, such as sufficient stability at ambient conditions and sufficient solubility in organic solvents, as the surface coating of the QCM is easily achieved in an electrospray process.[2] Hence, established concave building blocks for organic porous materials are, for example, crown ethers,[3] cyclodextrins,[4] or calixarenes.[5] Rigid dendrimers, such as dendritic polyphenylenes, have also proven to be excellent affinity materials for applications in QCMs.[6] The synthesis of such dendrimers, however, is very demanding, and therefore, we have recently explored smaller rigid hydrocarbon skeletons that exhibit voids and (extended) π-conjugated structural elements that can be accessed and functionalized in an easier manner. In the course of these studies, the 9,9′-spirobifluorene core proved to be very promising for such purposes.[7] However, it should be noted that these features are also required for a broad range of other applications of this particular class of compounds,[8] including molecular recognition,[9] catalysis,[10] coordination chemistry,[11] macromolecular chemistry,[12] and optoelectronics.[13]

Moreover, another interesting finding of our investigations with regards to efficient affinity materials is that azaheterocycles are clearly favorable in terms of chemical stability and binding properties.[7,14]

Results and Discussion

According to the criteria mentioned above, we decided to prepare two different classes to combine the rigid scaffold of a spirobifluorene with nitrogen-containing functional groups. Our first choice was to furnish the 9,9′-spirobifluorene with additional bipyridyl groups, whereas the second approach aimed at introducing the nitrogen function directly into the spirobifluorene core.

Following the first approach, we designed two molecules, **1** and **2** (Figure 1), in which the spirobifluorene moieties were either located in the periphery or the center of the molecule;

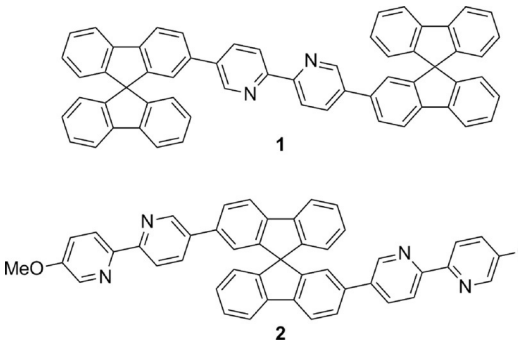

Figure 1. Structures of bipyridyl-functionalized 9,9′-spirobifluorenes **1** and **2**.

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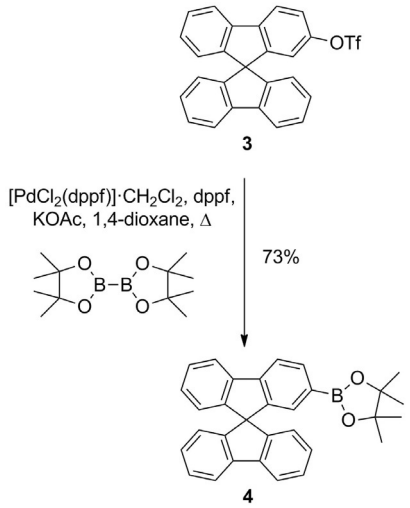
thus, requiring mono- and difunctionalized spirobifluorene building blocks, respectively.

The synthesis of **1** was achieved in a convergent ten-step synthesis, starting from 4-bromoanisol and 2,5-dibromopyridine (**9**). Following a synthetic protocol that we had developed earlier,[15] we prepared triflate **3** in a five-step synthesis, starting from 4-bromoanisol.

Miyaura cross-coupling of **3** with bis(pinacolato)diboron then resulted in the formation of boronic acid ester **4**, as displayed in Scheme 1.[16]

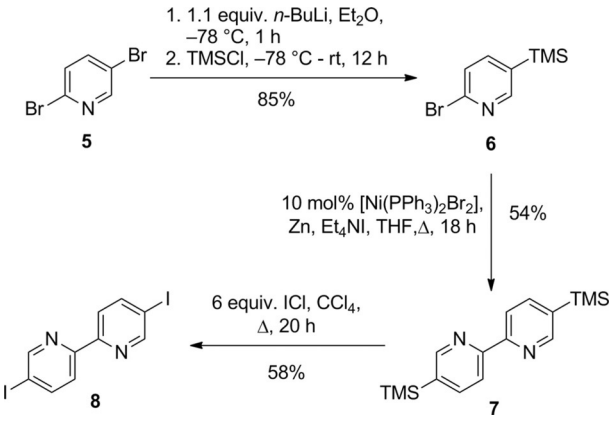


Scheme 1. Synthesis of mono-functionalized 9,9′-spirobifluorene building block **4** (OTf = triflate, dppf = 1,1′-bis(diphenylphosphino)ferrocene).

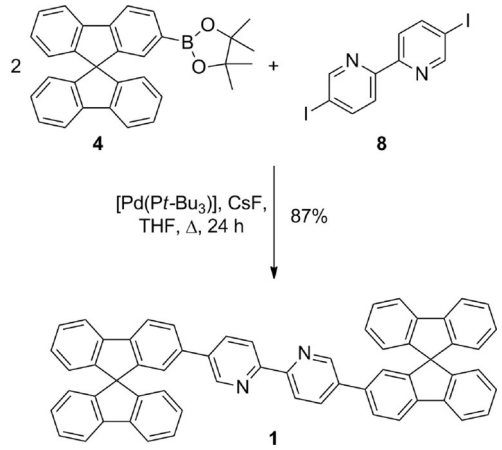
The synthesis of 5,5′-diiodo-2,2′-bipyridine (**8**) as the coupling partner for the final Suzuki reaction was best performed in a three-step sequence, starting from **9**.[17] Through adapting a protocol of Kira et al.,[18] regioselective lithiation and subsequent quenching with trimethylsilyl chloride (TMSCl) gave monosilylated pyridine **10** in very good yield. Nickel-catalyzed homocoupling[19] then gave 5,5′-disilylated bipyridine **11**, which was subjected to *ipso* substitution by using ICl to give the desired diiodinated bipyridine **12** in acceptable yield (Scheme 2).

Finally, Suzuki cross-coupling of **4** and **8** gave the first target compound **1** in very good yield (Scheme 3).

2,2′-Difunctionalized spirobifluorenes are chiral compounds, and hence, add another exciting property, with regard to use as an affinity material, in terms of aggregation in the affinity layer and the potential to achieve stereoselective recognition. Although, the last of these is not addressed in this study, because we focus on the detection of achiral compounds (see below), we still decided to prepare **2** in enantiomerically pure form to obtain, as much as possible, a homogenous affinity layer. Hence, we chose enantiomerically pure 2,2′-bis(4,4,5,5-tetamethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene ((*R*)-**9**) as a suitable building block that could be prepared starting from enantiomerically pure 2,2′-dihydroxy-9,9′-spirobifluorene,[20] as reported earlier.[20a]



Scheme 2. Synthesis of 5,5′-diiodo-2,2′-bipyridine (**8**).



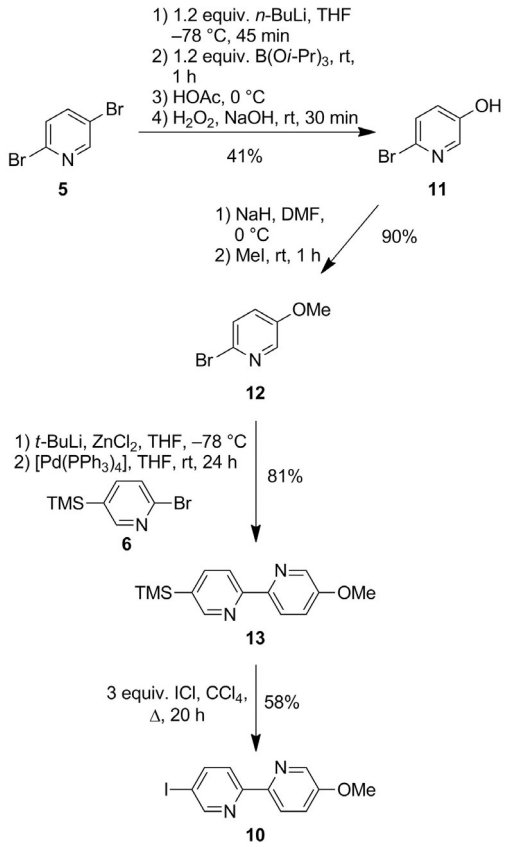
Scheme 3. Synthesis of bis(spirobifluorene)-capped 2,2′-bipyridine **1**.

The difunctionalized 2,2′-bipyridine **10** needed for coupling with (*R*)-**9** was prepared in five steps, again starting from dibromopyridine **5** (Scheme 4). Therefore, we first followed a protocol of Murakami et al. to prepare 2-bromo-5-hydroxypyridine (**11**) and 2-bromo-5-methoxypyridine (**12**).[21] Interestingly, we were able to increase the yields of both transformations significantly: compound **5** was first lithiated in a regioselective manner, and subsequently transformed into **11** via the corresponding boronic acid intermediate, according to the protocol of Murakami et al.[21] Methylation of **11** then gave **12**, which was subjected to a Negishi cross-coupling with **6** to give silylated bipyridine **13**, following a protocol that we had developed earlier.[22] Finally, compound **13** was converted into the desired iodinated bipyridine **10** through *ipso* substitution.

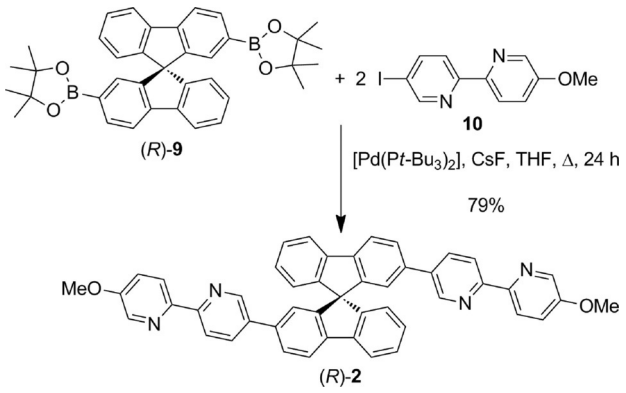
Thus, with both coupling partners (*R*)-**9** and **10** in hand, the synthesis of bis(bipyridine)-equipped spirobifluorene (*R*)-**2** was achieved in a Suzuki cross-coupling in very good yield (Scheme 5).

To introduce nitrogen functions directly into the spirobifluorene core, we decided to prepare 4,5-diaza-9,9′-spirobifluorenes **14**, **15**, and **16** as model compounds (Figure 2).

The synthesis of **14** started from 1,10-phenathroline, which was oxidized with potassium permanganate to give diazafluor-



Scheme 4. Synthesis of 5-iodo-5′-methoxy-2,2′-bipyridine (**10**).



Scheme 5. Synthesis of bis(bipyridine)-functionalized 9,9′-spirobifluorene **2**.

enone **17** in moderate yields, according to a protocol by Baxter et al.[23] The reaction of **17** with the Grignard reagent derived from 2-iodobiphenyl[24] then gave tertiary alcohol **18** in very good yield. Compound **18** was subsequently condensed to give the 4,5-diaza-9,9′-spirobifluorene **19** in an acceptable yield of 54%.[25] Regioselective electrophilic bromination led to **14** in a good yield of 71%, which was slightly better than the yield reported in the literature (Scheme 6).[25]

Single-crystal XRD analysis revealed that **14** crystallized in monoclinic space group *C*2/*c*, which formally contained one and a half independent molecules in its asymmetric unit because one molecule was located on a crystallographic C_2 axis.

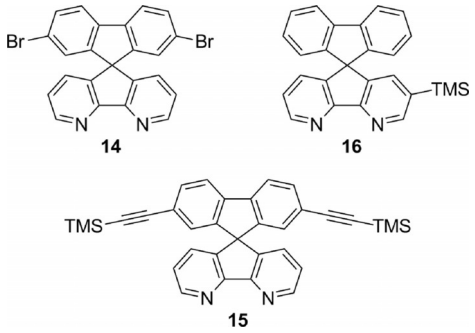
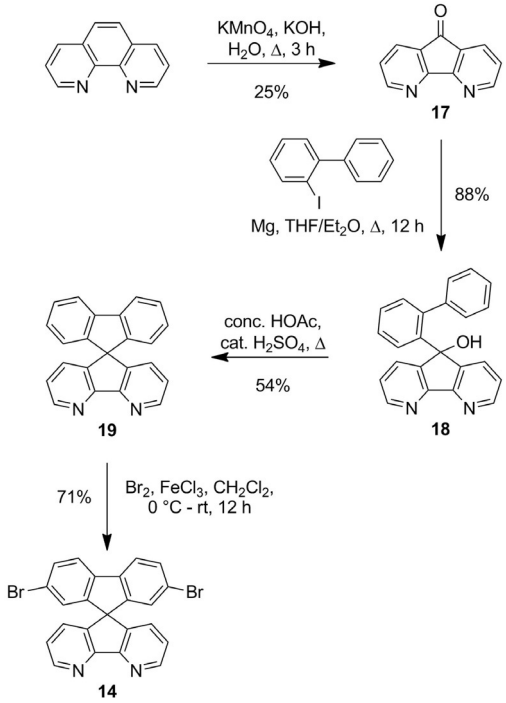


Figure 2. Structures of model compounds 4,5-diaza-9,9′-spirobifluorenes **18**–**20**.



Scheme 6. Synthesis of 4,5-diaza-9,9′spirobifluorenes **19** and **14**.

Interestingly, the molecules arrange in a pair-wise fashion stabilized by hydrogen bonds (Figure 3).

Compound **14** was then subjected to palladium-catalyzed cross-coupling reactions to obtain target compound **15** and bis(boronic acid ester) **20**, as a versatile derivative for the synthesis of further elaborated structures based on the diazaspirobifluorene skeleton (Scheme 7). Both reactions proceeded in acceptable yields for twofold cross-coupling reactions.

To obtain target compound **16**, which contains a functional group at one of the heterocycles of the diazaspirobifluorene skeleton, we had to develop a route to a functionalized diazafluorenone; this proved to be a rather difficult task. Starting from 2-bromonicotinic acid (**21**), we were finally able to prepare the desired silylated diazafluorenone in three steps in moderate yield (Scheme 8). Therefore, compound **21** was first transformed into methyl ester **22** upon treatment with methanol and sulfuric acid, according to a protocol of Stangeland

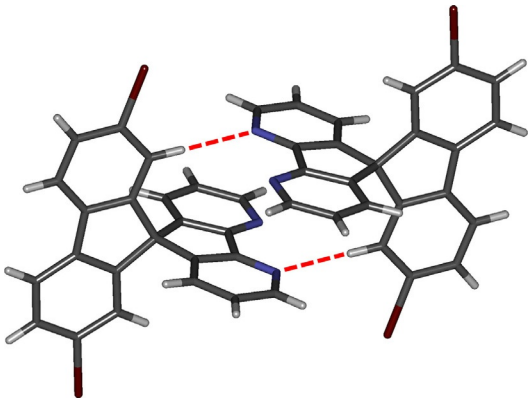
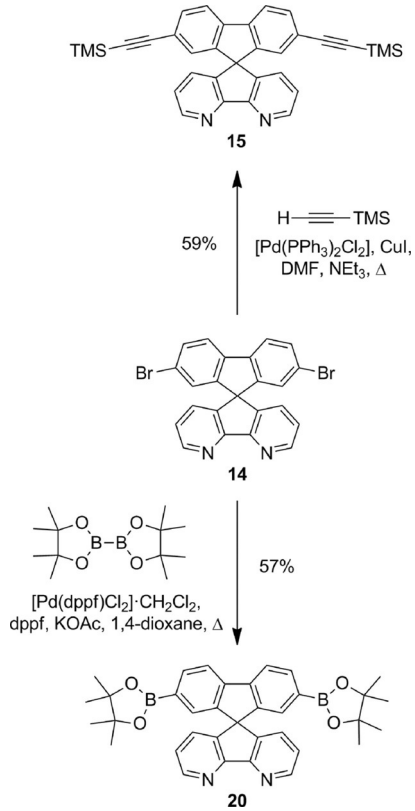
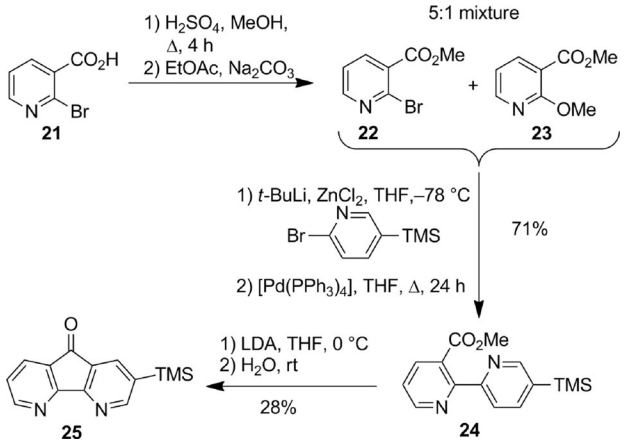


Figure 3. Molecular structure of **14**, as determined by XRD analysis. Carbon: dark gray, nitrogen: blue, bromide: orange, hydrogen: light gray.



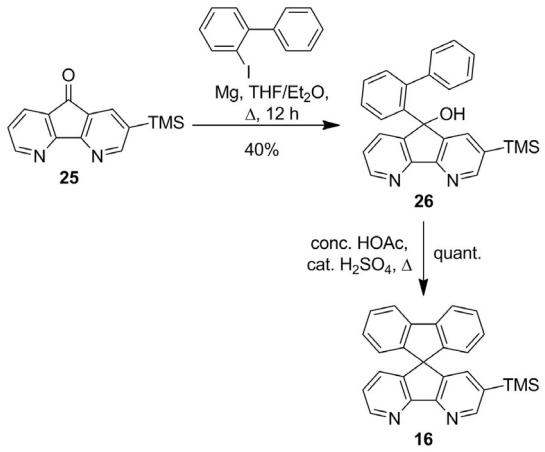
Scheme 7. Synthesis of 4,5-diaza-9,9′-spirobifluorenes **15** and **20**.

et al.[26] Please note that **22** was obtained as an inseparable 5:1 mixture together with 2-methoxynicotinic acid methyl ester (**23**) and none of our attempts to either increase the yields of the desired product or diminish the formation of the side product succeed. Nevertheless, we used the mixture directly in the subsequent coupling reaction with in situ zincated 5-trimethylsilylpyridine to give the difunctionalized 2,2′-bipyridine **24** in a good yield of 71%. Treatment of **24** with LDA then gave rise to the desired condensed diazafluorenone **25** in a moderate yield of 28%.



Scheme 8. Synthesis of 4,5-diazafluorenone **25**. LDA = lithium diisopropylamide.

Grignard reaction of **25** with 2-iodobiphenyl then gave rise to tertiary alcohol **26**, which was finally converted into **16** upon condensation under acidic conditions (Scheme 9).



Scheme 9. Synthesis of TMS-functionalized 4,5-diaza-9,9′-spirobifluorene **16**.

Compounds **1**, **2**, **14**–**16**, and **19** were then tested as affinity materials in gravimetric sensing based on QCMs. This study displays the unique interactions of these materials with volatile organic compounds (VOCs) in the vapor phase. Therefore, 195 MHz high fundamental frequency quartz crystal microbalances (HFF-QCMs) were used. The advantages of HFF-QCMs are the improved lower detection limit and the faster response time, compared with normal QCMs (5–20 MHz).[27] Depending on the particular vapor pressure, a detection limit in a range of ppm is achievable.[2b] Furthermore, it is a very temperature stable method. In addition, coated QCMs show stability over several weeks, right up to many months, even when increased flow rates of VOC are applied. The QCM modification with the spirobifluorene derivatives **1**, **2**, **14**–**16**, and **19** was performed by means of a well-known electrospray protocol,[2a] which allowed the deposition of a well-defined amount of affinity material (10.4 ng, 50 kHz) onto the electrode of the QCM. This

allows a consistent and highly reproducible determination by QCM. In a previous study, we revealed the preservation of the molecular properties of the deposited affinity material.[28] To evaluate the sensor responses to different analyte concentrations under equilibrium conditions, a continuous flow of nitrogen, enriched with a defined partial pressure of the analyte, was mixed and passed onto the coated QCMs. The analyte adsorption results in a frequency shift. The signal formation and recovery time of the sensor response takes place within seconds, so that an exact frequency read out is guaranteed (see Figures S6, S7, S32, and S33 in the Supporting Information). By fitting the sensor data with the Langmuir equation, the affinities of the individual affinity material were calculated. More details about the coating process, experimental setup, and determination of the affinities are given in the Supporting information.

To affect the adsorption behavior, the cavity size or microporosity of the affinity material and the intermolecular interaction towards the analyte are crucial. For instance, we have shown that more rigid affinity materials significantly affect the detection signal of the VOC; this is initiated by CH–π interactions and π–π stacking to a major degree.[7] Moreover, the design of functional groups that enable hydrogen[14b] or halogen bonding[29] favor the specific affinity towards a desired analyte. By utilizing various interactions between the affinity material and the VOC, detection limits down to the pictogram scale within seconds are possible.[28] A precoating of 1*H*,1*H*,2*H*,2*H*-perfluorooctylphosphonic acid on the electrode of the QCM suppresses interfering analyte signals, whereas the targeted analytes show enhanced signals.[30] Therefore, with this setup, the selectivity towards other ubiquitous vapors can be significantly improved, relative to most inorganic sensor materials.[31]

The selected spirobifluorene derivatives **1** and **2** combine the rigid spirobifluorene scaffold with additional bipyridyl groups for further intermolecular interactions. The analytes used to characterize the properties of the spirobifluorenes as affinity materials were common, yet hazardous to health and environment, aromatic compounds, such as benzene, toluene, and xylenes (BTX).[32] By comparison of the individual affinities of **1** and **2**, conclusions about the adsorption behavior can be drawn. So, if the selected analytes differ greatly in their boiling points (and therefore, vapor pressures), only affinities to a single analyte can be compared. Accordingly, the affinities are grouped by analyte in the following discussion.

Figure 4 displays the affinities of the spirobifluorenes **1** and **2** for the individual aromatic analytes. Thereby, compound **2** constantly exhibits higher affinities than those of **1**. This tendency became even more remarkable with *meta*-substitution of the analyte. Considering the clearly higher affinities for **2** than those of **1**, the major attraction takes place between the bipyridyl groups and the analyte in terms of π–π interactions. Additionally, compound **2** exhibits structural advantages that affect the adsorption behavior. Owing to the orthogonal arrangement of both fluorene moieties, twofold functionalization results in a structure in which both bipyridyl groups are oriented like a pincer. Therefore, the individual analyte could be able

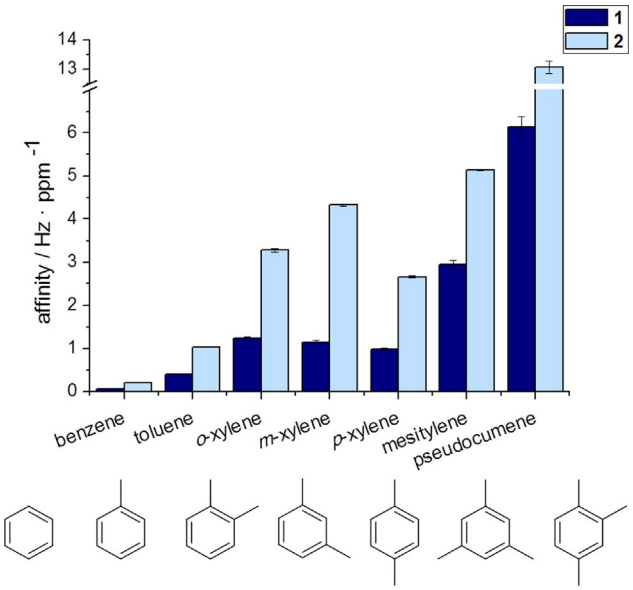


Figure 4. Affinities of **1** and **2** to a variety of aromatic analytes.

to interact with both bipyridyl surfaces. In contrast, spirobifluorene **1** consists of only a single bipyridyl group, which is potentially more shielded because of the rigid spirobifluorene scaffolds. A *meta*-substituted analyte shows an increased steric demand, resulting in less interaction with **1**, and therefore, a lower affinity.

To verify the assumption, the affinities of **1** and **2** for the ethyl-substituted aromatic analytes (Figure 5) were observed. Similarly, spirobifluorene **2** shows higher affinities than those of **1**. In particular, for the *meta*-substituted 1,3-DEB and 1,3,5-TEB, a great difference in the affinities occurs; this underlines the influence of the sterically demanding analytes.

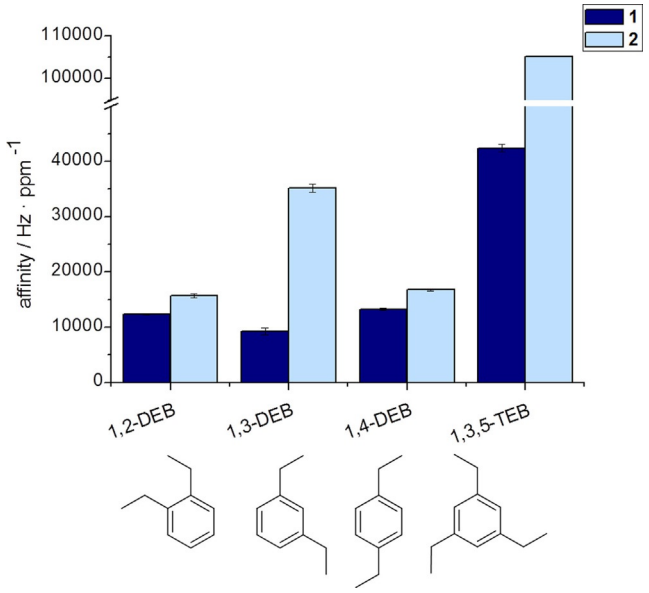


Figure 5. Affinities of **1** and **2** to ethyl-substituted aromatic analytes. DEB = diethylbenzene, TEB = triethylbenzene.

Apart from the detection of aromatic compounds, our aim is to find more selective and even better affinity materials for further hazardous and illicit compounds. In previous studies, we investigated a dendrimer-based affinity material that was highly sensitive and selective for the detection of triacetone triperoxide (TATP).[2b,6a] TATP is an extremely dangerous explosive,[33] which is attracting significant attention as a threat in terrorist attacks.[34] Müllen and co-workers synthesized a polyphenylene dendrimer (**27**) with an outstanding high affinity for TATP and simultaneously low cross-affinities for water or hydrogen peroxide (for the chemical structure of **27**, see the Supporting Information).[2b,6a] The high affinity is attributed to complementary voids in the dendrimer and CH–π and dipole–dipole interactions with the pyridine moieties. Based on the branched architecture with multiple pyridine moieties, the affinities of spirobifluorene **2** towards TATP and its cross-analytes were investigated and compared with the Müllen dendrimer **27** (Figure 6). Similar to dendrimer **27**, spirobifluorene **2** shows promising high affinities for TATP. Unfortunately, however, compound **2** also displays considerably higher cross-affinities to interfering compounds, such as water (factor of ca. 3) or hydrogen peroxide (factor of ca. 2.5), which complicates the selective detection of TATP in the presence of other analytes.

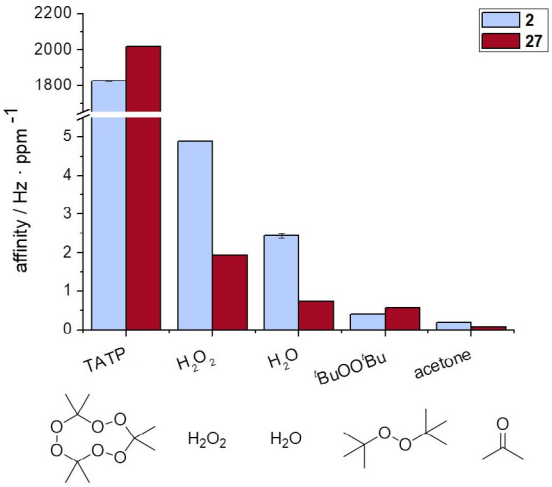


Figure 6. Affinities of **2** compared with **27**; the key sensor material for TATP tracing.

The second class of compounds investigated by QCM in this study is functionalized diazaspirobifluorenes, which contain the nitrogen functions directly in the spirobifluorene core. By differing in their number of functionalizations, the introduced functional groups, and in the functionalized position, conclusions about their binding behavior can be drawn. Figure 7 shows the affinities of diazaspirobifluorenes **14**–**16** and **19** towards benzene, toluene, *m*-xylene, and mesitylene. The unsubstituted diazaspirobifluorene **19** exhibits approximately similar, partly higher, affinities to those of **14**. Difunctionalization with bromine substituents results in no improvement in sensitivity, whereas the affinities of the TMS-substituted diazaspirobifluorenes **15** and **16** differ significantly from the affinities of **14** and **19**. This effect can be observed more clearly with increasing steric demand of the aromatic VOCs. Owing to the difunctionalization of the fluorene moiety of **15** with ethynyl-bridged TMS groups, a widened plane is generated, which induces additional interactions with the analyte. The triple bonds are also capable of interacting by means of π–π interactions, especially towards aromatic compounds, which results in higher affinity signals. Diazaspirobifluorene **16** sets itself apart from the other derivatives by its asymmetric monofunctionalization and by the particular functionalized diazafluorene moiety. Apart from CH–π and π-stacking interactions, breaking of symmetry could be responsible for the high affinities of **16** towards the analytes displayed in Figure 7. Even though the surfaces become more disordered it seems that more defined cavities could be generated. A stronger attraction between affinity material and analyte is a reasonable explanation for the measured affinities. The affinity comparison of the diazaspirobifluorenes towards a variety of aromatic compounds reveals this class as promising for the design of affinity materials.

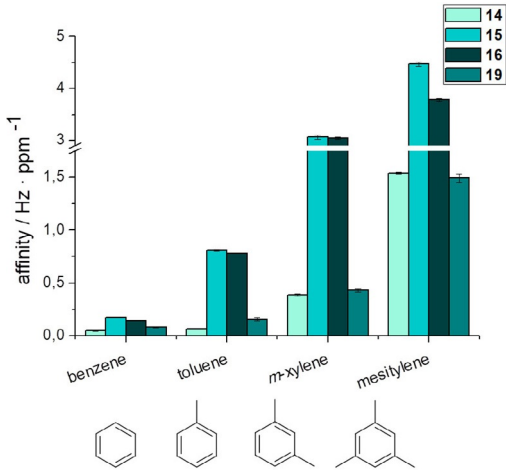


Figure 7. Affinities of diazaspirobifluorenes **14**–**16** and **19** to BTX analytes.

According to the interesting affinity behavior of **15** and **16**, the affinities towards a number of hazardous and illicit compounds, such as explosives, narcotics, or their precursors, were investigated (Figure 8). For example, phenol is a chemical commodity widely used in industrial productions that demonstrably damages the environment and health.[35] Therefore, a fast and reliable detection is of great interest. GBL is still abused as a prodrug for γ-hydroxybutyric acid (GHB),[36] but is barely distinguishable in the presence of ethanol or water.[14b] Furthermore, the detection of acetone in medical and veterinary aspects is of significant interest to indicate metabolic disorders or the progress of a disease.[37] Figure 8 shows the affinities of diazaspirobifluorenes **14**–**16** and **19** for those analytes. Compounds **14** and **19** exhibit no conspicuously high affinities for the aromatic analytes. Core functionalization, except halogen atoms, seems to have a positive influence on the affinity behavior. The diethynyl-bridged TMS derivative **15** displays similar unremarkable affinities for a number of analytes, except phenol, hydrogen peroxide, and water. A strong attraction be-

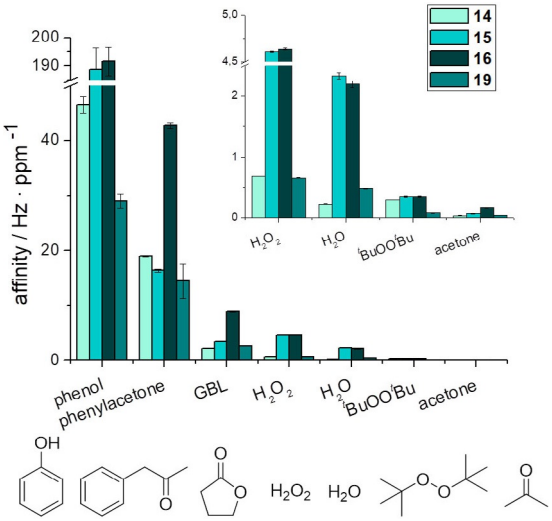


Figure 8. Affinities of diazaspirobifluorenes **14**–**16** and **19** to a variety of hazardous and illicit analytes. GBL = γ-butyrolactone.

tween **15** and the hydroxyl groups is conceivable. The superior affinities of **16** towards phenylacetone, GBL, and acetone are eye-catching. To elucidate the influence of TMS on the electronic structure, TMS-substituted pyridines were applied as a model system.[38] However, TMS groups substituted in the 3-position show only a slightly increase in pK_a value from 5.21 (protonated species) to 5.57 (TMS substituted), which indicates the electron-donating ability of the TMS substituent. A decrease in the pK_a value would increase the acidity of the pyridine derivative, which would favor an interaction between the pyridine nitrogen and the carbonyl oxygen atom of the analytes, resulting in high affinities. For a clarification of these remarkably affinities, further diazaspirobifluorene derivatives with other functional groups and varying substitution pattern will be the subject of future studies.

Conclusion

We presented two new classes of 9,9′-spirobifluorene-based supramolecular architectures with promising properties as affinity materials for the detection of VOCs by QCM. The installation of pyridyl moieties into the rigid spirobifluorene scaffold creates additional platforms for the analyte, resulting in further possibilities for guest interactions. In particular, the branched network of multiple pyridyl groups are convincing for the attraction of guest molecules. The 4,5-diaza-9,9′-spirobifluorene-type derivatives also show high potential for application as host compounds. Their gravimetric evaluation as affinity materials revealed the remarkable influence induced by the number and position of their functionalization. The lack of symmetry owing to monofunctionalization of the diazaspirobifluorene analogue is exposed to be a particularly suitable characteristic for the design of future affinity materials. Therefore, the disordered host surface exhibits more pronounced voids and distinctly increased interaction possibilities. The 4,5-diazaspirobifluorene derivatives seem to be a powerful class that will be investigated in more detail in the future because they open up a new way to increase sensitivity and selectivity for the detection of volatile analytes.

Experimental Section

General

Reactions under an inert gas atmosphere were performed under argon by using standard Schlenk techniques and glassware that was oven-dried prior to use. TLC was performed on aluminum TLC plates (silica gel 60F_{254} from Merck). Detection was performed under UV light ($\lambda = 254$ and 366 nm). Products were purified by column chromatography on silica gel 60 (70–230 mesh) from Merck. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer (300 K) operating at 500.1 (^{1}H) and 125.8 MHz (^{13}C), respectively; a Bruker AM 400 (298 K) spectrometer operating at 400.1 (^{1}H), 128.4 (^{11}B), and 100.6 MHz (^{13}C), respectively; or a Bruker Avance 300 (298 K) spectrometer operating at 300.1 (^{1}H) and 75.5 MHz (^{13}C), respectively. ^{1}H, ^{13}C, and ^{11}B NMR chemical shifts are reported on the δ scale (ppm) relative to signals of residual non-deuterated solvent (^{1}H), the deuterated solvent (^{13}C) as an internal standard, or BF_3·Et_2O in $CDCl_3$ (^{11}B) as an external standard. Signals were assigned on the basis of ^{1}H, ^{13}C, HMQC, and HMBC NMR spectroscopy experiments. For the numbering of the individual nuclei in the compounds, see the Supporting Information. Mass spectra were recorded with Finnigan 95XL (EI) or Bruker micrOTOF-Q (ESI) instruments. Elemental analyses were performed with a Heraeus Vario EL apparatus. Most solvents were dried, distilled, and stored under argon according to standard procedures. All chemicals were used as purchased from commercial sources. 2-(9,9′-Spirobifluorene-2-yl)trifluoromethansulfonate (**3**),[15] 2-bromo-5-(trimethylsilyl)-pyridine (**6**),[18] 5,5′-bis(trimethylsilyl)-2,2′-bipyridine (**7**),[19] 2,2′-bis(4,4,5,5-tetramethyl-1,2,3-dioxaborolan-2-yl)-9,9′-spirobifluorene ((*R*)-**9**),[20a] 2-bromo-5-hydroxypyridine (**11**),[21] 2-bromo-5-methoxypyridine (**12**),[21] 4,5-diazafluoren-9-one (**17**),[23,24] 4,5-diazafluoren-9-(2-biphenyl)ol (**18**),[26] 4,5-diaza-9,9′-spirobifluorene (**19**),[25] 2′,7′-dibromo-4,5-diaza-9,9′-spirobifluorene (**14**),[25] 2-bromo- (**22**) and 2-methoxynicotinic acid methyl ester (**23**),[26] and 2-iodobiphenyl[24] were prepared according to protocols reported in the literature.

Synthesis

5,5′-Bis(9,9′-spirobifluoren-2-yl)-2,2′-bipyridine (1): In a Schlenk flask equipped with reflux condenser and septum, compound **4** (120 mg, 0.27 mmol), **8** (50.0 mg, 0.12 mmol), cesium fluoride (150 mg, 0.98 mmol), and [Pd(PtBu$_3$)$_2$] (6.00 mg) were evacuated and flushed with argon several times. Then THF (5.00 mL) was added and the mixture was heated at reflux for 24 h. After cooling to room temperature water and dichloromethane were added. By the addition of a saturated solution of sodium carbonate, the pH was adjusted to eight and the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with brine and dried with sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: cyclohexane/ethyl acetate = 5/1 + 5% triethylamine). The product was obtained as a white solid (82 mg, 0.10 mmol, 87%). MS (ESI): *m/z* (%): 785.3 (100) $[M+H]^+$, 807.3 (25) $[M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{60}H_{36}N_2+Na]^+$, $[C_{60}H_{36}N_2+H]^+$: 807.2771, 785.2951; found: 807.2747, 785.2924.

Owing to its poor solubility in most organic solvents, compound **1** was transformed into its hydrochloride as follows for NMR spectroscopic measurements: 5,5′-di(9,9′-spirobifluoren-2-yl)-2,2′-bipyri-

dine (50.0 mg, 0.06 mmol) was suspended in methanol (30.0 mL). Hydrochloric acid (42.0 μL, 0.42 mmol) was added and the mixture was stirred for 2 h. After evaporation of the solvent, the product was obtained as a yellow solid that was highly soluble in organic solvents. ^{1}H NMR (500.1 MHz, $CD_3OD/CDCl_3$, 298 K): $\delta = 6.58$ (d, $^3J_{8,7} = {}^3J_{8',7'} = {}^3J_{1',3'} = 7.6$ Hz, 6H; H-8, H-1′/H-8′), 6.85 (s, 2H; H-1), 6.96 (dd, $^3J_{2',1'} = {}^3J_{7',8'} = 7.6$ Hz, $^3J_{2',3'} = {}^3J_{7',6'} = 7.3$ Hz, 4H; H-2′/H-7′), 7.01 (dd, $^3J_{7,6} = 7.3$ Hz, $^3J_{7,8} = 7.6$ Hz, 2H; H-7), 7.23 (dd, $^3J_{3',4'} = {}^3J_{6',5'} = 7.7$ Hz, $^3J_{3',2'} = {}^3J_{6',7'} = 7.3$ Hz, 4H; H-3′/H-6′), 7.25 (dd, $^3J_{6,7} = 7.3$ Hz, $^3J_{6,5} = 7.7$ Hz, 2H; H-6), 7.63 (d, $^3J_{3,4} = 7.5$ Hz, 2H; H-3), 7.72 (d, $^3J_{4',3'} = {}^3J_{5',6'} = 7.7$ Hz, 4H; H-4′/H-5′), 7.76 (d, $^3J_{5,6} = 7.7$ Hz, 2H; H-5), 7.88 (d, $^3J_{4,3} = 7.5$ Hz, 2H; H-4), 8.13 (brs, 2H; H-15), 8.27 (brs, 2H; H-16), 8.79 ppm (brs, 2H; H-18); ^{13}C NMR (125.8 MHz, $CD_3OD/CDCl_3$, 298 K): $\delta = 65.9$ (C-9/C-9′), 120.1 (C-4′/C-5′), 120.5 (C-5), 121.1 (C-4), 122.3 (C-1), 123.3 (C-16), 123.8 (C-1′/C-8′), 123.9 (C-8), 127.1 (C-3), 127.8 (C-2′/C-7′), 127.9 (C-6 and C-3′/C-6′), 128.7 (C-7), 133.5 (C-10), 139.6 (C-14), 139.8 (C-15), 140.2 (C-12), 141.6 (C-11′/C-12′), 143.8 (C-11), 143.9 (C-18), 145.0 (C-17), 147.8 (C-10′/C-13′), 149.1 (C-13), 150.3 ppm (C-2).

(*R*)-2,2′-Bis(5′-methoxy-2,2′-bipyridin-5-yl)-9,9′-spirobifluorene (2): In a Schlenk flask equipped with reflux condenser and septum, compound (*R*)-**9** (70.0 mg, 0.12 mmol), **10** (85.0 mg, 0.27 mmol), cesium fluoride (150 mg, 0.98 mmol), and $[Pd(PtBu_3)_2]$ (6.00 mg) were evacuated and flushed with argon several times. Then THF (5.00 mL) was added and the mixture was heated at reflux for 24 h. After cooling to room temperature, water and dichloromethane were added. By the addition of a saturated solution of sodium carbonate, the pH was adjusted to eight and the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with brine and dried with sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: cyclohexane/ethyl acetate = 5/1 + 5% triethylamine → ethyl acetate). The product was obtained as a light yellow solid (65.0 mg, 94.9 μmol, 79%). $[\alpha]_D^{20} = +541^\circ$ mL dm^{-1} g^{-1} ($c = 1.09$ mg mL^{-1}, $CHCl_3$); ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K): $\delta =$ 3.89 (s, 6H; H-24), 6.81 (d, $^3J_{8,7} = 7.4$ Hz, 2H; H-8), 7.04 (d, $^4J_{1,3} =$ 1.7 Hz, 2H; H-1), 7.16 (ddd, $^3J_{7,8} = 7.4$ Hz, $^3J_{7,6} = 7.5$ Hz, $^4J_{7,5} = 1.0$ Hz, 2H; H-7), 7.28 (dd, $^3J_{21,20} = 8.7$ Hz, $^4J_{21,23} = 2.8$ Hz, 2H; H-21), 7.42 (ddd, $^3J_{6,7} = 7.5$ Hz, $^3J_{6,5} = 7.6$ Hz, $^4J_{6,8} = 1.0$ Hz, 2H; H-6), 7.69 (dd, $^3J_{3,4} = 7.9$ Hz, $^4J_{3,1} = 1.7$ Hz, 2H; H-3), 7.81 (dd, $^3J_{15,16} = 8.4$ Hz, $^4J_{15,18} =$ 2.4 Hz, 2H; H-15), 7.91 (d, $^3J_{5,6} = 7.6$ Hz, 2H; H-5), 7.98 (d, $^3J_{4,3} =$ 7.9 Hz, 2H; H-4), 8.24 (dd, $^3J_{16,15} = 8.4$ Hz, $^5J_{16,18} = 0.7$ Hz, 2H; H-16), 8.30 (d, $^3J_{20,21} = 8.7$ Hz, 2H; H-20), 8.33 (d, $^4J_{23,21} = 2.8$ Hz, 2H; H-23), 8.72 ppm (dd, $^4J_{18,15} = 2.4$ Hz, $^5J_{18,16} = 0.7$ Hz, 2H; H-18); ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 55.8$ (C-24), 66.3 (C-9), 120.2 (C-16), 120.5 (C-5), 120.9 (C-4), 121.1 (C-21), 121.8 (C-20), 122.7 (C-1), 124.3 (C-8), 127.0 (C-3), 128.2 (C-6), 128.4 (C-7), 135.1 (C-15), 135.5 (C-14), 137.0 (C-23), 137.6 (C-2), 141.3 (C-12), 142.0 (C-11), 147.5 (C-18), 148.8 (C-19), 149.0 (C-13), 149.8 (C-10), 154.7 (C-17), 156.2 ppm (C-22); MS (ESI): *m/z* (%): 685.3 (100) $[M+H]^+$, 707.2 (61) $[M+Na]^+$, 1370.5 (18) $[4M+2H]^{2+}$, 1392.5 (11) $[4M+2Na]^{2+}$; HRMS (ESI): *m/z* calcd for $[C_{47}H_{32}N_4O_2+Na]^+$: 707.2417; found: 707.2411.

2-(4,4,5,5-Tetramethyl-1,2,3-dioxaborolan-2-yl)-9,9′-spirobifluorene (4): In a Schlenk flask equipped with reflux condenser and septum, compound **3** (300 mg, 0.65 mmol), potassium acetate (190 mg, 1.94 mmol), bis(pinacolato)diboron (180 mg, 0.71 mmol), $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (53.0 mg), and dppf (36.0 mg, 0.06 mmol) were evacuated and flushed with argon several times. Dry 1,4-dioxane (6.00 mL) was added and the mixture was heated at reflux for 2.5 days. After cooling to room temperature, the reaction was quenched by the addition of water. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water and brine and dried with magnesium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: cyclohexane/ethyl acetate = 20/1 → 5/1). The product was obtained as a light yellow solid (211 mg, 0.48 mmol, 73%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): $\delta =$ 1.27 (s, 12H; H-16), 6.70 (ddd, $^3J_{8,7} = 7.6$ Hz, $^4J_{8,6} = 1.0$ Hz, $^5J_{8,5} =$ 0.7 Hz, 1H; H-8), 6.73 (ddd, $^3J_{1',2'} = {}^3J_{8',7'} = 7.7$ Hz, $^4J_{1',3'} = {}^4J_{8',6'} = 0.7$ Hz, 2H; H-1′/H-8′), 7.10 (ddd, $^3J_{2',1'} = {}^3J_{7',8'} = 7.7$ Hz, $^3J_{2',3'} = {}^3J_{7',6'} = 7.5$ Hz, $^4J_{2',4'} = {}^4J_{7',5'} = 1.1$ Hz, 2H; H-2′/H-7′), 7.11 (ddd, $^3J_{7,6} = 7.5$ Hz, $^3J_{7,8} =$ 7.6 Hz, $^4J_{7,5} = 1.1$ Hz, 1H; H-7), 7.21 (s, 1H; H-1), 7.36 (ddd, $^3J_{6,7} =$ 7.5 Hz, $^3J_{6,5} = 7.5$ Hz, $^4J_{6,8} = 1.0$ Hz, 1H; H-6), 7.37 (ddd, $^3J_{3',4'} = {}^3J_{6',5'} =$ 7.5 Hz, $^3J_{3',2'} = {}^3J_{6',7'} = 7.5$ Hz, $^4J_{3',1'} = {}^4J_{6',8'} = 0.7$ Hz, 2H; H-3′/H-6′), 7.84–7.88 ppm (m, 5H; H-3, H-4, H-5, H-4′/H-5′); ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = 25.0$ (C-16), 66.1 (C-9/C-9′), 83.8 (C-15), 119.5 (C-4), 120.1 (C-4′/C-5′), 120.5 (C-5), 124.1 (C-8), 124.3 (C-1′/C-8′), 127.8 (C-6, C-3′/C-6′), 127.9 (C-2′/C-7′), 128.5 (C-7), 130.4 (C-1), 134.9 (C-3), 141.5 (C-12), 142.1 (C-11′/C-12′), 145.1 (C-11), 147.8 (C-10), 148.7 (C-10′/C-13′), 149.9 ppm (C-13); C-2 is invisible owing to its coupling with ^{11}B; ^{11}B NMR (128.4 MHz, $CDCl_3$, 298 K): $\delta = 30.8$ (B-14); MS (EI): *m/z* (%): 342.1 (50) $[M-C_6H_{12}O]^+$, 442.02(100) $[M]^+$; HRMS (EI): *m/z* calcd for $[C_{31}H_{27}BO_2]^+$: 441.2140; found: 441.2132; elemental analysis calcd (%) for $C_{31}H_{27}BO_2\cdot 1/20\,CH_2Cl_2$: C 83.51, H 6.12; found: C 83.34, H 6.21.

5,5′-Diiodo-2,2′-bipyridine (8): In a three-necked flask equipped with reflux condenser and a gas-washing bottle (filled with saturated solution of sodium thiosulfate), compound **7** (0.40 g, 1.33 mmol) **7** and iodine monochloride (0.42 mL, 1.30 g, 7.99 mmol) in tetrachloromethane (15.0 mL) were heated at reflux for 20 h. After cooling to room temperature, the reaction was quenched by the addition of a solution of sodium hydrogen sulfite (10% in water). The solution was then alkalized with a saturated solution of sodium hydroxide and extracted with dichloromethane. The combined organic layers were washed with water and brine, and finally dried with magnesium sulfate. After evaporation of the solvent, the residue was recrystallized from *n*-hexane to yield a light yellow solid (316 mg, 0.78 mmol, 58%). ^{1}H NMR (400.1 MHz, [D$_6$]DMSO, 298 K): $\delta = 8.16$ (dd, $^3J_{3,4} = 8.3$ Hz, $^5J_{3,6} = 0.7$ Hz, 2H; H-3), 8.33 (dd, $^3J_{4,3} = 8.3$ Hz, $^4J_{4,6} = 2.1$ Hz, 2H; H-4), 8.92 ppm (dd, $^4J_{6,4} =$ 2.1 Hz, $^5J_{6,3} = 0.7$ Hz, 2H; H-6); ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 298 K): $\delta = 95.6$ (C-5), 122.2 (C-3), 145.8 (C-4), 153.3 (C-2), 155.0 ppm (C-6); MS (EI): *m/z* (%): 280.9 (30) $[M-I]^+$, 407.8 (100) $[M]^+$; HRMS (EI): *m/z* calcd for $[C_{10}H_6I_2N_2]^+$: 407.8620; found: 407.8620; elemental analysis calcd (%) for $C_{10}H_6I_2N_2$: C 29.44, H 1.48, N 6.87; found: C 29.31, H 1.74, N 6.75.

5-Iodo-5′-methoxy-2,2′-bipyridine (10): In a three-necked flask equipped with reflux condenser and a gas-washing bottle (filled with a saturated solution of sodium thiosulfate), compound **13** (0.20 g, 0.77 mmol) and iodine monochloride (0.12 mL, 0.38 g, 2.32 mmol) in tetrachloromethane (10.0 mL) were heated at reflux for 20 h. After cooling to room temperature, the reaction was quenched by the addition of a saturated solution of sodium thiosulfate. The solution was then alkalized with a saturated solution of sodium hydroxide and extracted with dichloromethane. The combined organic layers were washed with water and brine, and finally dried with sodium sulfate. After evaporation of the solvent, the crude product was subjected to column chromatography (eluent: cyclohexane/ethyl acetate = 5/1 → 2/1) to yield a pearly solid (178 mg, 0.57 mmol, 74%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): $\delta = 3.91$ (s, 3H; H-7′), 7.30 (dd, $^3J_{4',3'} = 8.8$ Hz, $^4J_{4',6'} = 3.0$ Hz, 1H; H-4′), 8.07 (dd, $^3J_{4,3} = 8.4$ Hz, $^4J_{4,6} = 2.1$ Hz, 1H; H-4), 8.11 (dd, $^3J_{3,4} =$ 8.4 Hz, $^5J_{3,6} = 0.8$ Hz, 1H; H-3), 8.31 (d, $^3J_{3',4'} = 8.8$ Hz, 1H; H-3′), 8.34 (d, $^4J_{6',4'} = 3.0$ Hz, 1H; H-6′), 8.82 ppm (dd, $^4J_{6,4} = 2.1$ Hz, $^5J_{6,3} = 0.8$ Hz,

1H; H-6); ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 55.9 (C-7′), 92.8 (C-5), 121.0 (C-4′), 121.8 (C-3′), 122.3 (C-3), 137.2 (C-6′), 145.2 (C-4), 148.1 (C-2′), 155.0 (C-5′), 155.1 (C-6), 156.5 ppm (C-2); MS (ESI): *m/z* (%): 313.0 (13) $[M+H]^+$, 335.0 (100) $[M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{11}H_9IN_2O+Na]^+$: 334.965; found: 334.9643; elemental analysis calcd (%) for $C_{11}H_9IN_2O$: C 42.33, H 2.91, N 8.98; found: C 42.49, H 3.34, N 8.84.

5-Methoxy-5′-(trimethylsilyl)-2,2′-bipyridine (13): In a Schlenk flask equipped with reflux condenser and septum, THF (22.0 mL) was cooled to −78 °C. *tert*-Butyllithium (3.00 mL; 1.7 M in pentane) was added (yellow solution), followed by **12** (366 mg, 1.95 mmol), and the mixture was stirred for 30 min. After the addition of a suspension of zinc chloride (0.51 g, 3.75 mmol) in THF (9.00 mL), the mixture was allowed to warm to room temperature and stirred for 2.5 h (solution 1, colorless). In another Schlenk flask, compound **6** (345 mg, 1.50 mmol) and $[Pd(PPh_3)_4]$ (87.0 mg, 0.07 mmol) were dissolved in THF (5.00 mL; solution 2). Solution 2 was slowly added to solution 1 and the mixture was stirred for 24 h at room temperature (dark orange). After completion of the reaction (TLC control), it was quenched by adding a saturated solution of ethylenediaminetetraacetic acid (EDTA; 25.0 mL) and stirring for 15 min. By the addition of a saturated solution of sodium carbonate, the pH was adjusted to eight and the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with water and brine, and dried with sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: cyclohexane/ethyl acetate = 5/1 + 5% triethylamine). The product was obtained as a white solid (314 mg, 1.22 mmol, 81%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 0.31 (s, 9H; H-7′), 3.90 (s, 3H; H-7), 7.30 (dd, $^3J_{4,3}$ = 8.7 Hz, $^4J_{4,6}$ = 3.0 Hz, 1H; H-4), 7.88 (dd, $^3J_{4',3'}$ = 7.8 Hz, $^4J_{4',6'}$ = 1.8 Hz, 1H; H-4′), 8.26 (dd, $^3J_{3',4'}$ = 7.8 Hz, $^5J_{3',6'}$ = 1.0 Hz, 1H; H-3′), 8.35 (dd, $^3J_{3,4}$ = 8.7 Hz, $^5J_{3,6}$ = 0.8 Hz, 1H; H-3), 8.36 (d, $^4J_{6,4}$ = 3.0 Hz, 1H; H-6), 8.71 ppm (dd, $^4J_{6',4'}$ = 1.8 Hz, $^5J_{6',3'}$ = 1.0 Hz, 1H; H-6′); ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): δ = −1.2 (C-7′), 55.8 (C-7), 119.7 (C-3′), 121.0 (C-4), 121.8 (C-3), 134.3 (C-5′), 137.1 (C-6), 142.1 (C-4′), 149.2 (C-2), 153.4 (C-6′), 156.2 (C-5), 156.2 ppm (C-2′); MS (ESI): *m/z* (%): 259.1 (100) $[M+H]^+$, 281.1 (27) $[M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{14}H_{18}N_2OSi+H]^+$: 259.1261; found: 259.1266; elemental analysis calcd (%) for $C_{14}H_{18}N_2OSi{\cdot}2/5\,C_4H_8O_2$: C 63.81, H 7.28, N 9.54; found: C 63.39, H 7.08, N 9.88.

2′,7′-Bis({trimethylsilyl}ethynyl)-4,5-diaza-9,9′-spirobifluorene (15): In a Schlenk flask equipped with septum and reflux condenser, compound **14** (50.0 mg, 0.11 mmol), copper(I) iodide (2.00 mg, 0.01 mmol), and $[PdCl_2(PPh_3)_2]$ (7.40 mg, 0.01 mmol) were evacuated and flushed with argon several times. Triethylamine (5.00 mL) and DMF (3.00 mL) were added and the mixture was stirred at room temperature for 10 min. Ethynyltrimethylsilane (0.10 mL, 0.26 mmol) was added and the reaction mixture was heated at reflux overnight. After the reaction was complete (TLC control), it was cooled to room temperature and brine was added. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water and brine, and dried with sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: ethyl acetate). The product was obtained as a light brown solid (33 mg, 64.6 μmol, 59%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 0.15 (s, 18H; H-16), 6.82 (s, 2H; H-1′/H-8′), 7.02–7.13 (m, 4H; H-1/H-8 and H-2/H-7), 7.51 (dd, $^3J_{3',4'}$ = $^3J_{6',5'}$ = 8.0 Hz, $^4J_{3',1'}$ = $^4J_{6',8'}$ = 1.1 Hz, 2H; H-3′/H-6′), 7.76 (d, $^3J_{4',3'}$ = $^3J_{5',6'}$ = 8.0 Hz, 2H; H-4′/H-5′), 8.73 ppm (br s, 2H; H-3/H-6); ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): δ = −0.1 (C-16), 60.5 (C-9/C-9′), 95.8 (C-15), 104.7 (C-14), 120.6 (C-4′/C-5′), 123.2 (C-2′/C-7′), 123.9 (C-2/C-7), 127.6 (C-1′/C-8′), 131.9 (C-1/C-8), 132.6 (C-3′/C-6′), 141.4 (C-11′/C-12′), 142.8 (C-10/C-13), 146.5 (C-10′/C-13′), 150.7 (C-3/C-6), 159.0 ppm (C-11/C-12); MS (ESI): *m/z* (%): 533.2 (100) $[M+Na]^+$, 1043.4 (80) $[2M+Na]^+$, 1554.5 (20) $[3M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{33}H_{30}N_2Si_2+Na]^+$: 533.1840; found: 533.1842.

2-(Trimethylsilyl)-4,5-diaza-9,9′-spirobifluorene (16): Four drops of sulfuric acid were added as a catalyst to a boiling solution of **26** (120 mg, 0.29 mmol) in glacial acetic acid (9.00 mL) and the mixture was heated at reflux overnight. After cooling to room temperature, the reaction was quenched by the addition of cold water. The mixture was then alkalized with a 6 N solution of sodium hydroxide and the aqueous layer was extracted with chloroform. The combined organic layers were dried with sodium sulfate. After evaporation of the solvent, the crude product was subjected to column chromatography (eluent: cyclohexane/ethyl acetate = 2/1). The product was obtained as a light brown solid (82 mg, 0.21 mmol, 71%). ^{1}H NMR (400.1 MHz in $CDCl_3$, 298 K): δ = 0.18 (s, 9H; H-14), 6.72 (d, $^3J_{1',2'}$ = $^3J_{8',7'}$ = 7.6 Hz, 2H; H-1′/H-8′), 7.06 (dd, $^3J_{8,7}$ = 7.8 Hz, $^4J_{8,6}$ = 1.7 Hz, 1H; H-8), 7.09 (dd, $^3J_{7,8}$ = 7.8 Hz, $^3J_{7,6}$ = 4.6 Hz, 1H; H-7), 7.13 (dd, $^3J_{2',1'}$ = $^3J_{7',8'}$ = 7.6 Hz, $^3J_{2',3'}$ = $^3J_{7',6'}$ = 7.5 Hz, $^4J_{2',4'}$ = $^4J_{7',5'}$ = 1.0 Hz, 2H; H-2′/H-7′), 7.19 (d, $^4J_{1,3}$ = 1.4 Hz, 1H; H-1), 7.41 (ddd, $^3J_{3',2'}$ = $^3J_{6',7'}$ = 7.5 Hz, $^3J_{3',4'}$ = $^3J_{6',5'}$ = 7.6 Hz, $^4J_{3',1'}$ = $^4J_{6',8'}$ = 0.9 Hz, 2H; H-3′/H-6′), 7.87 (d, $^3J_{4',3'}$ = $^3J_{5',6'}$ = 7.6 Hz, 2H; H-4′/H-5′), 8.72 (dd, $^3J_{6,7}$ = 4.6 Hz, $^4J_{6,8}$ = 1.7 Hz, 1H; H-6), 8.82 ppm (d, $^4J_{3,1}$ = 1.4 Hz, 1H; H-3); ^{13}C NMR (100.6 MHz in $CDCl_3$, 298 K): δ = −1.06 (C-14), 61.9 (C-9/C-9′), 120.5 (C-4′/C-5′), 123.9 (C-7), 124.0 (C-1′/C-8′), 128.3 (C-2′/C-7′), 128.5 (C-3′/C-6′), 131.8 (C-8), 136.1 (C-2), 136.7 (C-1), 142.0 (C-11′/C-12′), 142.9 (C-10), 144.3 (C-13), 146.4 (C-10′/C-13′), 150.4 (C-6), 154.6 (C-3), 159.0 (C-12), 159.3 ppm (C-11); MS (ESI), *m/z* (%): 391.2 (37.5) $[M+H]^+$, 413.1 (100) $[M+Na]^+$, 803.3 (19) $[2M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{26}H_{22}N_2Si+H]^+$, $[C_{26}H_{22}N_2Si+Na]^+$: 391.1625, 413.1444; found: 391.1626, 413.1424; elemental analysis calcd (%) for $C_{26}H_{22}N_2Si{\cdot}3/10\,C_4H_8O_2$: C 78.56, H 5.61, N 7.02; found: C 78.19, H 5.94, N 6.96.

2′,7′-Bis(4,4,5,5-tetramethyl-1,2,3-dioxaborolan-2-yl)-4,5-diaza-9,9′-spirobifluorene (20): In a Schlenk flask equipped with reflux condenser and septum, compound **14** (50 mg, 0.11 mmol), potassium acetate (61.8 mg, 0.63 mmol), bis(pinacolato)diboron (58.7 mg, 0.23 mmol), $[PdCl_2(dppf)]{\cdot}CH_2Cl_2$ (8.6 mg, 0.01 mmol), and dppf (5.80 mg, 0.01 mmol) were evacuated and flushed with argon several times. Dry 1,4-dioxane (5.00 mL) was added and the mixture was heated at reflux overnight. After cooling to room temperature, the reaction was quenched by the addition of water. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine and dried with sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: ethyl acetate). The product was obtained as a light brown solid (36 mg, 63.1 μmol, 57%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 1.24 (s, 24H; H-16), 7.07 (dd, $^3J_{1,2}$ = $^3J_{8,7}$ = 7.7 Hz, $^4J_{1,3}$ = $^4J_{8,6}$ = 1.7 Hz, 2H; H-1/H-8), 7.11 (dd, $^3J_{2,1}$ = $^3J_{7,8}$ = 7.7 Hz, $^3J_{2,3}$ = $^3J_{7,6}$ = 4.6 Hz, 2H; H-2/H-7), 7.14 (s, 2H; H-1′/H-8′), 7.85–7.89 (m, 4H; H-3′/H-6′ and H-4′/H-5′), 8.73 ppm (dd, $^3J_{3,2}$ = $^3J_{6,7}$ = 4.6 Hz, $^4J_{3,1}$ = $^4J_{6,8}$ = 1.7 Hz, 2H; H-3/H-6); ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 24.9 (C-16), 61.6 (C-9/C-9′), 84.0 (C-15), 120.2 (C-4′/C-5′)*; 123.9 (C-2/C-7), 130.2 (C-1′/C-8′), 132.2 (C-1/C-8), 135.3 (C-3′/C-6′)*; 143.6 (C-10/C-13), 144.6 (C-11′/C-12′), 146.0 (C-10′/C-13′), 150.3 (C-3/C-6), 159.2 ppm (C-11/C-12); *assignment might be interchanged; C-2′/C-7′ is not visible owing to its coupling with ^{11}B; ^{11}B NMR (128.4 MHz, $CDCl_3$, 298 K): δ = 33.0 ppm (B-14); MS (ESI): *m/z* (%): 354.2 (25) $[M+2\,NaHCOO+2H]^+$, 593.3 (100) $[M+Na]^+$,

1163.6 (56) $[2M+Na]^+$, 1733.9 (25) $[3M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{35}H_{36}B_2N_2O_4+Na]^+$: 593.2765; found: 593.2767.

Methyl-5′-(trimethylsilyl)-2,2′-bipyridine-3-carboxylate (24): In a Schlenk flask equipped with reflux condenser and septum, THF (22.0 mL) was cooled to −78 °C. *tert*-Butyllithium (3.30 mL, 5.55 mmol; 1.7 M in pentane) was added (yellow solution), followed by **6** (800 mg, 3.47 mmol), and the mixture was stirred for 30 min. After the addition of a suspension of zinc chloride (1.14 g, 8.33 mmol) in THF (17.0 mL), the mixture was allowed to warm to room temperature and stirred for 2.5 h (solution 1, colorless). In another Schlenk flask, compound **22** (500 mg, 2.31 mmol) and $[Pd(PPh_3)_4]$ (134 mg, 0.12 mmol) were dissolved in THF (5.00 mL; solution 2). Solution 2 was slowly added to solution 1 and the mixture was stirred for 24 h at room temperature (dark orange). After completion of the reaction (TLC control), it was quenched by adding a saturated solution of EDTA (25.0 mL) and stirred for 15 min. By the addition of a saturated solution of sodium carbonate, the pH was adjusted to eight and the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with water and brine, and dried with sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: cyclohexane/ethyl acetate = 5/1→1/1). The product was obtained as a colorless oil (468 mg, 1.63 mmol, 71 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): $\delta = 0.33$ (s, 9H; H-7′), 3.82 (s, 3H; H-8), 7.37 (dd, $^3J_{5,4} = 7.8$ Hz, $^3J_{5,6} = 4.8$ Hz, 1H; H-5), 7.93–7.96 (m, 2H; H-4′ and H-4), 8.11 (dd, $^3J_{3',4'} = 7.8$ Hz, $^5J_{3',6'} = 1.0$ Hz, 1H; H-3′), 8.67 (dd, $^4J_{6',4'} = 1.6$ Hz, $^5J_{6',3'} = 1.0$ Hz, 1H; H-6′), 8.74 ppm (dd, $^3J_{6,5} = 4.8$ Hz, $^4J_{6,4} = 1.7$ Hz, 1H; H-6); ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = -1.2$ (C-7′), 52.6 (C-8), 121.9 (C-5), 122.8 (C-3′), 128.6 (C-5′), 135.5 (C-3), 137.0 (C-4′), 142.2 (C-4), 150.5 (C-6′), 152.6 (C-6), 155.5 (C-2), 156.1 (C-2′), 169.7 ppm (C-7); MS (EI): *m/z* (%): 213.1 (20) $[M-C_3H_9Si]^+$, 228.1 (15) $[M-C_2H_2O_2]^+$, 241.1 (30) $[M-C_3H_9]^+$, 255.1 (75) $[M-CH_3O]^+$, 271.1 (100) $[M-CH_3]^+$, 286.1 (20) $[M]^+$; HRMS (EI): *m/z* calcd for $[C_{15}H_{18}N_2O_2Si]^+$: 286.1138; found: 286.1138; elemental analysis calcd (%) for $C_{15}H_{18}N_2O_2Si \cdot 1/5\,C_6H_{12} \cdot 3/5\,H_2O$: C 61.96, H 6.94, N 9.80; found: C 61.52, H 7.43, N 9.39.

2-(Trimethylsilyl)-4,5-diazafluoren-9-one (25): In a Schlenk flask with a septum, diisopropylamine (1.41 mL, 1.02 g, 10.1 mmol) was dissolved in THF (13.0 mL) and cooled to 0 °C. *n*-Butyllithium (3.77 mL, 0.60 g, 9.44 mmol; 2.5 M in hexane) was added and the mixture was stirred for 15 min at 0 °C (LDA solution). Compound **24** (800 mg, 2.79 mmol) in THF (17.0 mL) was cooled to 0 °C and slowly added to the LDA solution. After stirring for 2 h at room temperature, water (55.0 mL) was added and the mixture was stirred overnight. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine and dried with sodium sulfate. After evaporation of the solvent, the crude product was subjected to column chromatography (eluent: cyclohexane/ethyl acetate = 1/1→ethyl acetate). The product was obtained as a brown solid (197 mg, 0.77 mmol, 28 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): $\delta = 0.36$ (s, 9H; H-14), 7.34 (dd, $^3J_{7,8} = 7.5$ Hz, $^3J_{7,6} = 5.1$ Hz, 1H; H-7), 7.98 (dd, $^3J_{8,7} = 7.5$ Hz, $^4J_{8,6} = 1.6$ Hz, 1H; H-8), 8.10 (d, $^4J_{1,3} = 1.6$ Hz, 1H; H-1), 8.79 (dd, $^3J_{6,7} = 5.1$ Hz, $^4J_{6,8} = 1.6$ Hz, 1H; H-6), 8.85 ppm (d, $^4J_{3,1} = 1.6$ Hz, 1H; H-3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = -1.2$ (C-14), 124.9 (C-7), 128.6 (C-10), 129.5 (C-2), 131.6 (C-8), 136.4 (C-1), 137.7 (C-13), 155.3 (C-6), 159.5 (C-3), 163.7 (C-11), 163.8 (C-12), 190.4 ppm (C-9); MS (ESI): *m/z* (%): 255.1 (20) $[M+H]^+$, 277.1 (100) $[M+Na]^+$, 531.2 (40) $[2M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{14}H_{14}N_2OSi+Na]^+$: 277.0768, found: 277.0770; elemental analysis calcd (%) for $C_{14}H_{14}N_2OSi$: C 66.11, H 5.55, N 11.01; found: C 65.68, H 5.53, N 10.74.

4,5-Diaza-2-(trimethylsilyl)fluorene-9-(2-biphenyl)-ol (26): For this synthesis, two setups were needed, each consisting of a three-necked flask equipped with a dropping funnel and reflux condenser, which was evacuated and flushed with argon several times. In one of the setups, magnesium flakes (40.0 mg, 1.57 mmol) were coated with dry diethyl ether (2.00 mL). To this, a solution of 2-iodobiphenyl (440 mg, 1.57 mmol) in dry diethyl ether (6.00 mL) was added through a dropping funnel, so that the reaction mixture boiled gently. After the solution was added completely, the mixture was heated at reflux for 2 h. After cooling to room temperature, the Grignard solution was transferred to the dropping funnel of the second setup. It was then slowly added to a boiling solution of **25** (200 mg, 0.79 mmol) in THF (15.0 mL). The mixture was heated at reflux for 24 h after the complete addition of the Grignard solution and then cooled to room temperature. The reaction was quenched by the addition of water and the aqueous layer was extracted with chloroform. The combined organic layers were washed with water and brine, and dried with sodium sulfate. The first product fraction was obtained as follows: after evaporation of the solvent, cyclohexane was added to the residue and the suspension was kept in the refrigerator overnight. The light brown precipitate was filtered off, washed with cyclohexane, and dried (99 mg). A second product fraction was obtained by concentrating the filtrate to dryness and purification of the residue by column chromatography (eluent: cyclohexane/ethyl acetate = 1/1). The product was obtained as a light brown solid (130 mg, 0.32 mmol, 40 %). ^{1}H NMR (400.1 MHz in $CDCl_3$, 298 K): $\delta = 0.29$ (s, 9H; H-14), 5.73 (d, $^3J_{8',9'} = 7.1$ Hz, 1H; H-8′), 5.88 (d, $^3J_{12',11'} = 7.1$ Hz, 1H; H-12′), 6.54 (dd, $^3J_{9',10'} = {}^3J_{11',10'} = 7.5$ Hz, $^3J_{9',8'} = {}^3J_{11',12'} = 7.1$ Hz, 2H; H-9′/H-11′), 6.79 (ddd, $^3J_{10',9'} = {}^3J_{10',11'} = 7.5$ Hz, $^4J_{10',12'} = {}^4J_{10',8'} = 1.1$ Hz, 1H; H-10′), 6.89 (dd, $^3J_{6',5'} = 7.1$ Hz, $^4J_{6',4'} = 1.8$ Hz, 1H; H-6′), 6.91 (dd, $^3J_{7,6} = 4.9$ Hz, $^3J_{7,8} = 7.6$ Hz, 1H; H-7), 7.33 (ddd, $^3J_{5',6'} = 7.1$ Hz, $^3J_{5',4'} = 7.5$ Hz, $^4J_{5',3'} = 1.3$ Hz, 1H; H-5′), 7.48 (dd, $^3J_{8,7} = 7.6$ Hz, $^4J_{8,6} = 1.4$ Hz, 1H; H-8), 7.56 (ddd, $^3J_{4',5'} = 7.5$ Hz, $^3J_{4',3'} = 8.1$ Hz, $^4J_{4',6'} = 1.8$ Hz, 1H; H-4′), 7.58 (d, $^4J_{1,3} = 1.4$ Hz, 1H; H-1), 8.12 (dd, $^3J_{6,7} = 4.9$ Hz, $^4J_{6,8} = 1.4$ Hz, 1H; H-6), 8.23 (d, $^4J_{3,1} = 1.4$ Hz, 1H; H-3), 8.55 ppm (dd, $^3J_{3',4'} = 8.1$ Hz, $^4J_{3',5'} = 1.3$ Hz, 1H; H-3′); ^{13}C NMR (100.6 MHz in $CDCl_3$, 298 K): $\delta = -1.0$ (C-14), −78.7 (C-9), 123.5 (C-7), 126.4 (C-9′/C-11′), 126.5 (C-10′), 127.0 (C-3′), 127.5 (C-5′), 127.7 (C-4′), 128.3 (C-8′), 129.1 (C-12′), 131.4 (C-6′), 132.3 (C-8), 135.4 (C-2), 136.8 (C-1), 138.0 (C-2′), 139.8 (C-7′), 140.6 (C-1′), 145.0 (C-10), 146.1 (C-13), 150.2 (C-6), 154.3 (C-3), 157.6 (C-11), 157.7 ppm (C-12); MS (ESI): *m/z* (%): 409.2 (65) $[M+H]^+$, 431.2 (100) $[M+Na]^+$, 817.3 (12.5) $[2M+H]^+$, 839.3 (50) $[2M+Na]^+$; HRMS (ESI): *m/z* calcd for $[C_{26}H_{24}N_2OSi+H]^+$: 409.1731; found: 409.1738; elemental analysis calcd (%) for $C_{26}H_{24}N_2OSi \cdot 2/5\,CH_2Cl_2$: C 71.72, H 5.65, N 6.34; found: C 71.40, H 5.97, N 6.16.

X-ray structure determination

Single-crystal XRD studies on compound **14** were performed on a Nonius KappaCCD diffractometer at 123(2) K with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction on equivalent reflections was performed. Direct methods (SHELXS-97) were used to solve the structures. All non-hydrogen atoms were refined anisotropically by using a full-matrix least-squares refinement on F^2 (SHELXL-2014).[39] Crystal dimensions: 0.30 × 0.20 × 0.20 mm; $C_{23}H_{12}Br_2N_2$; $M_r = 476.17$; monoclinic; space group *C*2/*c*; $a = 18.5334(5)$, $b = 9.9804(4)$, $c = 30.1597(8)$ Å; $\alpha = 90$, $\beta = 96.905(6)$, $\gamma = 90°$; $V = 5538.2(3)$ Å^3; $Z = 12$; $\rho = 1.713$ g cm^{-3}; $\mu = 4.401$ mm^{-1}; $F(000) = 2808$; 10465 reflections ($2\theta_{max} = 26.0°$) measured (5172 unique, $R_{int} = 0.0461$, completeness = 95.6 %); R ($I > 2\sigma(I)$) = 0.0353; wR_2 (all data) = 0.0803. GOF = 0.926 for 366 parameters and no restraint, largest difference between peak and hole 0.56/−0.61 e Å^{-3}.

CCDC 1533190 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

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