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Synthesis of Molecular Tripods Based on a Rigid 9,9′-Spirobifluorene Scaffold

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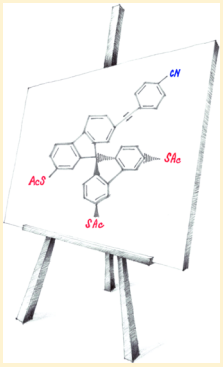
Supporting Information

ABSTRACT: The efficient synthesis of a new tripodal platform based on a rigid 9,9′-spirobifluorene with three acetyl protected thiol groups in the positions 2, 3′ and 6′ for deposition on Au(111) surfaces is reported. The modular 9,9′-spirobifluorene platform provides both a vertical arrangement of the molecular rod in position 7 and its electronic coupling to the gold substrate. To demonstrate the validity of the molecular design, the model compound **24** exposing a *para*-cyanophenylethynyl rod is synthesized. Our synthetic approach is based on a metal−halogen exchange reaction of 2-iodobiphenyl derivative and his subsequent reaction with 2,7-disubstituted fluoren-9-one to afford the carbinol **16**. Further electrophilic cyclization and separation of regioisomers provided the corresponding 2,7,3′,6′-tetrasubstituted 9,9′-spirobifluorene **17** as the key intermediate. The molecular structure of **17** was determined by single-crystal X-ray diffraction crystallography. The self-assembly features of the target compound **24** were analyzed in preliminary UHV-STM experiments. These results already demonstrated the promising potential of the concept of the tripodal structure to stabilize the molecule on a Au(111) surface in order to control the spatial arrangement of the molecular rod.



INTRODUCTION

The spatial control of molecular structures on planar substrates is a remaining challenge. Flat delocalized π-systems have the tendency to spread with the entire π-surface over the substrate driven by van der Waals interactions. While delocalized π-systems are the ideal model compounds of numerous electronic and optical applications, a more perpendicular arrangement with the surface would be desired to profit from their properties. In optical experiments the quenching of molecular excited states is reduced by a perpendicular arrangement, and in electronic applications a perpendicular arrangement is required to separate the π-system from the substrate and to profit from the entire dimension of the molecule. While for most optical set-ups the perpendicular arrangement is the only prerequisite, in electronic applications also the contact point of the molecule with the substrate, which defines the coupling between molecule and electrode (substrate), must be controlled.

Several attempts to increase the spatial control over the arrangement of rigid-rod type structures on Au(111) as flat substrate have been reported. A few examples even profit from the interaction of delocalized π-systems with the flat substrate to arrange a subunit perpendicular to the surface like, e.g., the triazatriangulenium platforms from Herges and co-workers[1] or the [4-(4-pyridyl)phenyl]methyl platform from Aso and co-workers.[2] The most commonly used immobilization chemistry on gold electrodes is the formation of covalent bonds between thiols and gold substrates. To gain spatial control over the molecule's arrangement, structures comprising several thiol groups as anchor points were suggested. Using several anchor points for one molecule not only increases the stability of its binding to the surface but also restricts its tilting with respect to the surface. In order to orient the structures with respect to the surface plane, C_3-symmetric tripods are particularly appealing. A number of tripodal model compounds were synthesized and chemisorbed on gold substrates. As tripodal branching structures carbon atoms (e.g., tetraphenylmethanes),[2−6] silicon atoms (e.g., tetraphenylsilanes),[7−10] or adamantane cages[11−15] were used. The three branches of the tripod were functionalized with identical sulfur-[3,4,6−15] or selenium-[5] containing anchor groups. While some synthetic papers focused mainly on the concept,[7−9,11] initial studies revealed an increased stability of the tripodal contact,[3,4] and surface analysis by scanning probe methods[6,12] or X-ray absorption techniques[14] displayed an enlarged separation due to the increased footprint of the tripod. Further evidence for a perpendicular arrangement of separated molecules were obtained by optical[6,15] and electrochemical[10,13,14] analysis of the samples.

While several of these tripods enable a perpendicular arrangement of rod-type molecular structures, the electronic coupling to the rod's π-system to the metal states is limited due to the tripod architectures comprising sp^3 hybridized atoms. This electronic decoupling of the functional subunit is on the one hand desired to profit from the subunit's optical properties, but on the other hand it represents a considerable handicap for molecular electronic applications.

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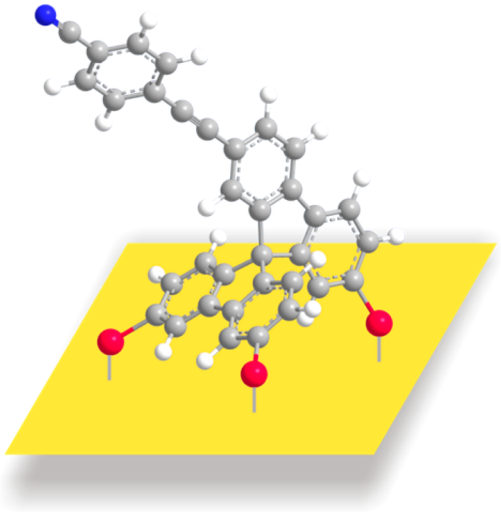
Here we develop a tripodal platform as modular anchoring subunit providing both a vertical arrangement of the molecular rod and its electronic coupling to the gold substrate. In particular we describe a rigid three-dimensional 9,9′-spirobifluorene with thiol anchoring groups in the positions 2, 3′ and 6′ and a synthetic variable position 7 allowing to introduce rigid-rod type structures experiencing an efficient coupling to the metal electrode in a modular manner. A first model compound demonstrating the concept is reported here and displayed in Chart 1, namely, the platform comprising a *para*-cyanophenylethynyl as rigid-rod subunit.

Chart 1



Within this paper the synthesis of the platform is presented in details and the optical properties of the target structures and of key intermediates are discussed. Furthermore, preliminary surface deposition experiments are presented, supporting the hypothesis of the concept of a rigid tripodal platform as well-defined anchor group exposing the rigid rod subunit.

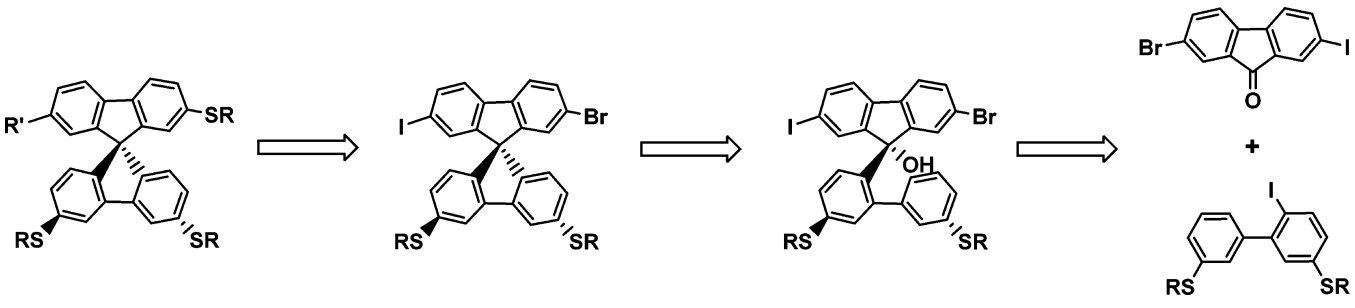
RESULTS AND DISCUSSION

Molecular Design. This core structure was chosen because 9,9′-spirobifluorene and its derivatives form an intriguing class of molecules that exhibit a three-dimensional rigid topology and possess electronic characteristics reflective of two separated conjugated biphenyl moieties fused at a common spiro center. The system can be described electronically as $\pi-\sigma-\pi$, where conjugation between the orthogonal biphenyl groups is limited. While the fluorene subunit with a thiol anchor group in position 2 and ethynyl substituent in position 7 becomes an intrinsic part of the backbone of the immobilized rigid rod, the task of the electronically decoupled second fluorene subunit with thiol anchor groups in positions 3′ and 6′ is to fix and stabilize the upright standing of the rigid rod. The *para*-position of the anchor group immobilizing the molecular rod maximizes its electronic coupling to the electrode[16] and thiol functionalized fluorene model compounds already displayed favorable electronic transport features in single molecule experiments.[17] In order to provide modular variability of the anchoring platform, the extension of the molecular rod *para*-cyanophenylethynyl is introduced at a late stage of the synthesis. Furthermore, the cyano group may serve as spectroscopic marker for further surface measurements.[18]

From a synthetic viewpoint the assembly of the target structure profits from an already developed rich synthetic chemistry forming differently functionalized 9,9′-spirobifluorene. These π-conjugated spiro compounds have attracted much attention because of their promising application in the field of enantioselective molecular recognition,[19] molecular tectonics,[20,21] molecular electronics,[22] catalysis,[23] and optoelectronic materials for the production of organic light-emitting diodes and dye-sensitized solar cells[24] owing to their unique photophysical properties.[25] The first synthesis of 9,9′-spirobifluorene was reported by Clarkson and Gomberg, whom started from 2-iodobiphenyl and fluoren-9-one.[26] At the present time, there are several variations of this procedure with high yield up to 90%. One of the advantages of 9,9′-spirobifluorene is its easy functionalization at the four *para*-positions 2,2′,7,7′. The same strategy was used for 6-fold substitution in the 2,2′,4,4′,7,7′ positions. Also 2,2′-substituted 9,9′-spirobifluorene can be obtained directly by disubstitution of spirobifluorene if deactivating substituents are used. Selective 2,7-substitution and other further advanced substitution patterns have to be arranged in the precursors before the formation of the central spirobifluorene core. Spirobifluorene-based oligomers and polymers usually consist of *para*-interlinked subunits derived from 2- or 2,7-substituted 9,9′-spirobifluorene building blocks, and only few reports dealing with alternative substitution patterns have been reported.

Synthesis. Our retrosynthetic approach is using a similar strategy, which was first described by Clarkson and Gomberg,[26] based on a metal−halogen exchange reaction of 2-iodobiphenyl derivative and his subsequent reaction with 2,7-disubstituted fluoren-9-one to afford the carbinol. Further electrophilic cyclization provided the corresponding 2,7,3′,6′-tetrasubstituted 9,9′-spirobifluorene, which is shown in Chart 2. It should be noted that 2,7,3′,6′-tetrasubstituted 9,9′-spirobifluorene has been reported once so far.[27]

Chart 2. Retrosynthetic Strategy to 2,7,3′,6′-Tetrasubstituted 9,9′-Spirobifluorenes



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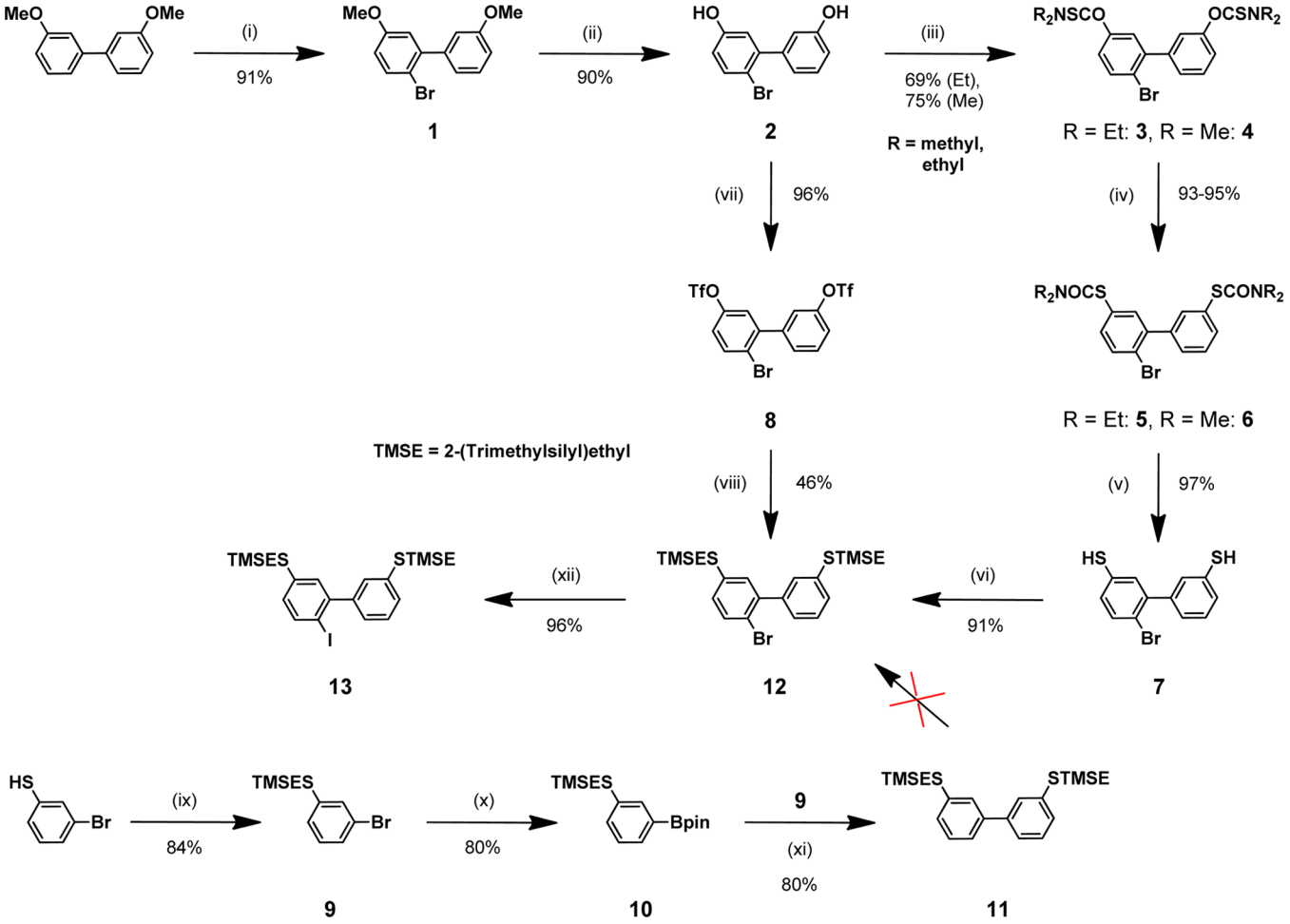
Scheme 1. Synthesis of 2-Iodobiphenyl Derivative 13 by Different Synthetic Pathways[a]



[a]Reagents and conditions: (i) NBS, CH_3CN; (ii) BBr_3, CH_2Cl_2; (iii) NaH, R_2NCSCl, DMF, Δ, (R = Me, Et); (iv) Ph_2O, Δ; (v) (a) KOH, MeOH, (b) H^+; (vi) vinyltrimethylsilane, AIBN, Δ; (vii) Tf_2O, CH_2Cl_2, Et_3N; (viii) $TMS(CH_2)_2SH$, Xantphos, $Pd_2(dba)_3$, iPr_2EtN, dioxane; (ix) vinyltrimethylsilane, $(tert\text{-}BuO)_2$, Δ; (x) (a) *n*-BuLi, THF, (b) $(iPrO)_3B$, (c) H^+, (d) pinacol, Δ; (xi) **9**, $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O; (xii) (a) *n*-BuLi, THF, (b) I_2, THF.

The synthetic strategy to the 2-iodobiphenyl derivative **13**, the first key building block for the preparation of 9,9′-spirobifluorene, is outlined in Scheme 1. The synthesis started with regioselective monobromination of commercially available 3,3′-dimethoxybiphenyl with equimolar amount of NBS in acetonitrile at 0 °C to provide 2-bromobiphenyl derivative **1** in 91% yield. Subsequent demethylation with BBr_3 gave almost quantitatively biphenyl-5,3′-diol **2**. Our following strategy was to introduce the sufur via a Newman−Kwart rearrangement as an efficient method to convert phenols to thiophenols by the thermally activated rearrangement of an *O*-thiocarbamate to the corresponding *S*-thiocarbamate.[28] The *O*,*O*′-dialkylthiocarbamates **3**, **4** were synthesized by treating diol **2** with diethylcarbamoyl chloride, dimethylcarbamoyl chloride respectively using sodium hydride (NaH) as base. We expected that *O*,*O*′-dimethylthiocarbamate **4** tends to crystallize and can therefore by purified more simply. Both *O*,*O*′-dimethyl **4** and *O*,*O*′-diethylthiocarbamate **3** were prepared in order to improve purification of *O*,*O*′-thiocarbamates from the reaction mixture; however, the yield of both derivatives **3**, **4** was almost the same. On the contrary to our expectation, final purification of *O*,*O*′-diethylthiocarbamate **3** was easier, due to the bigger polarity differences between the desired product and byproducts. Then *O*,*O*′-diethyl **3** respectively *O*,*O*′-dimethylthiocarbamate **4** was dissolved in anhydrous diphenyl ether and heated up to 250−260 °C under an argon atmosphere to afford the *S*,*S*′-dialkylthiocarbamates **5**, **6** respectively in almost quantitative yields. After hydrolysis with KOH in methanol, biphenyl-5,3′-dithiol **7** was obtained in 97% yield. Subsequently, the dithiol **7** was protected in a form of 2-(trimethylsilyl)ethyl derivative **12**, profiting from the radical reaction of the thiol groups with vinyltrimethylsilane in the presence of 2,2′-azobis(2-methylpropionitrile) (AIBN) as a radical initiator.[29,30] To have in hand more reactive 2-iodobiphenyl **13** for the further halogen-metal exchange and formation of carbinol **16**, 2-bromobiphenyl **12** was treated with *n*-BuLi and iodinated to provide 2-iodobiphenyl derivative **13** in 96% yield. We have also tried to establish alternative synthetic routes to prepare 2-bromobiphenyl **12** faster, these attempts are outlined in Scheme 1. The first alternative approach is based on triflatation of diol **2** with triflic anhydride to afford triflate **8** in 96% yield. Then the resulting triflate **8** was converted by the C−S cross-coupling reaction with 2-(trimethylsilyl)ethanethiol in the presence of 5 mol % of $Pd_2(dba)_3$ and 2.5 mol % of Xantphos at 60 °C to the desired product **12**.[31,32] This strategy suffers from the poor selectivity of the substitution reaction between both triflates in

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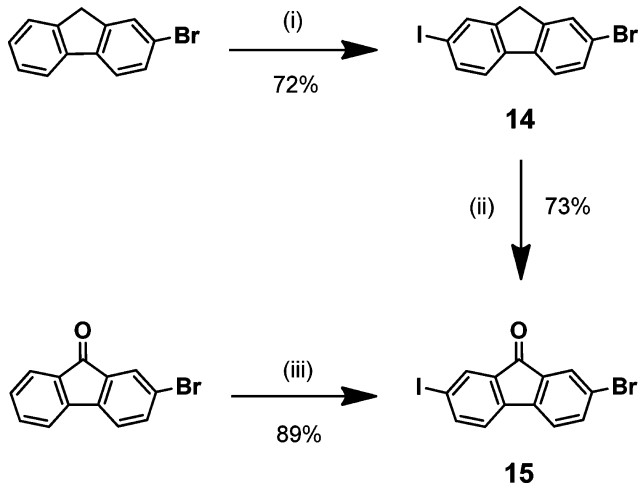
positions 5 and 3′ and the bromine in position 2. The title product **12** was isolated in a low yield, and still contains other regioisomers, which cannot be completely separated. In this case, the chromatography separation does not offer a feasible means for complete separation of the reaction mixture. Another synthetic approach to 2-bromobiphenyl **12** started from the commercial available 3-bromothiophenole, which was protected in a form of 2-(trimethylsilyl)ethyl derivative **9**. Subsequently, the boronic acid was introduced by treating compound **9** with *n*-BuLi solution to perform a bromine−lithium exchange. The lithiated species is quenched by trisopropyl borate to provide boronic acid which was further reacted with pinacol to afford the target pinacol ester **10** in 80% yield. The corresponding biphenyl **11** was prepared via Suzuki cross-coupling reaction of bromide **9** with pinacol ester **10** in 80% yield. For the further monobromination of 2-(trimethylsilyl)ethylsulfanylated biphenyl **11**, many mild methods have been employed to prepare monobrominated biphenyl **12**, but all of these attempts produced mixtures instead of pure single product. We have used NBS as a bromine source and various solvents like acetonitrile, THF and dichloromethane at 0 °C and at an ambient temperature, but the monobromination did not proceed cleanly, and among the desired product **12** also other isomers together with disulfides as byproducts have been observed from the NMR and GC−MS analysis.

We conclude that the most effective and convenient method for the synthesis of the first key intermediate **13** is via a Newman−Kwart rearrangement, as discussed in the beginning of this paragraph.

Two synthetic protocols outlined in Scheme 2 have been developed to obtain 2-bromo-7-iodofluoren-9-one **15**, the second key intermediate for the preparation of 9,9′-spirobifluorene core structure. The first method is based on regioselective monobromination and subsequent iodination of the commercial available 9*H*-fluorene to provide 2-bromo-7-iodo-9*H*-fluorene **14** in 72% yield, which was further oxidized with chromium oxide to the desired fluoren-9-one **15** in 73% yield. However, a more convenient and highly efficient method for the preparation of 2-bromo-7-iodofluoren-9-one **15** is via the regioselective iodination of commercially available 2-bromo-fluoren-9-one, which provided the desired product in 89% yield.

Scheme 2. Synthesis of 2-Bromo-7-iodofluoren-9-one 15[a]



[a]Reagents and conditions: (i) I_2, KIO_3, H^+; (ii), CrO_3, AcOH, Ac_2O; (iii) I_2, H_5IO_6, H^+.

With the both key intermediate **13** and **15** in hand, we have build up the spirobifluorene core via halogen-metal exchange in **13** and following addition of 2-bromo-7-iodofluoren-9-one **15**. Many metalation agents (*n*-BuLi, *tert*-BuLi, Li metal, *i*PrMgCl·LiCl, and Mg turnings) have been employed for the halogen-metal exchange of 2-iodobiphenyl **13**, and it was discovered that both halogen-lithium and halogen-magnesium exchanges work well. However, in case of lithiated species, subsequent addition of 2-bromo-7-iodofluoren-9-one **15** did not afford the desired carbinol **16**, but mainly provided the starting 2-iodobiphenyl derivative **13**. We prepared and used several 2-halogenated biphenyl (2-bromobiphenyl, 2-iodobiphenyl, 2-bromo-5,3′-dimethoxybiphenyl, 2-iodobiphenyl derivative **13**) for the metalation with *n*-BuLi respectively *tert*-BuLi at −78 °C in both THF and diethyl ether to understand this unexpected substitution. After lithiation, subsequent addition of 2-bromo-7-iodofluoren-9-one provided in all cases the reaction mixture containing mainly 2-iodobiphenyl derivatives, which is shown in Scheme 3. The results of these experiments provided evidence, that lithiation proceed almost quantitative with both *n*-BuLi and *tert*-BuLi, but obtained 2-lithiated biphenyl rather eliminated iodine from the position 7 of **15** than attack the carbonyl of fluoren-9-one derivative **15** to afford the desired carbinol **16**. The halogen-magnesium exchange of iodobiphenyl **13** was employed to circumvent the problem. The best results were obtained with *i*PrMgCl·LiCl complex ("turbo-Grignard")[33] as metalation agent at −40 °C, and following addition of fluoren-9-one **15** afforded the corresponding carbinol **16** in 59% yield. This "turbo-Grignard" reagent possesses a high kinetic basicity, favoring halogen/magnesium exchange on substituted aromatic halides over nucleophilic attack on sensitive functional groups. Furthermore, the solubility of the resulting aryl magnesium species is improved, due to the presence of LiCl. Reaction with "turbo-Grignard" reagent formed an organometallic species, which reacted with 2-bromo-7-iodofluornen-9-one **15** exclusively via addition to the carbonyl group and forming the desired carbinol **16**, which is outlined in Scheme 4.

Subsequent electrophilic cyclization of carbinol **16** leads to the regioisomeric mixture of 9,9′-spirobifluorenes **17** and **18**. However, the separation of the two isomers by column chromatography turned out to be problematic due to the small difference in the retention factors between the isomers, which handicapped the isolation of pure regioisomers. Preliminary attempts showed that the desired regioisomer **17** can be separated by fractional crystallization, but only from a **17** enriched solution. Thus, it was important to understand and control the formation of the desired isomer over the other, in order to produce the isomerically pure building block **17** for subsequent functionalization. Screening for acids, solvents and temperatures allowed us to slightly increase the amount of the desired isomer **17** over preferred **18**. Many of the cyclization reactions were attempted with Brønsted acids (HCl, $MeSO_3H$, CF_3COOH), Lewis acid ($BF_3{\cdot}Et_2O$), and solvents (acetic acid, dichloromethane, acetonitrile) at different temperatures −78 to 80 °C and concentrations, and the best ratio (>2/1) of isomers **17**/**18** was obtained with the mixture of hydrochloric acid and acetic acid equal to 1:10 (v/v) at 10 °C, where the concentration of carbinol **16** is 10 mmol/L. This method was used on a multigram scale and reproducibly provided the mixture of regioisomers **17**/**18** with the ratio more than 2/1,

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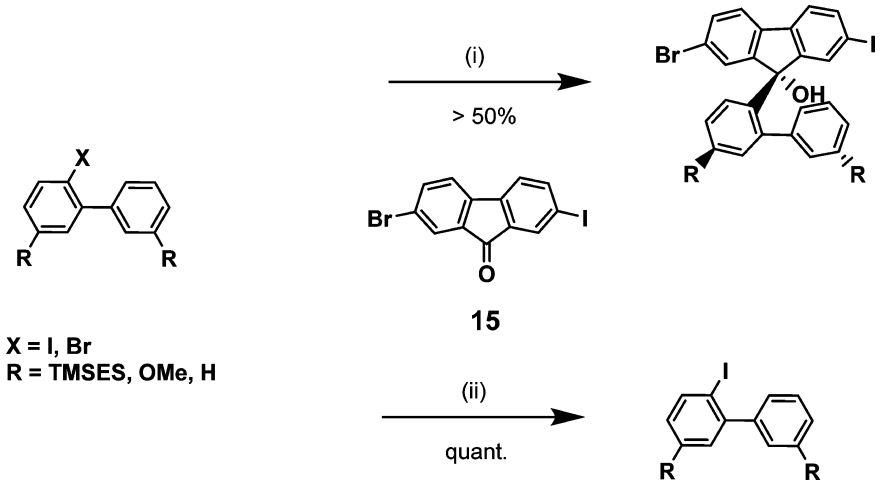
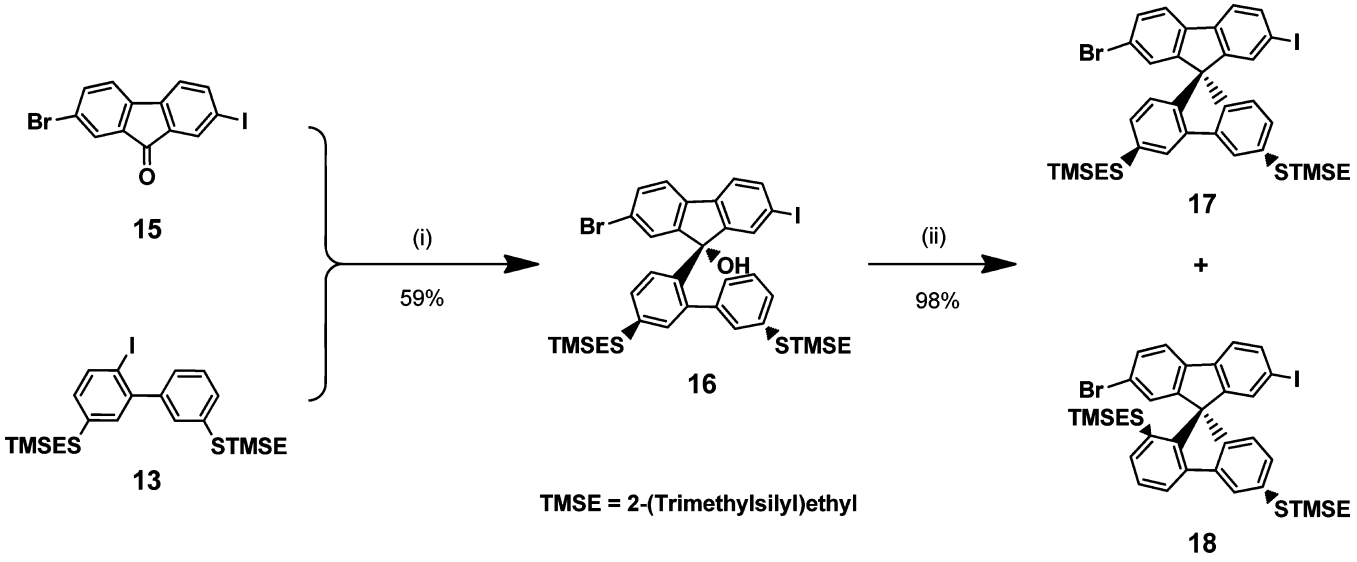
Scheme 3. Synthetic Attempts toward Carbinol[a]



[a]Reagents and conditions: (i) (a) *i*PrMgCl·LiCl, THF, −40 °C, resp. Mg, THF, 50 °C; (b) **15** in THF. (ii) (a) *n*-BuLi, resp. *tert*-BuLi, THF, −78 °C; (b) **15** in THF.

Scheme 4. Synthesis of the Spirobifluorene Regioisomers 17 and 18[a]



[a]Reagents and conditions: (i) *i*PrMgCl·LiCl, THF, −40 °C, (ii) AcOH, HCl.

which was determined from the ^{1}H NMR spectrum of the crude isomeric mixture. To have in hand regioisomeric mixture enriched with the desired isomer **17** is the crucial step for the successful separation. If the ratio is lower than 1.5/1, the separation has not been achieved by fractional crystallization. Further slow recrystallization of the isomeric mixture from ethanol and toluene (10:1, v/v) provided a first crop of the symmetric isomer **17**, a second crop was obtained by the column chromatography of the mother liquor on a large excess of silica gel. The crystals obtained from **17** were of single crystal quality, enabling solid state structure analysis by X-ray diffraction further corroborating the identity of the regioisomer **17** (Figure 1).

With the isomerically pure spirobifluorene derivative **17** in hand, the subsequent functionalization via Sonogashira cross-coupling with acetylenes chemoselectively provided substitution in position 7, which is based on the differential reactivity of iodine and bromine toward the Pd catalyzed substitution conditions. For the assembly of the target compound **21**, 4-ethynylbenzonitrile **20** was required. The synthesis of **20** started from the commercial available 4-iodobenzonitrile, which was coupled with trimethylsilylacetylene via Sonogashira coupling to afford trimethylsilyl protected acetylene derivative **19** in 90% yield. Subsequent cleavage of trimethylsilyl protecting group under basic conditions afforded **20** in almost quantitative yield. For the following Sonogashira coupling of **20** with the 9,9′-spirobifluorne unit, we have used both isomerically pure derivative **17** and the regioisomeric mixture of **17**/**18**, and found out, that the presence of the polar nitrile group permits separation of the target isomeric compounds **21** and **22** by column chromatography on silica gel. Sonogashira coupling reaction of both, **17** and the isomeric mixture of **17**/**18** with 4-ethynylbenzonitrile **20**, gave the desired isomer **21** after column chromatography in yields of 88% and 86% respectively (Scheme 5).

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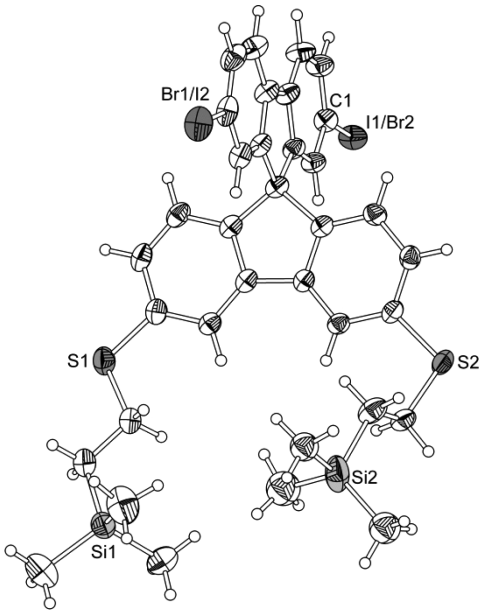


Figure 1. Molecular structure of spirobifluorene **17** determined by single-crystal X-ray diffraction (50% probability of thermal ellipsoids).

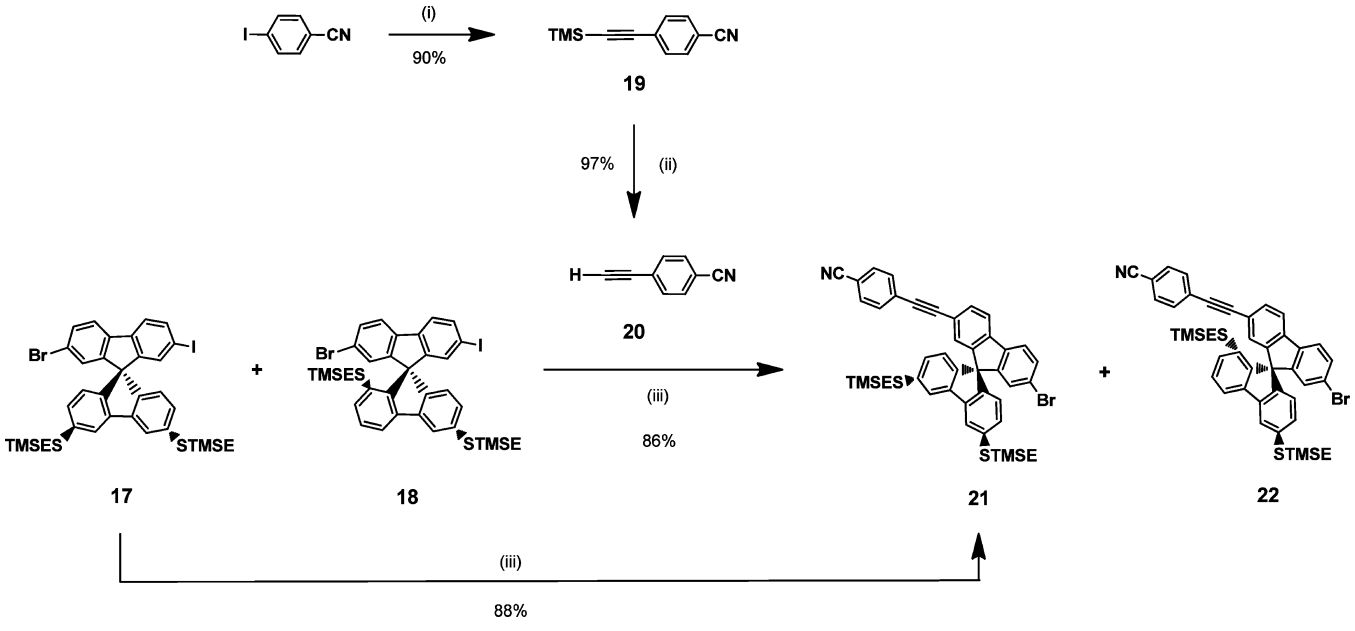
To introduce the third alkylsulfanyl group, isomerically pure spirobifluorene derivative **21** was treated with 2-(trimethylsilyl)ethanthiol in the presence of $Pd_2(dba)_3$, Xantphos and Hünig's base to provide the desired tripodal spirobifluorene **23** in 95% yield which is shown in Scheme 6. For the transprotection of the 2-(trimethylsilyl)ethylsulfanyl groups of compound **23** to acetylsulfanyl groups, several alternative protocols have been reported.[30,34] While the 2-(trimethylsilyl)ethylsulfanyl groups were easily cleaved with tetrabutylammonium fluoride (TBAF), the subsequent treatment with acetyl chloride resulted in the complex mixture of acetylated products and side products, considerably reducing the yield of the desired product **24**. Transprotection of the thiols has been successfully performed using $AgBF_4$ and acetyl chloride (AcCl) in dichloromethane to afford the desired thioacetate **24** in 79% yield.[35] The presence of terminal thioacetate groups allows the spirobifluorene tripod to be bound to a gold surface. The acetyl works as a labile thiol protecting group and can mildly and efficiently be cleaved prior to the physical investigations or in situ upon binding to the gold surface.

All new compounds were fully characterized by conventional analytical and spectroscopy techniques like ^1H and ^{13}C NMR spectroscopy, mass spectrometry, IR, UV–vis and florescence spectrometry, as well as by elemental analysis.

Single-Crystal X-ray Diffraction. The molecular structure of regioisomerically pure spirobifluorene **17** obtained by single-crystal X-ray diffraction is shown in Figure 1. Compound **17** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. As expected the molecules are disordered in a way that the positions of the halogen atoms are occupied in a 0.5:0.5 ratio with iodine or bromine, respectively. Also the methyl groups of one TMS group (at Si2) are disordered over two positions. The planes between the two π-systems are nearly orthogonal (87.3°). The solid state structure of **17** allowed first estimations of the spatial arrangement of the protruding molecular rod. On a plane defined by both sulfur atoms (S1, S2) and Br1/I2 as proxy for the surface the rod direction is the straight through C1 and I1/Br2. The angle between this straight and this surface is 52.8° providing a first approximation of the arrangement of the molecular rod with respect to the surface plane. Details of the crystallographic data, as well as bond lengths and angles, can be found in the Supporting Information.

Optical Properties. The π-conjugation in the spirobifluorenes was investigated by UV–vis measurements. As reported in Figure 2 and Table 1, the absorption spectra of spirobifluorenes **17**–**18** and **21**–**24** in 10^{-5} M dichloromethane solutions at room temperature showed the presence of one sharp band about 260 nm in addition to a broad one around 310–400 nm,

Scheme 5. Coupling of the Rigid Rod Subunit to the Spirobifluorene Subunit 17[a]



[a]Reagents and conditions: (i) Trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF; (ii) K_2CO_3, MeOH, THF; (iii) **20**, $PdCl_2(PPh_3)_2$, CuI, Et_3N.

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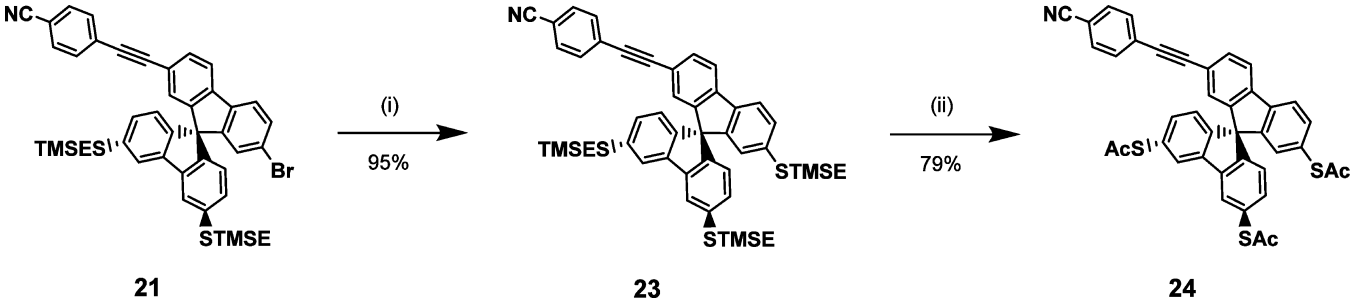
Scheme 6. Introduction of the Third Masked Thiol Group and Subsequent Transprotection[a]



[a]Reagents and conditions: (i) $TMS(CH_2)_2SH$, $Pd_2(dba)_3$, Xantphos, iPr_2EtN, dioxane, Δ; (ii) $AgBF_4$, AcCl, CH_2Cl_2.

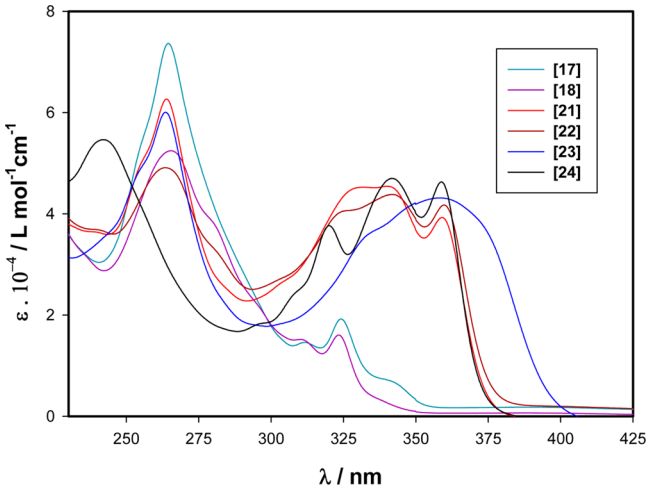


Figure 2. UV−vis spectra of the spirobifluorenes **17**, **18**, **21**−**24** (10^{-5} M solution in CH_2Cl_2).

Table 1. UV−Vis Absorption and Emission Spectral Data of Spirobifluorenes 17, 18, 21−24

	λ_{abs}/nm	ε/L mol^{-1} cm^{-1}	Absorption onset nm (eV)	λ_{em}/ nm
[**17**]	264, 312, 324, 342 (sh)	73 692, 14 615, 19 230, 6604	358 (3.46)	362
[**18**]	266, 310, 324	52 443, 15 204, 16 063	355 (3.49)	367
[**21**]	264, 332, 340, 359	62 687, 45 299, 45 448, 39 254	388 (3.19)	413
[**22**]	263, 326, 342, 360	49 107, 40 682, 43 839, 41 786	395 (3.13)	406
[**23**]	264, 358	60 088, 43 109	420 (2.95)	453
[**24**]	242, 320, 342, 359	54 673, 37 664, 47 009, 46 261	390 (3.17)	396

both laying in the UV region that can be attributed to $\pi-\pi^*$ transmissions. The high energy band of spirobifluorenes **17**−**18** and **21**−**23** at about 260 nm is almost the same and slightly dependent on the substitution. This strong band in UV−vis spectrum of spirobifluorne **18** is about 2 nm bathochromically shifted as compared to the more symmetric isomer **17**. In contrary, the energy band of thioacetate **24** is strongly hypsochromically shifted by 22 nm as compared to 2-(trimethylsilyl)ethylsulfanyl derivative **23**. The broad low energy absorption band about 310−400 nm, in which one can distinguish three maxima, has significantly lower absorption intensity and is further hypsochromically shifted by 20 nm for **17** and **18** compared with the spirobifluorenes **21**−**24**. Which is clearly signing an extension of the conjugation of the core π-spirobifluorene system with 4-cyanophenylethynyl group in position 7. The broadness of the **21**−**24** spectra is due to a rotational freedom of the aryl ring around the C−C bond joining the spirobifluorene unit. The more symmetric regioisomers **17** and **21** exhibit the first maximum at 312 nm, 332 nm respectively bathochromically shifted by 2 nm, 6 nm respectively compared to the corresponding regioisomers **18** and **22**. The UV−vis spectrum also shows the strong bathochromic shift between thioacetate **24** and 2-(trimethylsilyl)ethyl protected spirobifluorene **23**.

The fluorescence spectra of regioisomeric spirobifluorenes **17** and **18** in dichloromethane present the emission peaks at λ_{max} = 362 nm, 367 nm respectively (Figure 3). The emission peak of

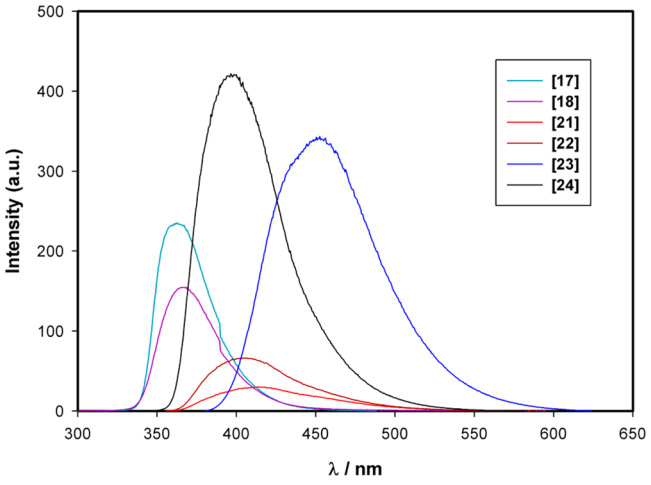


Figure 3. Emission spectra of the spirobifluorenes **17**, **18**, **21**−**24** (λ_{exc} = 264 nm, 10^{-5} M solution in CH_2Cl_2, measured for **17**, **18** with both emission and adsorption slit width = 5 nm, and for **21**−**24** slit widths were 2.5 nm).

spirobifluorene derivatives **21** and **22** (413, 406 nm) is red-shifted with respect to spirobifluorenes **17** and **18** (362, 367 nm) due to the important contribution of the 4-cyanophenylethynyl substituent leading to a more conjugated excited state. Introduction of the third 2-(trimethylsilyl)ethylsulfanyl group in **23** has a remarkable effect not only on the emission maximum, which is strongly red-shifted by 40 nm, but also on the fluorescence intensity. In contrary, transprotection of 2-(trimethylsilyl)ethyl group in **23** to acetyl in **24** leads to the strong blue shift of 57 nm. Both spirobifluorenes **23** and **24** are highly fluorescent blue emitting compounds.

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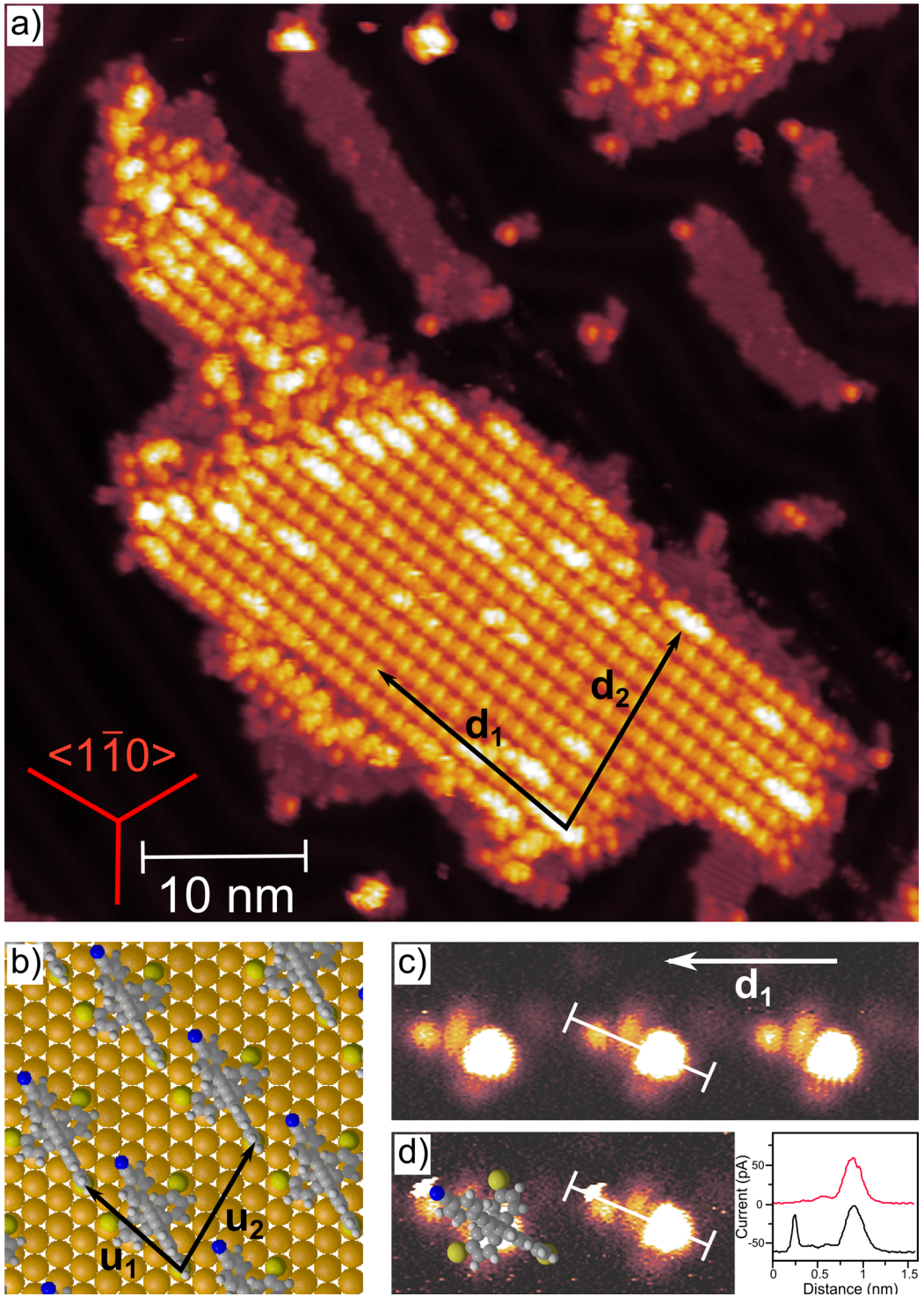

Figure 4. (a) Highly ordered island of molecular tripods (yellow) and remaining CH_2Cl_2 (dark purple) on the Au(111) surface. (b) Unit cell of the molecular islands as extracted from the directions and distances in (a) with the molecular configuration as extracted from (c). (c) Constant height mode image with submolecular resolution. (d) STM image of the same molecules as in (c) scanned at lower distance with a model of the molecule superimposed (model size is to scale). The inset cross sections show the distance between cyano group and the spirobifluorene core.

Surface Deposition of the Tripod 24 and STM Analysis. Of particular interest was the immobilization and the spatial arrangement of the target tripod **24** on an Au(111) surface. The tripod is considered as modular platform enabling the surface deposition of macromolecular structures with increased spatial control, and thus, deposition techniques from dissolved samples are more suitable than sublimation from the solid phase. Here we applied a technique of depositing **24** dissolved in dichloromethane via a pulse-valve, spraying the dissolved molecules into the vacuum and onto the surface (for more details see the Experimental Section). The deposition method allows for higher molecule concentrations in the solution, i.e., a better molecule/impurity ratio as compared to

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the droplet-deposition[36] used for the tripod structures comprising metal complexes.[37]

Figure 4(a) displays a typical STM image recorded from a sample prepared as described in the Experimental Section. Two different island structures can be seen. The dark elongated islands consist of remaining CH_2Cl_2 situated in the *fcc* areas of the herringbone reconstruction of the Au(111) surface, as could be confirmed from deposition of pure CH_2Cl_2. The brighter islands consist of ordered arrays of molecule **24**. The striped pattern of the herringbone reconstruction of the gold is not superimposed to the island structure (in contrast to islands of weakly/physisorbed molecules).[38] This is a first indication that the molecules indeed bind chemically due to the sulfur−gold bond that lifts the herringbone reconstruction.[39] The molecules arrange in periodic rows (direction d_1) that enclose an angle of 11.6° ± 1.5° with the $\langle 1\bar{1}0\rangle$ directions of the gold surface. The direction of periodicity across the rows (direction d_2) encloses an angle of α = 79° ± 2° with respect to direction 1 or 28° ± 2° with respect to $\langle 1\bar{1}0\rangle$. The unit vectors are $\mathbf{u_1}$ = 1.36 nm and $\mathbf{u_2}$ = 1.52 nm, respectively. From the length of the unit vectors and the orientation with respect to the underlying Au(111) surface we can infer a commensurate $\sqrt{21} \times 3\sqrt{3}$ structure for the molecules as shown in Figure 4(b). The commensurability also indicates a strong interaction with the surface. Therefore, the applied deposition procedure from CH_2Cl_2 and subsequent annealing at 400 K apparently promotes the on-surface deprotection, enabling the S−Au bond and immobilization by covalent S−Au bonds of the tripod structures with all three anchoring groups.

By recording images in constant height mode (mapping the current while keeping the distance to the gold sample constant), we were able to resolve a submolecular structure (Figure 4(c)). The elongated form of the molecule is clearly imaged. The middle part of the molecule, where the side legs couple very well to the surface carries large currents and is brightly imaged, while the neck obviously shows weaker coupling, therefore is imaged fainter. The region of the third leg is so far from the tip, that we do not map a current any more (note that in cc mode, the tip does not compensate for height differences and that the tunneling current decreases by an order of magnitude if the distance increases by 1 Å.). If we record constant height images at a distance, where the tip touches the molecule, we will measure a direct and, therefore, strongly increased current. Narrowing the gap between tip and sample this will first occur at the most protruding position, above other parts of the molecules we still obtain a tunneling current and the image is only slightly altered there. This situation is shown in Figure 4(d). The contact is made at the very end of the elongated structure and coincides with the position of the cyano group. The distances in the constant height images fit perfectly with the distances of the corresponding subunits of the molecule. From Figure 4(c) we can infer the angle between the long axis of the molecule with respect to the unit vectors of the unit cell. Figure 4(b) shows the molecules arranged according to these angles. In this orientation all three of the sulfur legs anchor in equivalent positions (in the model we chose on-top for clarity).

All together the quenching of the gold reconstruction, the commensurability with the surface structure and the orientation of the molecule as found by constant height imaging, support the concept of the tripodal structure to stabilize the molecule on the Au(111) surface and to control the spatial arrangement of the molecular rod in an upright orientation.

CONCLUSION

In conclusion we profit from the rigid three-dimensional structure of 9,9′-spirobifluorene as scaffold to control the arrangement of a rigid-rod subunit on a surface. In particular the synthesis of a 9,9′-spirobifluorene derivative with sulfur anchor groups in positions 2, 3′ and 6′ in combination with a modularly addressable position 7 is developed as tripodal platform in order to gain control over the spatial arrangement of the rigid-rod subunit. Interestingly the platform not only provides an emerging rigid-rod subunit, but also its efficient electronic coupling to the (electrode) surface. As first model compound the 4-cyanophenylethynyl derivative **24** is synthesized and fully characterized. Preliminary STM experiments not only display promising self-assembly features of the model compound, but corroborate the validity of the molecular design by a protruding rigid-rod molecular subunit.

The electronic coupling of the rod-type subunit to the substrate is currently under investigation. Synthetically we are interested in investigating modular approaches to other positions of the rigid tripodal platform to increase the spatial control of attached subunits.

EXPERIMENTAL SECTION

Materials. All starting materials and reagents were obtained from commercial suppliers and used without further purification. TLC was performed on silica gel 60 F_{254} plates, spots were detected by fluorescence quenching under UV light at 254 nm, and/or staining with appropriate solutions (anisaldehyde, phosphomolybdic acid, $KMnO_4$). Column chromatography was performed on silica gel 60 (0.040−0.063 mm). All experimental manipulations with anhydrous solvents were carried out in flame-dried glassware under inert atmosphere of argon. Degassed solvents were obtained by three cycles of the freeze−pump−thaw. Tetrahydrofuran, dioxane, toluene and diethyl ether were dried and distilled from sodium/benzophenone under argon atmosphere. Acetonitrile, dichlormethane and triethylamine were dried and distilled from CaH_2 under argon atmosphere. Diphenyl ether was dried over 4 Å molecular sieves. 2-Bromo-9*H*-fluorene was prepared according to published procedure.[40]

Equipment and Measurements. All NMR spectra were recorded at 25 °C in $CDCl_3$, CD_2Cl_2 or acetone-d_6. ^{1}H NMR (500.16 MHz) spectra were referenced to TMS as internal standard (δ_H = 0 ppm) or to the solvent residual proton signal ($CDCl_3$, δ_H = 7.24 ppm; CD_2Cl_2, δ_H = 5.32 ppm; acetone-d_6, δ_H = 2.05 ppm). ^{13}C NMR (125.78 MHz) spectra with total decoupling of protons were referenced to the solvent ($CDCl_3$, δ_C = 77.23 ppm, CD_2Cl_2, δ_C = 54.00 ppm, acetone-d_6, δ_C = 29.92 ppm). ^{19}F{^{1}H} NMR (470.57 MHz) spectra were referenced to $CFCl_3$ as an external standard in a coaxial capillary (δ_F = 0.00 ppm). ^{11}B{^{1}H} NMR (160.47 MHz) spectra were referenced to $BF_3{\cdot}Et_2O$ as an external standard in a coaxial capillary (δ_B = 0.00 ppm). For correct assignment of both ^{1}H and ^{13}C NMR spectra, the ^{1}H−^{1}H COSY, ^{13}C DEPT-135, HSQC and HMBS experiments were performed; EI MS spectra were recorded with a GC−MS instrument (samples were dissolved in diethyl ether, chloroform or introduced directly using direct injection probes DIP, DEP) and *m*/*z* values are given along with their relative intensities (%) at an ionizing voltage of 70 eV. UV−vis spectra were recorded with a UV−vis spectrophotometer in a 1 cm quartz cell at ambient temperature (extinction coefficients are given below in units of L mol^{-1} cm^{-1}). Fluorescence spectra were measured at room temperature in a 1 cm quartz cell. HRMS spectra were obtained with an ESI-TOF mass spectrometer. IR spectra were measured in KBr pellets. Analytical samples were dried at 40−100 °C under reduced pressure (10^{-2} mbar). Melting points were measured with a melting point apparatus and are not corrected. Elemental analyses were obtained using an elemental analyzer. Molecules have been deposited onto an Au(111) surface by spray deposition. The gold single crystal was cleaned by repeated cycles of argon ion sputtering and annealing to 720 K. The clean crystal was transferred to a simple

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vacuum chamber (ca. 5 mbar). A droplet of **24** dissolved in CH_2Cl_2 (conc. approximately 9×10^{-5} M) was sprayed into the chamber by opening the pulse valve for 10 ms. This way, a mist including the dissolved molecules is deposited onto the sample. The sample was then transferred to UHV and mildly annealed at T = 400 K for 60 min to remove remaining solvent molecules. The sample was then transferred to our custom built scanning tunneling microscope (STM). STM images were measured in constant current mode at 5 K.

*2-Bromo-5,3′-dimethoxy-1,1′-biphenyl (**1**).*[20,41] To a solution of 3,3′-dimethoxybiphenyl (12 g, 56 mmol) in dry acetonitrile (130 mL) stirred under argon at −5 °C was dropwise added a solution of NBS (10 g, 56 mmol) in dry acetonitrile (130 mL) over 1 h. The slightly yellow solution was stirred at 0 °C for an additional 4 h, after which the reaction mixture was heated up to room temperature and stirred overnight. The completion of the reaction was checked by TLC (Hex:CH_2Cl_2 = 2:1). Water (50 mL) was added, and organic solvents were evaporated under reduced pressure. The aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic layer was subsequently washed with Na_2SO_3 (60 mL, 10%), brine (60 mL), and dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude light yellow oil was purified by column chromatography on silica gel (2000 g) in the mixture of hexane:CH_2Cl_2 equal to 8:1 to afford pure product **1** (14.95 g, 91%) as a colorless oil that crystallized on standing (R_f = 0.28, Hex:CH_2Cl_2 = 4:1): mp 64−66 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 3.80 (s, 3H, CH_3), 3.83 (s, 3H, CH_3'), 6.80 (dd, J = 9 Hz, J = 3.5 Hz, 1H, C^{4}H), 6.89 (d, J = 3.5 Hz, 1H, C^{6}H), 6.85−6.90 (m, 1H, C$^{4'}$H), 6.91−6.95 (m, 1H, C$^{2'}$H), 6.96−7.00 (dt, J = 8 Hz, J = 1 Hz, 1H, C$^{6'}$H), 7.31−7.37 (td, J = 7.5 Hz, J = 1 Hz, 1H, C$^{5'}$H), 7.54 (d, J = 8.5 Hz, 1H, C^{3}H); ^{13}C NMR (125.8 MHz, CD_2Cl_2) δ ppm 55.8 (CH_3), 56.1 (CH_3'), 113.2 (C^2), 113.7 (C$^{4'}$H), 115.3 (C^{4}H), 115.6 (C$^{2'}$H), 117.2 (C^{6}H), 122.2 (C$^{6'}$H), 129.6 (C$^{5'}$H), 134.2 (C^{3}H), 143.0 (C^1), 143.8 (C$^{1'}$), 159.5 (C^5), 159.8 (C$^{3'}$); EI MS m/z (%) 294 (99), 292 (100, M$^+$), 213 (12), 198 (25), 139 (26), 86 (26); IR (KBr) ν cm^{-1} 3006 (w, ν(=CH)), 2958 (m) and 2936 (m, ν_{as}(CH_3)), 2857 (m, ν_s(CH_3)), 1591 (s) and 1567(s, ν(CC), Ph), 1491 (m), 1464 (s), 1438 (s), 1285 (s), 1254 (s), 1231 (vs), 1204 (s), 1174 (m), 1049 (m, Ph), 1031 (vs, Ph), 1013 (s), 873 (m, β_{as}(CH_3)), 804 (s), 781 (m), 700 (m) and 601 (m, ν(CH)). Anal. Calcd for $C_{14}H_{13}BrO_2$ (293.16): C, 57.36; H, 4.47. Found: C, 57.08; H, 4.61.

*2-Bromo-1,1′-biphenyl-5,3′-diol (**2**).*[27] To a solution of **1** (15 g, 51 mmol) in dry dichloromethane (350 mL) stirred under argon at −78 °C was dropwise added BBr_3 (150 mL, 150 mmol, 1 M in CH_2Cl_2) over 30 min. The dark red reaction mixture was stirred at −78 °C for an additional 1 h, and then allowed to warm to room temperature and stirred at room temperature for 26 h. The completion of the reaction was checked by TLC (Hex:CH_2Cl_2 = 2:1, Hex:EtOAc = 1:1). The flask was placed in an ice bath and water (250 mL) was slowly added. The aqueous layer was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic layer was subsequently washed with Na_2SO_3 (100 mL, 10%), brine (100 mL), and dried over magnesium sulfate. After filtration and evaporation of the solvent, the crude light brown oil was purified by column chromatography on silica gel (1500 g) in the gradient of hexane:EtOAc equal to 8:1−2:1. The product **2** was isolated as a light brown solid (12.15 g) in 90% yield (R_f = 0.58, Hex:EtOAc = 1:1): mp 142−144 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ ppm 6.75−6.81 (td, J = 8.5 Hz, J = 3 Hz, 1H, C^{4}H), 6.82−6.88 (m, 4H, C$^{2,2',4',6'}$H), 7.25 (m, 1H, C$^{5'}$H), 7.48 (d, J = 8.5 Hz, 1H, C^{5}H), 8.61 (bs, 2H, OH); ^{13}C NMR (125.8 MHz, acetone-d_6) δ ppm 111.8 (C^6), 115.5 (C$^{4'}$H), 117.1 (C$^{2'}$H), 117.2 (C^{4}H), 119.0 (C^{2}H), 121.3 (C$^{6'}$H), 130.0 (C$^{5'}$H), 134.7 (C^{5}H), 143.5 (C$^{1'}$), 144.4 (C^1), 157.8 (C$^{3'}$), 157.9 (C^5); IR (KBr) ν cm^{-1} 3234 (bs, ν(OH)), 1582 (s, ν(CC), Ph), 1458 (s), 1453 (s), 1429 (s), 1308 (s), 1255 (m), 1236 (vs), 1218 (vs), 1178 (vs), 1021 (w), 941 (w), 858 (m), 832 (m), 808 (m), 780 (m), 696 (m, ν(CH)); ESI(−) HRMS Calcd for $C_{12}H_8BrO_2$ ([M − H]$^-$, 262.9713), found m/z 262.9710. Anal. Calcd for $C_{12}H_9BrO_2$ (265.11): C, 54.37; H, 3.42. Found: C, 55.09; H, 3.80.

*O,O′-(2-Bromo-1,1′-biphenyl-5,3′-diyl) bis(diethylthiocarbamate) (**3**).* A 500 mL three-necked flask fitted with a dropping funnel, a reflux condenser, an argon inlet and a magnetic stirring bar was charged with NaH (3.63 g, 90.6 mmol, 60% in mineral oil) and dry DMF (80 mL) under argon. After cooling to −5 °C (ice bath, NaCl) a solution of **2** (6 g, 2.65 mmol) in dry DMF (80 mL) was dropwise added over 30 min. [Note: Where the reaction mixture solidifies, more DMF was added to enable efficient stirring.] After the addition was complete, stirring was continued for 2 h at room temperature, then the reaction suspension was cooled down to ∼0 °C, and *N*,*N*-diethylthiocarbamoyl chloride (15.2 g, 100 mmol) was added portionwise as a solid. The reaction mixture was allowed to warm to room temperature, stirred at room temperature for 2 h, and then at 80 °C for 12 h. After cooling to room temperature, the yellow suspension was poured into a mixture of crushed ice (ca. 500 g) and CH_2Cl_2 (400 mL), and the two phases were separated. The aqueous phase was washed with CH_2Cl_2 (3 × 150 mL). The combined organic layer was subsequently washed with NaOH (150 mL, 2% aqueous solution), brine (100 mL), and dried over magnesium sulfate. After filtration and evaporation of all solvents, the crude brown oil was purified by column chromatography on silica gel (1200 g) in the gradient of hexane:CH_2Cl_2 equal to 2:1−1:2 to provide *O*-thiocarbamate **3** as a pale yellow oil (7.74 g) in 69% yield (R_f = 0.28, Hex:EtOAc = 5:1): ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 1.27−1.35 (m, 12H, CH_3), 3.65−3.72 (m, 4H, CH_2), 3.84−3.91 (m, 4H, CH_2), 6.97 (dd, J = 9 Hz, J = 3 Hz, 1H, C^{4}H), 7.08−7.10 (m, 1H, C$^{4'}$H), 7.10−7.12 (m, 1H, C^{2}H), 7.13−7.15 (m, 1H, C$^{2'}$H), 7.32 (dt, J = 8 Hz, J = 1H, C$^{6'}$H), 7.45 (td, J = 8 Hz, J = 1H, C$^{5'}$H), 7.67 (d, J = 9 Hz, 1H, C^{5}H); ^{13}C NMR (125.8 MHz, CD_2Cl_2) δ ppm 12.06 (CH_3), 12.12 (CH_3), 13.88 (CH_3), 13.90 (CH_3), 44.95 (CH_2), 45.00 (CH_2), 48.9 (CH_2), 49.0 (CH_2), 119.1 (C^6), 122.9 (C^{2}H), 124.3 (C^{4}H), 124.5 (C$^{2'}$H), 126.3 (C$^{4'}$H), 127.2 (C$^{6'}$H), 129.2 (C$^{5'}$H), 134.1 (C^{5}H), 141.8 (C$^{1'}$), 142.7 (C^1), 153.8 (C^3), 154.4 (C$^{3'}$), 186.7 (C=S), 187.2 (C=S); IR (KBr) ν cm^{-1} 3056 (w, ν(=CH)), 2976 (m) and 2934 (m, ν_{as}(CH_2, CH_3)), 2873 (w, ν_s(CH_2, CH_3)), 1584 (w) and 1569 (w, ν(CC), Ph), 1513 (vs), 1458 (s), 1428 (s), 1316 (s), 1286 (s), 1231 (s), 1197 (s), 1174 (s), 1118 (m), 1094 (m), 1022 (m), 965 (w), 944 (w), 909 (w), 875 (w, β_{as}(CH_2, CH_3)), 789 (m), 697 (m) and 667 (w, ν(CH)); EI MS m/z (%) 496 (2), 494 (2, M$^+$), 415 (1), 116 (100), 100 (77), 88 (92), 84 (28), 72 (67), 60 (49). Anal. Calcd for $C_{22}H_{27}BrN_2O_2S_2$ (495.49): C, 53.33; H, 5.49; N, 5.65. Found: C, 53.41; H, 5.45; N, 5.71.

*O,O′-(2-Bromo-1,1′-biphenyl-5,3′-diyl) bis-(dimethylthiocarbamate) (**4**).* The desired product was prepared according to the method described for the preparation of **3**, starting from **2** (34 g, 128 mmol) in dry DMF (300 mL), NaH (14.8 g, 370 mmol, 60% in mineral oil) in dry DMF (300 mL) and *N*,*N*-dimethylthiocarbamoyl chloride (47.5 g, 384 mmol). The reaction mixture was heated at 80 °C for 26 h under argon atmosphere. The completion of the reaction was checked by TLC (Hex:EtOAc = 1:1). The crude reaction mixture was purified by column chromatography on silica gel (4000 g) in the gradient of hexane:CH_2Cl_2 equal to 2:1−1:2. The *O*-thiocarbamate **4** was isolated as a white foamy solid (42.1 g) in 75% yield (R_f = 0.38, CH_2Cl_2): mp 67−68 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.32 (m, 6H, CH_3), 3.43 (m, 6H, CH_3), 6.93 (dd, J = 8.5 Hz, J = 3 Hz, 1H, C^{4}H), 7.04−7.08 (m, 1H, C$^{4'}$H), 7.08−7.10 (m, 1H, C^{2}H), 7.11−7.14 (m, 1H, C$^{2'}$H), 7.32 (dt, J = 8.5 Hz, J = 1H, C$^{6'}$H), 7.42 (td, J = 8 Hz, J = 1H, C$^{5'}$H), 7.63 (d, J = 8.5 Hz, 1H, C^{5}H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 38.98 (CH_3), 39.00 (CH_3), 43.48 (CH_3), 43.54 (CH_3), 119.2 (C^6), 122.5 (C^{2}H), 123.8 (C^{4}H), 124.1 (C$^{2'}$H), 125.9 (C$^{4'}$H), 127.2 (C$^{6'}$H), 128.9 (C$^{5'}$H), 133.8 (C^{5}H), 141.4 (C$^{1'}$), 142.4 (C^1), 153.2 (C^3), 153.8 (C$^{3'}$), 187.4 (C=S), 187.8 (C=S); IR (KBr) ν cm^{-1} 3054 (vw, ν(=CH)), 2932 (m, ν_{as}(CH_3)), 2870 (w, ν_s(CH_3)), 1573 (m, ν(CC), Ph), 1538 (vs), 1459 (s), 1393 (vs), 1285 (s), 1254 (m), 1203 (vs), 1181 (s), 1126 (vs), 1062 (m), 1021 (m), 974 (w), 909 (vw), 875 (w, β_{as}(CH_3)), 838 (m), 818 (w), 793 (m), 698 (m, ν(CH)); EI MS m/z (%) 440 (2), 438 (2, M$^+$), 88 (100), 86 (72), 84 (93), 72 (92), 51 (31), 49 (82), 47 (14), 44 (11). Anal. Calcd for $C_{18}H_{19}BrN_2O_2S_2$ (439.39): C, 49.20; H, 4.36; N, 6.38. Found: C, 49.51; H, 4.48; N, 6.25.

*S,S′-(2-Bromo-1,1′-biphenyl-5,3′-diyl) bis(diethylthiocarbamate) (**5**).* A 250 mL Schlenk flask fitted with a reflux condenser, an argon inlet and a boiling chips was charged with *O*-thiocarbamate **3** (7.1 g, 14.3 mmol) and dry diphenyl ether (80 mL) under argon. The flask

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was heated at 250−260 °C for 10 h under argon in a mineral oil bath. After cooling to room temperature, diphenyl ether was distilled off under the reduced pressure (10^{-2} mbar) at 130 °C, and the crude brown oil was purified by column chromatography on silica gel (2300 g) in the gradient of hexane:CH_2Cl_2 = 1:6−pure CH_2Cl_2 to provide *S*-thiocarbamate **5** as a pale yellow oil (6.8 g) in 95% yield (R_f = 0.21, CH_2Cl_2:MeOH = 100:1): ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.15 and 1.25 (bs, 12H, CH_3), 3.37−3.45 (m, 8H, CH_2), 7.32 (dd, J = 8 Hz, J = 2 Hz, 1H, C^4H), 7.39−7.45 (m, 2H, $C^{6'}$H, $C^{5'}$H), 7.45−7.47 (m, 1H, C^2H), 7.50−7.55 (m, 2H, $C^{4'}$H, $C^{2'}$H), 7.64 (d, J = 8 Hz, 1H, C^5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 13.4 (CH_3), 14.1 (CH_3), 42.7 (CH_2), 124.0 (C^6), 128.6 ($C^{6'}$H, C^3), 128.9 ($C^{3'}$), 130.4 ($C^{5'}$H), 133.7 (C^5H), 135.3 ($C^{4'}$H), 136.2 (C^4H), 136.4 ($C^{2'}$H), 138.2 (C^2H), 141.0 ($C^{1'}$), 142.3 (C^1), 165.00 (C═O), 165.6 (C═O); IR (KBr) ν cm^{-1} 3058 (w, ν(═CH)), 2974 (m) and 2934 (w, $\nu_{as}(CH_2, CH_3)$), 2873 (w, $\nu_s(CH_2, CH_3)$), 1664 (vs, ν(C═O)), 1593 (vw) and 1576 (vw, ν(CC), Ph), 1453 (m), 1405 (s), 1380 (m), 1362 (m), 1307 (m), 1248 (s), 1217 (s), 1117 (s), 1098 (s), 1071 (m), 1019 (m), 941 (w), 887 (w, $\beta_{as}(CH_2, CH_3)$), 853 (s), 790 (m), 697 (w) and 659 (m, ν(CH)); EI MS m/z (%) 496 (6), 494 (6, M^+), 100 (100), 86 (73), 84 (85), 72 (71), 51 (42), 49 (77), 44 (19). Anal. Calcd for $C_{22}H_{27}BrN_2O_2S_2$ (495.49): C, 53.33; H, 5.49; N, 5.65. Found: C, 53.50; H, 5.37; N, 5.52.

*S,S′-(2-Bromo-1,1′-biphenyl-5,3′-diyl) bis-(dimethylthiocarbamate) (**6**).* The product was prepared according to the method described for the preparation of *S*-thiocarbamate **5**, starting from **4** (13 g, 29.6 mmol) in dry diphenyl ether (120 mL). The reaction mixture was heated at 250−260 °C for 16 h under argon atmosphere. The crude reaction mixture was purified by column chromatography on silica gel (3000 g) in the gradient of hexane:EtOAc equal to 3:1−2:1. The pure product **6** was isolated as a clear sticky solid (12.1 g) in 93% yield (R_f = 0.31, Hex:EtOAc = 1:1): ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.01 (bs, 6H, CH_3), 3.05 (bs, 6H, CH_3), 7.30 (dd, J = 8 Hz, J = 2 Hz, 1H, C^4H), 7.34−7.44 (m, 2H, $C^{6'}$H, $C^{5'}$H), 7.44−7.46 (m, 1H, C^2H), 7.46−7.54 (m, 2H, $C^{4'}$H, $C^{2'}$H), 7.64 (d, J = 8 Hz, 1H, C^5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 37.1 (CH_3), 124.1 (C^6), 128.5 (C^3), 128.6 ($C^{6'}$H), 128.8 ($C^{3'}$), 130.4 ($C^{5'}$H), 133.7 (C^5H), 135.2 ($C^{4'}$H), 136.1 (C^4H), 136.4 ($C^{2'}$H), 138.1 (C^2H), 141.0 ($C^{1'}$), 142.2 (C^1), 166.2 (C═O), 166.8 (C═O); IR (KBr) ν cm^{-1} 3054 (w, ν(═CH)), 2931 (m, $\nu_{as}(CH_3)$), 2865 (w, $\nu_s(CH_3)$), 1669 (vs, ν(C═O)), 1592 (w) and 1534 (m, ν(CC), Ph), 1455 (m), 1396 (s), 1363 (s), 1286 (m), 1256 (s), 1203 (s), 1120 (bs), 1094 (s), 1062 (m), 1018 (m), 904 (m, $\beta_{as}(CH_3)$), 815 (w), 792 (m), 687 (m) and 652 (m, ν(CH)); EI MS m/z (%) 440 (11), 438 (10, M^+), 88 (18), 86 (87), 84 (95), 72 (100), 51 (42), 49 (92), 47 (16), 44 (13). Anal. Calcd for $C_{18}H_{19}BrN_2O_2S_2$ (439.39): C, 49.20; H, 4.36; N, 6.38. Found: C, 49.01; H, 4.53; N, 6.26.

*2-Bromo-1,1′-biphenyl-5,3′-dithiol (**7**).* Solid KOH was added portionwise to a degassed solution of *S*-thiocarbamate **5** (2.1 g, 4.24 mmol) in the mixture of methanol (100 mL) and water (6 mL). The reaction mixture was heated to reflux (ca. 100 °C) and stirred for 5 h under argon. The solution was cooled to 0 °C and acidified with HCl (1 M) to pH ≈ 1. After removal of methanol under reduced pressure, the aqueous residue was washed with CH_2Cl_2 (3 × 120 mL). The combined organic layer was washed with water (100 mL), brine (100 mL), and dried over magnesium sulfate. After filtration and evaporation of the solvent, the product was isolated as a pale brown oil (1.22 g) in 97% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.45 (s, 1H, SH′), 3.49 (s, 1H, SH), 7.09 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H, C^4H), 7.13−7.17 (m, 1H, $C^{4'}$H), 7.18−7.20 (m, 1H, C^2H), 7.25−7.30 (m, 3H, $C^{6'}$H, $C^{5'}$H, $C^{2'}$H), 7.49 (d, J = 8.5 Hz, 1H, C^5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 119.7 (C^6), 126.9 ($C^{4'}$H), 128.95 ($C^{6'}$H), 128.98 ($C^{2'}$H), 130.0 (C^4H), 130.2 ($C^{5'}$H), 130.8 ($C^{3'}$), 131.0 (C^3H), 131.8 (C^2H), 133.8 (C^5H), 141.4 ($C^{1'}$), 142.6 (C^1); IR (KBr) ν cm^{-1} 3050 (w, ν(═CH)), 2566 (m, ν(S−H)), 1592 (m) and 1575 (m, ν(CC), Ph), 1452 (vs), 1405 (m), 1375 (m), 1292 (vw), 1268 (vw), 1245 (vw), 1140 (m), 1108 (s), 1018 (s), 920 (w), 878 (m), 843 (w), 811 (s), 787 (vs), 729 (w), 708 (w), and 696 (s, ν(CH)); ESI(−) HRMS Calcd for $C_{12}H_8BrS_2$ ([M − H]$^-$, 294.9245), found m/z 294.9239. Anal. Calcd for $C_{12}H_9BrS_2$ (297.23): C, 48.49; H, 3.05. Found: C, 48.70; H, 3.18.

*2-Bromo-1,1′-biphenyl-5,3′-diyl bis(trifluoromethansulfonate) (**8**).* Triflic anhydride (11.7 g, 7 mL, 41.6 mmol) was added dropwise to a solution of **2** (5 g, 18.9 mmol) in dry triethylamine (8.1 g, 11 mL, 80 mmol) and dichloromethane (120 mL) at −78 °C under argon. The solution was stirred for 4 h, and then allowed to warm to room temperature and stirred for an additional 6 h. The resulting solution was passed through a pad of silica gel (60 g), and washed with CH_2Cl_2 (100 mL). After extraction with NH_4Cl (100 mL, 10%) and drying with magnesium sulfate, the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (800 g) in hexane:EtOAc (30:1) to give triflate **8** (9.6 g) as a clear, colorless oil in 96% yield (R_f = 0.38, Hex:EtOAc = 20:1): ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.19 (dd, J = 8.5 Hz, J = 3 Hz, 1H, C^4H), 7.23 (d, J = 4 Hz, 1H, C^2H), 7.33−7.37 (m, 2H, $C^{2'}$H, $C^{4'}$H), 7.40 (dt, J = 7.5 Hz, J = 1 Hz, 1H, $C^{6'}$H), 7.55 (td, J = 8 Hz, J = 0.5 Hz, 1H, $C^{5'}$H), 7.76 (d, J = 8.5 Hz, 1H, C^5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 118.9 (d, $^1J_{CF}$ = 320.7 Hz, CF_3), 119.0 (d, $^1J_{CF}$ = 320.7 Hz, CF_3), 121.7 ($C^{4'}$H), 122.3 (C^6), 122.61 ($C^{2'}$H), 122.64 (C^4H), 124.1 (C^2H), 129.4 ($C^{6'}$H), 130.6 ($C^{5'}$H), 135.3 (C^5H), 141.6 ($C^{1'}$), 142.7 (C^1), 148.7 (C^3), 149.4 ($C^{3'}$); ^{19}F{^{1}H} NMR (470.6 MHz, $CDCl_3$) δ ppm −72.61 (s, CF_3), −72.71 (s, CF_3); IR (KBr) ν cm^{-1} 3086 (bw, ν(═CH)), 1598 (w), 1579 (w) and 1567 (w, ν(CC), Ph), 1460 (s), 1429 (vs), 1242 (vs), 1212 (vs, $\nu(CF_3)$), 1027 (m, $\nu_s(SO_3)$), 945 (s), 888 (vs), 829 (s), 797 (w), 694 (w), 626 (m), 609 (s, $\delta_s(CF_3)$), and 515 (m, $\delta_{as}(CF_3)$); EI MS m/z (%) 530 (83), 528 (81, M^+), 397 (81), 395 (82), 369 (89), 367 (89), 305 (54), 303 (55), 155 (100), 84 (64). Anal. Calcd for $C_{14}H_7BrF_6O_6S_2$ (529.22): C, 31.77; H, 1.33. Found: C, 31.82; H, 1.35.

*1-Bromo-3-[2-(trimethylsilyl)ethylsulfanyl]benzene (**9**).* A 25 mL pressure tube was charged with 3-bromothiophenol (14.3 g, 75.5 mmol), vinyltrimethylsilane (8.9 g, 13 mL, 88.8 mmol) and di-*tert*-butyl peroxide (2 mL, 10.6 mmol) under argon. The tube was sealed, and stirred at 100 °C for 20 h. After cooling to room temperature, the solution was diluted with hexane (400 mL), washed with NaOH (100 mL, 2 M), water (100 mL), and brine (100 mL). The combined organic layer was dried with magnesium sulfate, and solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (800 g) in hexane to provide product **9** (18.4 g) as a pale yellow oil in 84% yield (R_f = 0.44, Hexane): ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.04 (s, 9H, CH_3), 0.91 (m, 2H, $C\underline{H_2}Si$), 2.94 (m, 2H, $SC\underline{H_2}$), 7.09−7.13 (m, 1H, C^5H), 7.16−7.20 (m, 1H, C^6H), 7.24−7.28 (m, 1H, C^4H), 7.38−7.41 (m, 1H, C^2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.6 (CH_3), 16.8 ($\underline{C}H_2Si$), 29.5 ($S\underline{C}H_2$), 123.0 (C^1), 127.1 (C^6H), 128.7 (C^4H), 130.3 (C^5H), 130.9 (C^2H), 140.1 (C^3); IR (KBr) ν cm^{-1} 3060 (w, ν(═CH)), 2951 (m, $\nu_{as}(CH_2, CH_3)$), 2895 (w, $\nu_s(CH_2, CH_3)$), 1577 (s) and 1556 (m, ν(CC), Ph), 1460 (s), 1400 (w), 1250 (s), 1165 (w), 1083 (w), 1068 (w), 1011 (w), 991 (w), 856 (s), 841 (s), 769 (m), 755 (m), 693 (w) and 677 (w, ν(CH)); EI MS m/z (%) 290 (3), 288 (3, M^+), 262 (5), 260 (5), 247 (4), 245 (4), 88 (10), 86 (64), 84 (100), 73 (52), 51 (29), 49 (90), 44 (49), 28 (24). Anal. Calcd for $C_{11}H_{17}BrSSi$ (289.31): C, 45.67; H, 5.92. Found: C, 45.78; H, 6.05.

*3-[2-(Trimethylsilyl)ethylsulfanyl]phenylboronic acid pinacol ester (**10**).* In a 500 mL Schlenk flask, bromide **9** (8 g, 27.5 mmol) was dissolved in THF (150 mL) under argon and cooled to −78 °C. The solution was treated with *n*-BuLi (14.1 g, 21 mL, 33 mmol, 15% in hexane) and the reaction mixture was stirred for 30 min at −78 °C. Triisopropyl borate (7.3 g, 39 mmol) was added dropwise, and the reaction mixture was stirred for 1 h at −78 °C, and then allowed to warm to room temperature and stirred overnight. The milky solution was quenched with water (50 mL), and HCl solution (50 mL, 1 M) was added. After evaporation of the organic solvents, an additional HCl solution (100 mL, 1 M) was added and white suspension was quickly stirred for 1 h. White solid was filtered off, washed with water (3 × 60 mL), pentane (2 × 50 mL) and vacuum-dried (10^{-2} mbar, 40 °C). The boronic acid was isolated as a white solid (5.85 g) in 84% yield. The product was further converted to the pinacol ester, which was prepared from the boronic acid (5.8 g, 22.8 mmol), pinacol (4.6 g,

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39 mmol) and toluene (100 mL) by azeotropic distillation. After 12 h of reflux, toluene was distilled off, and the light yellow residue was purified by sublimation on a Kugelrohr apparatus at 180 °C and 3 × 10^{-1} mbar to provide 7.4 g of pure pinacol ester **10** as a white solid in 80% yield (after two steps): mp 53−54 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 0.05 (s, 9H, CH_3, TMS), 0.93 (m, 2H, C$\underline{H_2}$Si), 1.33 (s, 12H, CH_3, Bpin), 2.99 (m, 2H, SC$\underline{H_2}$), 7.26−7.32 (m, 1H, C^5H), 7.36−7.42 (m, 1H, C^6H), 7.52−7.57 (m, 1H, C^4H), 7.68−7.72 (m, 1H, C^2H); ^{13}C NMR (125.8 MHz, CD_2Cl_2) δ ppm −1.6 (CH_3, TMS), 17.5 (C$\underline{H_2}$Si), 25.2 (CH_3, Bpin), 29.8 (S$\underline{C}H_2$), 84.5 (C, Bpin), 128.8 (C^5H), 132.0 (C^6H), 132.3 (C^4H), 135.4 (C^2H), 137.4 (C^3); ^{11}B{^{1}H} NMR (160.5 MHz, CD_2Cl_2) δ ppm 30.8; IR (KBr) ν cm^{-1} 3054 (w, ν(=CH)), 2954 and 2975 (s, $\nu_{as}(CH_2, CH_3)$), 2893 (m, $\nu_s(CH_2, CH_3)$), 1593 (s) and 1561 (m, ν(CC), Ph), 1478 (s, $\delta_{as}(CH_3)$, Bpin), 1400 (bs, $\delta_s(CH_3)$, Bpin), 1353 (vs) and 1322 (vs, ν(CC), Bpin), 1273 (vs), 1250 (vs, $\delta_s(CH_3)$, TMS), 1213 (m), 1162 (s), 1143 (s), 1112 (s), 1087 (m), 965 (s, Bpin), 885 (s), 865 (vs, $\beta_{as}(CH_3)$, Bpin, $\delta_{as}(CH_3)$, TMS), 793 (s), 724 (s), 705 (s, $\nu_{as}(SiC_3)$, TMS), 667 (m, ν(CH), Bpin); EI MS *m*/*z* (%) 336 (8, M^+), 308 (26), 208 (15), 166 (36), 151 (20), 86 (60), 84 (86), 73 (100), 49 (80). Anal. Calcd for $C_{17}H_{29}BO_2SSi$ (336.37): C, 60.70; H, 8.69. Found: C, 60.98; H, 8.51.

*3,3′-Bis[2-(trimethylsilyl)ethylsulfanyl]-1,1′-biphenyl (**11**).* A 500 mL Schlenk flask was charged with aryl bromide **9** (2.9 g, 10 mmol), pinacol ester **10** (3.5 g, 10.4 mmol), sodium carbonate (4.2 g, 40 mmol) and put under argon. Toluene (100 mL) and water (10 mL) were added, and the resulting solution was degassed before $Pd(PPh_3)_4$ (693 mg, 0.6 mmol) was added. The reaction mixture was again degassed (3×), and then heated at 95 °C for 18 h. The completion of the reaction was checked by TLC (Hex:CH_2Cl_2 = 50:1). After cooling to room temperature, the dark reaction mixture was passed through a short pad of silica gel (40 g) and washed with CH_2Cl_2 (300 mL). Solvents were evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (800 g, Hex:CH_2Cl_2 = 80:1) to provide biphenyl **11** (3.4 g) as a clear, colorless oil in 80% yield (R_f = 0.24, Hex:CH_2Cl_2 = 50:1): ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 0.06 (s, 18H, CH_3), 0.97 (m, 4H, C$\underline{H_2}$Si), 3.03 (m, 4H, SC$\underline{H_2}$), 7.27−7.32 (m, 2H, $C^{6,6'}$H), 7.34−7.40 (m, 4H, $C^{4,4'}$H, $C^{5,5'}$H), 7.49−7.52 (m, 2H, $C^{2,2'}$H); ^{13}C NMR (125.8 MHz, CD_2Cl_2) δ ppm −1.5 (CH_3), 17.4 (C$\underline{H_2}$Si), 29.9 (S$\underline{C}H_2$), 125.0 ($C^{4,4'}$H), 127.8 ($C^{2,2'}$H), 128.1 ($C^{6,6'}$H), 129.8 ($C^{5,5'}$H), 138.8 ($C^{3,3'}$), 141.9 ($C^{1,1'}$); IR (KBr) ν cm^{-1} 3057 (w, ν(=CH)), 2952 (bs, $\nu_{as}(CH_2, CH_3)$), 2918 (m, $\nu_s(CH_2, CH_3)$), 1586 (s) and 1561 (m, ν(CC), Ph), 1465 (m), 1422 (w), 1384 (w), 1260 (s), 1251 (s, $\delta_s(CH_3)$, TMS), 1162 (s), 1106 (w), 1088 (w), 1009 (m), 852 (bs, $\delta_{as}(CH_3)$, TMS), 773 (m), 701 (m, $\nu_{as}(SiC_3)$, TMS); EI MS *m*/*z* (%) 418 (12, M^+), 362 (24), 347 (8), 101 (11), 73 (100), 51 (31). Anal. Calcd for $C_{22}H_{34}S_2Si_2$ (418.80): C, 63.09; H, 8.18. Found: C, 63.17; H, 8.23.

*2-Bromo-5,3′-bis[2-(trimethylsilyl)ethylsulfanyl]-1,1′-biphenyl (**12**). Method A*: A 25 mL pressure tube was charged with thiol **7** (2.9 g, 9.8 mmol), vinyltrimethylsilane (7.8 g, 11.5 mL, 78.1 mmol) and AIBN (82 mg, 0.5 mmol) under argon. The tube was sealed and stirred at 100 °C for 30 h. After cooling to room temperature, the solution was diluted with CH_2Cl_2 (150 mL), passed through a short pad of silica gel (20 g, CH_2Cl_2), and evaporated. The residue was purified by column chromatography on silica gel (900 g) in Hexane:CH_2Cl_2 (10:1) to provide product **12** (4.5 g) as a colorless oil in 91% yield (R_f = 0.37, Hex:CH_2Cl_2 = 5:1). *Method B*: A dry 25 mL flask was charged with triflate **8** (1 g, 1.9 mmol), Xantphos (58 mg, 100 μmol), $Pd_2(dba)_3$ (52 mg, 50 μmol), and dry dioxane (15 mL). The tube was evacuated under a vacuum and refilled with argon three times. Then *N*,*N*-diisopropylethylamine (776 mg, 1 mL, 6 mmol), and 2-(trimethylsilyl)ethanethiol (537 mg, 4 mmol) were added under argon and the tube was quickly capped with a rubber septum. The reaction mixture was stirred at 60 °C for 14 h, and at 90 °C for 6 h. The completion of the reaction was checked by TLC (Hex:EtOAc = 20:1). After cooling, the reaction mixture was diluted with diethyl ether (60 mL), filtered through a pad of silica gel (30 g, diethyl ether), and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (800 g, hexane:ethyl acetate equal to 50:1) to provide the title compound **12** (432 mg) as a pale yellow oil (which contains about 10% of other isomers) in 46% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.02 (s, 18H, CH_3), 0.93 (m, 4H, C$\underline{H_2}$Si), 2.96 (m, 4H, SC$\underline{H_2}$), 7.10 (dd, J = 7.5 Hz, J = 2 Hz, 1H, C^4H), 7.16 (dt, J = 7 Hz, J = 2 Hz, 1H, $C^{6'}$H), 7.21 (d, J = 2.5 Hz, 1H, C^2H), 7.28−7.35 (m, 2H, $C^{4'}$H, $C^{5'}$H), 7.30 (d, J = 2 Hz, 1H, $C^{2'}$H), 7.53 (d, J = 8.5 Hz, 1H, C^5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.52 and −1.50 (CH_3), 17.0 and 17.1 (C$\underline{H_2}$Si), 29.69 and 29.71 (S$\underline{C}H_2$), 119.6 (C^6), 126.8 ($C^{6'}$H), 128.3 ($C^{5'}$H), 128.7 ($C^{4'}$H), 129.1 (C^4H), 129.7 ($C^{2'}$H), 131.2 (C^2H), 133.5 (C^5H), 137.3 (C^3), 137.4 ($C^{3'}$), 141.5 ($C^{1'}$), 142.6 (C^1); IR (KBr) ν cm^{-1} 3053 (vw, ν(=CH)), 2952 (s, $\nu_{as}(CH_2, CH_3)$), 2914 (w, $\nu_s(CH_2, CH_3)$), 1591 (w), 1572 (m) and 1546 (w, ν(CC), Ph), 1452 (m), 1420 (w), 1366 (w), 1260 (m), 1249 (s, $\delta_s(CH_3)$, TMS), 1164 (w), 1102 (m), 1017 (m), 858 (vs) and 842 (vs, $\delta_{as}(CH_3)$, TMS), 789 (m), 752 (w), 733 (w), 698 (m, $\nu_{as}(SiC_3)$, TMS); EI MS *m*/*z* (%) 498 (5), 496 (4, M^+), 442 (14), 440 (12), 101 (16), 73 (100). Anal. Calcd for $C_{22}H_{33}BrS_2Si_2$ (497.70): C, 53.09; H, 6.68. Found: C, 53.22; H, 6.56.

*2-Iodo-5,3′-bis[2-(trimethylsilyl)ethylsulfanyl]-1,1′-biphenyl (**13**).* In a 100 mL Schlenk flask, 2-bromobiphenyl **12** (2 g, 4 mmol) was dissolved in anhydrous THF (30 mL) under argon, cooled to −78 °C and degassed. Afterward *n*-BuLi (1.9 g, 2.8 mL, 4.4 mmol, 15% in hexane) was added dropwise over 10 min and the resulting yellow solution was stirred at −78 °C for 40 min. In a second 100 mL Schlenk flask, iodine (1.2 g, 4.8 mmol) was dissolved in THF (30 mL) under argon, and cooled to −78 °C. The iodine solution was cannulated dropwise into the flask containing lithiated biphenyl. The dark solution was stirred at −78 °C for 1 h, then allowed to warm to room temperature and stirred for an additional 10 h. The reaction mixture was quenched with Na_2SO_3 (60 mL, 10%). The aqueous layer was extracted with diethyl ether (3 × 80 mL). The combined organic layer was subsequently washed with brine (100 mL), and dried over magnesium sulfate. After filtration over a short pad of silica gel (80 g, diethyl ether), evaporation, and drying under a vacuum (10^{-2} mbar), the pure product was isolated as a light yellow oil (2.1 g) in 96% yield (R_f = 0.40, Hex:CH_2Cl_2 = 50:1): ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.02 (s, 18H, CH_3), 0.92 (m, 2H, C$\underline{H_2}$Si), 0.96 (m, 2H, C$\underline{H_2}$Si′), 2.94 (m, 2H, SC$\underline{H_2}$), 2.98 (m, 2H, SC$\underline{H_2}$′), 6.93 (dd, J = 8 Hz, J = 2 Hz, 1H, C^4H), 7.16 (m, 1H, $C^{6'}$H), 7.18 (d, J = 2.5 Hz, 1H, C^2H), 7.23 (m, 1H, $C^{2'}$H), 7.29−7.35 (m, 2H, $C^{4'}$H, $C^{5'}$H), 7.79 (d, J = 8 Hz, 1H, C^5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.52 and −1.46 (CH_3), 16.9 and 17.1 (C$\underline{H_2}$Si), 29.4 and 29.7 (S$\underline{C}H_2$), 94.4 (C^6), 126.7 ($C^{6'}$H), 128.3 ($C^{4'}$H), 128.7 ($C^{5'}$H), 128.9 (C^4H), 129.6 ($C^{2'}$H), 129.8 (C^2H), 137.4 ($C^{3'}$), 138.4 (C^3), 139.8 (C^5H), 144.5 ($C^{1'}$), 146.7 (C^1); IR (KBr) ν cm^{-1} 3054 (vw, ν(=CH)), 2951 (s, $\nu_{as}(CH_2, CH_3)$), 2916 (w, $\nu_s(CH_2, CH_3)$), 1590 (w), 1567 (m) and 1539 (w, ν(CC), Ph), 1476 (w), 1448 (m), 1421 (w), 1365 (w), 1260 (m), 1249 (s, $\delta_s(CH_3)$, TMS), 1164 (w), 1101 (m), 1008 (m), 858 (vs) and 841 (vs, $\delta_{as}(CH_3)$, TMS), 786 (w), 753 (w), 731 (w), 697 (m, $\nu_{as}(SiC_3)$, TMS); EI MS *m*/*z* (%) 544 (5, M^+), 488 (13), 101 (14), 73 (100). Anal. Calcd for $C_{22}H_{33}IS_2Si_2$ (544.70): C, 48.51; H, 6.11. Found: C, 48.78; H, 6.23.

*2-Bromo-7-iodo-9H-fluorene (**14**)*..[42,43] A 500 mL Schlenk flask was charged with 2-bromo-9*H*-fluorene (15 g, 61 mmol), iodine (6.6 g, 26 mmol), and potassium iodate (3.2 g, 15 mmol), flushed with argon, and then water (12 mL), acetic acid (260 mL) and concentrated sulfuric acid (6 mL) were added. The reaction mixture was heated at 90 °C for 2 h under argon. After cooling to room temperature, the purple suspension was filtered off, washed with acetic acid (150 mL), Na_2SO_3 (150 mL, 10%), water (300 mL), and air-dried. A light yellow solid was recrystallized from toluene (120 mL) to provide 16.3 g of a white solid in 72% yield (R_f = 0.33, Hex:CH_2Cl_2 = 20:1): mp 180−181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.81 (s, 2H, C^9H_2), 7.45 (d, J = 8 Hz, 1H, C^5H), 7.47 (dd, J = 8 Hz, J =1 Hz, 1H, C^3H), 7.57 (d, J = 8 Hz, 1H, C^4H), 7.63 (d, J = 2 Hz, 1H, C^1H), 7.67 (dd, J = 8 Hz, J =1 Hz, 1H, C^6H), 7.84 (d, J = 1 Hz, 1H, C^8H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 36.6 (C^9H_2), 92.5 (C^7), 121.3 (C^2), 121.5 (C^4H), 121.7 (C^5H), 128.5 (C^1H), 130.3 (C^3H), 134.4 (C^8H), 136.2 (C^6H), 140.0 (C^{11}), 140.5 (C^{12}), 144.8 (C^{10}), 145.2 (C^{13}); IR (KBr) ν cm^{-1} 3056 (vw, ν(=CH)), 2890 (w, $\nu_s(CH_2)$),

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1596 (w) and 1567 (w, ν(CC), Ph), 1419 (m), 1396 (s), 1273 (m), 1161 (m), 1128 (w), 1050 (m), 951 (w), 930 (w), 832 (m) and 804 (vs, ν(CH)); EI MS m/z (%) 372 (91), 370 (93, M^+), 291 (52), 245 (51), 243 (52), 164 (89), 163 (100), 146 (35), 82 (30), 81 (86). Anal. Calcd for $C_{13}H_8BrI$ (371.02): C, 42.09; H, 2.17. Found: C, 42.14; H, 2.16.

*2-Bromo-7-iodofluoren-9-one (**15**).* *Method A*: To a suspension of 9*H*-fluorene **14** (6 g, 16 mmol) in the mixture of acetic acid (100 mL) and acetic anhydride (100 mL) was portionwise added CrO_3 (8 g, 80 mmol) over 3 h. The reaction mixture was vigorously stirred at room temperature for 16 h, and then poured into crushed ice (ca. 2 kg), and carefully neutralized with saturated $NaHCO_3$ solution. The yellow precipitate was filtered off, washed with water (2 L), and air-dried. The crude product was treated with chloroform (600 mL), and passed through a short silica gel column (500 g, $CHCl_3$). After evaporation in vacuo, the residue was recrystallized from ethanol to provide product **15** (4.5 g) as a yellow solid in 73% yield (R_f = 0.42, Hex:CH_2Cl_2 = 2:1). *Method B*: A 500 mL two-necked flask fitted with a reflux condenser, and a magnetic stirring bar was charged with 2-bromofluoren-9-one (10 g, 38.6 mmol), water (20 mL), acetic acid (120 mL), and concentrated sulfuric acid (4 mL), and heated at 60 °C for 1 h. Then iodine (9.9 g, 39 mmol), and periodic acid (4.3 g, 19 mmol) were added, and the reaction mixture was stirred at 85 °C for 18 h. After cooling to room temperature, the reaction mixture was poured into Na_2SO_3 (200 mL, 10%) solution, and a yellow solid was filtered off, washed with water (600 mL), and air-dried. A bright yellow solid was recrystallized from ethyl acetate to give 13.2 g of yellow needles in 89% yield: mp 197−198 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.22 (d, J = 8 Hz, 1H, C^5H), 7.34 (d, J = 8 Hz, 1H, C^4H), 7.59 (dd, J = 8 Hz, J =2 Hz, 1H, C^3H), 7.71 (d, J = 2 Hz, 1H, C^1H), 7.80 (dd, J = 8 Hz, J =1.5 Hz, 1H, C^6H), 7.91 (d, J = 1.5 Hz, 1H, C^8H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 94.6 (C^7), 122.1 (C^4H), 122.3 (C^5H), 123.7 (C^2), 127.9 (C^1H), 133.8 (C^8H), 135.1 (C^{13}), 135.4 (C^{10}), 137.6 (C^3H), 142.5 (C^{11}), 143.0 (C^{12}), 143.6 (C^6H), 191.1 (C^9O); IR (KBr) ν cm^{-1} 3054 (vw, ν(=CH)), 1723 (vs) and 1709 (s, ν(C=O), CpCO), 1603 (w) and 1589 (m, ν(CC), Ph), 1445 (m), 1415 (s), 1274 (w), 1242 (m), 1221 (w), 1203 (w), 1184 (s), 1153 (m), 1052 (m), 1028 (m), 905 (m), 841 (w), 822 (s) and 780 (vs, ν(CH)), 675 (bm); EI MS m/z (%) 386 (77), 384 (77, M^+), 231 (20), 229 (20), 150 (73), 86 (74), 84 (100), 75 (32), 51 (32), 49 (87). Anal. Calcd for $C_{13}H_6BrIO$ (385.00): C, 40.56; H, 1.57. Found: C, 40.49; H, 1.53.

*(R,S)-9-{5,3′-Bis[2-(trimethylsilyl)ethylsulfanyl]-1,1′-biphen-2-yl}-2-bromo-7-iodofluoren-9-ol (**16**).* A dry and argon-flushed 100 mL Schlenk flask was charged with 2-iodobiphenyl **13** (1.4 g, 2.57 mmol), and anhydrous THF (30 mL) was added. The solution was cooled to −40 °C (acetonitrile/CO_2(*s*)), and *i*PrMgCl·LiCl complex solution ("turbo-Grignard", 2.4 mL, 3.1 mmol, 1.3 M in THF) was added dropwise over 10 min. The reaction mixture was stirred at −40 °C for 4 h under argon. The reaction mixture was stirred at the same temperature until completion of the I/Mg exchange was detected by GC−MS analysis. In a second 100 mL Schlenk flask, fluoren-9-one **15** (1.2 g, 3.1 mmol) was dissolved in dry THF (40 mL), cooled to −40 °C, and degassed. This solution was slowly added via a cannula into the flask containing the Grignard reagent, and the mixture was stirred at −40 °C for 2 h, then allowed to warm to room temperature and stirred for an additional 16 h. The reaction mixture was quenched with saturated aq. NH_4Cl solution (80 mL). The aqueous layer was washed with diethyl ether (3 × 80 mL). The combined organic layer was subsequently washed with brine (100 mL), dried over magnesium sulfate, and filtered. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (800 g) in hexane:EtOAc (50:1) to afford 1.23 g of the title product **16** (R_f = 0.21, Hex:EtOAc = 20:1) as a light yellow foamy solid in 59% yield. The title carbinol **16** is a mixture of two diastereomers in a ratio ∼1:1, which was determined by NMR analysis at different temperatures: mp 65−67 °C; ^{1}H NMR (500.0 MHz, $CDCl_3$) δ ppm 0.02, 0.03 (2 × s, 2 × 9H, 2 × $CH_3^{(\rightarrow 3'')}$), 0.04 (s, 18H, 2 × $CH_3^{(\rightarrow 3')}$), 0.83 (m, 4H, 2 × $C\underline{H}_2Si^{(\rightarrow 3'')}$), 0.97 (m, 4H, 2 × $C\underline{H}_2Si^{(\rightarrow 3')}$), 2.25 (s, 2H, 2 × OH), 2.68 (m, 4H, 2 × $SC\underline{H}_2^{(\rightarrow 3'')}$), 2.99 (m, 4H, 2 × $SC\underline{H}_2^{(\rightarrow 3')}$), 5.88, 5.89 (2 × m, 2 × 1H, 2 × $C^{6''}$H), 5.90, 5.93 (2 × m, 2 × 1H, 2 × $C^{2''}$H), 6.59, 6.61 (2 × m, 2 × 1H, 2 × $C^{5''}$H), 6.78 (m, 2H, 2 × $C^{4''}$H), 6.83 (d, J = 2.1 Hz, 2H, 2 × $C^{2'}$H), 6.90 (m, 1H, C^5H), 6.96 (d, J = 7.9 Hz, 1H, C^5H), 7.02 (m, 1H, C^4H), 7.09 (d, J = 8.1 Hz, 1H, C^4H), 7.29−7.33 (m, 3H, 2 × C^1H, C^3H), 7.37 (dd, J = 8.1 Hz, J = 1.9 Hz, 1H, C^3H), 7.42 (dd, J = 8.4 Hz, J = 2.1 Hz, 2H, 2 × $C^{4'}$H), 7.50−7.53 (m, 3H, 2 × C^8H, C^6H), 7.57 (dd, J = 7.9 Hz, J = 1.6 Hz, 1H, C^6H), 8.30 (d, J = 8.4 Hz, 2H, 2 × $C^{5'}$H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ ppm −1.73 ($CH_3^{(\rightarrow 3')}$), −1.67, −1.59 ($CH_3^{(\rightarrow 3'')}$), 16.46, 16.52 ($\underline{C}H_2Si^{(\rightarrow 3'')}$), 16.63 ($\underline{C}H_2Si^{(\rightarrow 3')}$), 28.3, 28.5 ($S\underline{C}H_2^{(\rightarrow 3'')}$), 28.7 ($S\underline{C}H_2^{(\rightarrow 3')}$), 81.8 ($C^9$), 93.1, 93.2 ($C^7$), 121.5, 121.6 ($C^4$H), 121.7, 121.8 ($C^5$H), 122.0, 122.1 ($C^2$), 125.5, 125.6 ($C^{4''}$H), 126.16, 126.22 ($C^{6''}$H), 126.5 ($C^{4'}$H), 126.76, 126.78, 126.80 ($C^{5'}$H, $C^{5''}$H), 127.6 (C^1H), 127.75, 127.76 (C^1H, $C^{2''}$H), 128.1 ($C^{2''}$H), 130.2 ($C^{2'}$H), 131.9, 132.4 (C^3H), 133.4, 133.6 (C^8H), 135.28, 135.29 ($C^{6'}$), 136.1 ($C^{3''}$), 137.2 ($C^{3'}$), 137.88 (C^{11}), 137.90 (C^6H), 138.2 (C^{11}), 138.41 (C^6H), 138.43, 138.8 (C^{12}), 140.127, 140.134 ($C^{1''}$), 140.6 ($C^{1'}$), 151.4, 151.7 (C^{10}), 151.7, 152.0 (C^{13}); IR (KBr) ν cm^{-1} 3400 (bm, ν(OH)), 3050 (vw, ν(=CH)), 2950 (m, ν_{as}(CH_2, CH_3)), 2893 (w, ν_s(CH_2, CH_3)), 1582 (m), 1565 (w) and 1540 (w, ν(CC), Ph), 1460 (m), 1446 (m), 1410 (m), 1396 (m), 1371 (w), 1248 (vs, δ_s(CH_3), TMS), 1164 (m), 1090 (m), 1054 (m), 1006 (bm), 925 (w), 879 (m), 858 (vs) and 839 (vs, δ_{as}(CH_3), TMS), 809 (s), 786 (m), 751 (m), 727 (m), 704 (m, ν_{as}(SiC_3), TMS), 670 (m), 640 (w); ESI(+) HRMS Calcd for $C_{35}H_{40}BrIONaS_2Si_2$ ([M + Na]$^+$, 825.0185), found m/z 825.0186. Anal. Calcd for $C_{35}H_{40}BrIOS_2Si_2$ (803.80): C, 52.30; H, 5.02. Found: C, 52.19; H, 4.92.

*2-Bromo-7-iodo-3′,6′-bis[2-(trimethylsilyl)ethylsulfanyl]-9,9′-spirobifluorene (**17**) and (R,S)-2-Bromo-7-iodo-1′,6′-bis[2-(trimethylsilyl)ethylsulfanyl]-9,9′-spirobifluorene (**18**).* An argon-flushed 100 mL Schlenk flask was charged with carbinol **16** (0.5 g, 0.62 mmol), and glacial acetic acid (50 mL) was added. The solution was cooled to 10 °C, and concentrated HCl (1 mL, 37%) was added. The reaction mixture was keep stirring at 10 °C for 6 h under argon, and then allowed to warm to room temperature and stirred for an additional 12 h. The reaction mixture was diluted with water (30 mL), and after 20 min of stirring, the white precipitate was filtered off, washed with water (ca. 400 mL), air and vacuum-dried to provide 476 mg (98% yield) of a white solid as a mixture of two regioisomers **17** and **18** in a ratio of 2:1 (R_f = 0.35, Hex:CH_2Cl_2 = 5:1). The ratio of regioisomers was determined by ^{1}H NMR of the crude reaction mixture. The regioisomeric mixture was further purified by the slow crystallization from the mixture of ethanol and toluene (10:1) to give a first crop of the pure symmetric isomer **17** (160 mg) as a white crystalline material. The mother liquor was evaporated, and the residue was purified by column chromatography on a large excess of silica gel (1400 g) in the mixture of hexane:EtOAc (50:1) to give a second crop of the symmetric isomer **17** (120 mg) and the isomer **18** (135 mg) as a light yellow foamy solid. For the isomer **17**: mp 165−166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.06 (s, 18H, CH_3), 0.99 (m, 4H, $C\underline{H}_2Si$), 3.03 (m, 4H, $SC\underline{H}_2$), 6.60 (d, J = 8 Hz, 2H, $C^{1'}$H, $C^{8'}$H), 6.81 (d, J = 1.5 Hz, 1H, C^1H), 7.01 (d, J = 1.5 Hz, 1H, C^8H), 7.06 (dd, J = 8 Hz, J = 1.5 Hz, 2H, $C^{2'}$H, $C^{7'}$H), 7.46 (dd, J = 8.5 Hz, J = 2 Hz, 1H, C^3H), 7.51 (d, J = 8 Hz, 1H, C^5H), 7.63 (d, J = 8.5 Hz, 1H, C^4H), 7.67 (dd, J = 8 Hz, J = 1.5 Hz, 1H, C^6H), 7.71 (d, J = 1.5 Hz, 2H, $C^{4'}$H, $C^{5'}$H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.5 (CH_3), 17.1 ($\underline{C}H_2Si$), 29.9 ($S\underline{C}H_2$), 65.1 (C^9), 93.6 (C^7), 120.5 ($C^{4'}$H, $C^{5'}$H), 121.7 (C^4H), 122.0 (C^5H), 122.3 (C^2), 124.6 ($C^{1'}$H, $C^{8'}$H), 127.5 (C^1H), 128.8 ($C^{2'}$H, $C^{7'}$H), 131.4 (C^3H), 133.4 (C^8H), 137.3 (C^6H), 138.1 ($C^{3'}$, $C^{6'}$), 139.8 (C^{11}), 140.4 (C^{12}), 142.1 ($C^{11'}$, $C^{12'}$), 145.1 ($C^{10'}$, $C^{13'}$), 150.2 (C^{10}), 150.5 (C^{13}); IR (KBr) ν cm^{-1} 3044 (w, ν(=CH)), 2946 (s, ν_{as}(CH_2, CH_3)), 2891 (m, ν_s(CH_2, CH_3)), 1595 (s), 1568 (m) and 1546 (w, ν(CC), Ph), 1469 (m), 1454 (s), 1440 (m), 1415 (m), 1405 (m), 1397 (m), 1282 (m), 1277 (m), 1258 (s), 1248 (vs, δ_s(CH_3), TMS), 1161 (m), 1108 (w), 1099 (w), 1090 (w), 1083 (m), 1063 (m), 1054 (m), 1006 (s), 955 (w), 949 (w), 932 (m), 886 (m), 850 (vs) and 833 (bs, δ_{as}(CH_3), TMS), 811 (s), 807 (s), 804 (s), 766 (w), 751 (m), 736 (w), 704 (m) and 690 (m, ν_{as}(SiC_3), TMS), 665 (m), 635 (m); EI MS m/z (%) 786 (3), 784 (3, M^+), 730 (6), 728

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(6), 626 (7), 73 (100). Anal. Calcd for $C_{35}H_{38}BrIS_2Si_2$ (785.79): C, 53.50; H, 4.87. Found: C, 53.56; H, 4.89.

For the isomer **18**: mp 153−154 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm −0.12 (s, 9H, $CH_3^{(\rightarrow 1')}$), 0.06 (s, 9H, $CH_3^{(\rightarrow 6')}$), 0.40 (m, 2H, $C\underline{H}_2Si^{(\rightarrow 1')}$), 0.98 (m, 2H, $C\underline{H}_2Si^{(\rightarrow 6')}$), 2.47 (m, 2H, $SC\underline{H}_2^{(\rightarrow 1')}$), 3.01 (m, 2H, $SC\underline{H}_2^{(\rightarrow 6')}$), 6.47 (d, J = 8 Hz, 1H, C$^{8'}$H), 6.81 (d, J = 1.5 Hz, 1H, C^{1}H), 7.01 (d, J = 1.5 Hz, 1H, C^{8}H), 7.02 (dd, J = 8 Hz, J = 1.5 Hz, 1H, C$^{7'}$H), 7.14 (d, J = 7.5 Hz, 1H, C$^{4'}$H), 7.40 (td, J = 7.5 Hz, J = 1 Hz, 1H, C$^{3'}$H), 7.47 (dd, J = 8 Hz, J = 2 Hz, 1H, C^{3}H), 7.53 (d, J = 8 Hz, 1H, C^{5}H), 7.63−7.69 (m, 3H, C^{4}H, C$^{2'}$H, C^{6}H), 7.71 (d, J = 1 Hz, 1H, C$^{5'}$H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.6 ($CH_3^{(\rightarrow 1')}$), −1.5 ($CH_3^{(\rightarrow 6')}$), 17.0 ($\underline{C}H_2Si^{(\rightarrow 1')}$), 17.2 ($\underline{C}H_2Si^{(\rightarrow 6')}$), 29.8 ($S\underline{C}H_2^{(\rightarrow 1')}$), 29.9, 30.00 ($S\underline{C}H_2^{(\rightarrow 6')}$), 65.8 (C^9), 93.3 (C^7), 117.7 (C$^{2'}$H), 120.7 (C$^{5'}$H), 121.6 (C^{4}H), 121.9 (C^{5}H), 122.0 (C^2), 124.1 (C$^{8'}$H), 127.0 (C^{1}H), 128.9 (C$^{7'}$H), 129.2 (C$^{4'}$H), 129.4 (C$^{3'}$H), 131.1 (C^{3}H), 132.8 (C^{8}H), 135.2 (C$^{1'}$), 137.0 (C^{6}H), 137.6 (C$^{6'}$), 141.0 (C^{11}), 141.5 (C^{12}), 141.7 (C$^{12'}$), 142.7 (C$^{11'}$), 145.5 (C$^{13'}$), 146.0 (C$^{10'}$), 149.0 (C^{10}), 149.3 (C^{13}); IR (KBr) ν cm^{-1} 3054 (vw, ν(=CH)), 2952 (s) and 2920 (s, $\nu_{as}(CH_2, CH_3)$), 2851 (m, $\nu_s(CH_2, CH_3)$), 1730 (bm), 1594 (w), 1567 (w) and 1517 (w, ν(CC), Ph), 1448 (m), 1422 (w), 1406 (w), 1389 (w), 1260 (m), 1249 (s, $\delta_s(CH_3)$, TMS), 1162 (m), 1104 (w), 1079 (m), 1054 (w), 1006 (m), 946 (vw), 934 (w), 856 (bs) and 840 (bs, $\delta_{as}(CH_3)$, TMS), 807 (s), 768 (m), 746 (m), 722 (w), 703 (w, $\nu_{as}(SiC_3)$, TMS), 664 (m), 635 (m).

*4-[(Trimethylsilyl)ethynyl]benzonitrile (**19**).*[44,45] A 500 mL Schlenk flask was charged with 4-iodobenzonitrile (7.5 g, 32.7 mmol), $PdCl_2(PPh_3)_2$ (1.2 g, 1.7 mmol), CuI (630 mg, 3.3 mmol) under argon, and dry THF (60 mL), and dry triethylamine (100 mL) were added. Then trimethylsilylacetylene (4.9 g, 7.1 mL, 50 mmol) was added, and the mixture was stirred at room temperature for 10 h. The reaction mixture was treated with diethyl ether (300 mL), and the precipitate was filtered through a pad of silica gel (30 g, diethyl ether), and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (600 g, hexane:CH_2Cl_2 equal to 2:1) to afford the title compound **19** (5.9 g) as a white solid in 90% yield (R_f = 0.35, Hex:CH_2Cl_2 = 2:1): mp 102−103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.24 (s, 9H, CH_3), 7.51 (dd, J = 7.5 Hz, J = 2 Hz, 2H, C^{3}H, C^{5}H), 7.57 (dd, J = 6.5 Hz, J = 2 Hz, 2H, C^{2}H, C^{6}H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −0.1 (CH_3), 99.8 (≡C—Si), 103.2 (Ar—C≡), 112.0 (C^1), 118.7 (CN), 128.2 (C^4), 132.1 (C^{2}H, C^{6}H), 132.7 (C^{3}H, C^{5}H); IR (KBr) ν cm^{-1} 3064 (w) and 3048 (vw, ν(=CH)), 2964 (m) and 2956 (m, $\nu_{as}(CH_3)$), 2898 (w, $\nu_s(CH_3)$), 2235 (m, ν(C≡N)), 2158 (m, ν(C≡C)), 1603 (w, ν(CC), Ph), 1499 (m), 1407 (w), 1272 (w), 1251 (m), 1246 (m, $\delta_s(CH_3)$, TMS), 1217 (w), 1177 (w), 862 (vs) and 842 (vs, $\delta_{as}(CH_3)$, TMS), 758 (s), 724 (m), 699 (w, $\nu_{as}(SiC_3)$, TMS), 630 (w), 557 (m); EI MS m/z (%) 197 (4, M$^+$), 183 (8), 165 (8), 139 (10), 101 (22), 73 (100). Anal. Calcd for $C_{12}H_{13}NSi$ (199.33): C, 72.31; H, 6.57; N, 7.03. Found: C, 72.42; H, 6.51; N, 7.09.

*4-Ethynylbenzonitrile (**20**).*[6,46] In a 250 mL flask, the silylated acetylene **19** (3.6 g, 18.1 mmol) was dissolved in the mixture of THF (60 mL) and methanol (60 mL). Potassium carbonate (25 g, 181 mmol) was added, and suspension was vigorously stirred at room temperature for 14 h. The reaction mixture was filtered through a pad of Celite (diethyl ether), and the remaining solution concentrated under reduced pressure. The crude product was treated with diethyl ether (200 mL), and passed through a short pad of silica gel (100 g, diethyl ether). After evaporation, and drying under vacuo at room temperature, the title compound **20** (2.24 g) was isolated as a white solid in 97% yield (R_f = 0.28, Hex:CH_2Cl_2 = 2:1): mp 158−159 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.28 (s, 1H, CH), 7.55 (dd, J = 7 Hz, J = 1.5 Hz, 2H, C^{3}H, C^{5}H), 7.60 (dd, J = 7 Hz, J = 1.5 Hz, 2H, C^{2}H, C^{6}H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm 81.8 (≡C—H), 82.1 (Ar—C≡), 112.5 (C^1), 118.5 (CN), 127.2 (C^4), 132.2 (C^{2}H, C^{5}H), 132.9 (C^{3}H, C^{5}H); IR (KBr) ν cm^{-1} 3052 (vw, ν(=CH)), 2228 (m, ν(C≡N)), 2103 (m, ν(C≡C)), 1602 (w, ν(CC), Ph), 1408 (w), 1272 (w), 841 (s), 731 (m), 688 (w), 556 (m); EI MS m/z (%) 127 (100, M$^+$), 100 (18), 86 (11), 84 (16), 49 (15), 44 (21). Anal. Calcd for C_9H_5N (127.15): C, 85.02; H, 3.96; N, 11.02. Found: C, 85.20; H, 3.85; N, 10.93.

*4-({2-Bromo-3′,6′-bis[2-(trimethylsilyl)ethylsulfanyl]-9,9′-spirobifluoren-7-yl}ethynyl)benzonitrile (**21**) and 4-({2-Bromo-1′,6′-bis[2-(trimethylsilyl)ethylsulfanyl]-9,9′-spirobifluoren-7-yl}ethynyl)benzonitrile (**22**).* An argon-flushed 50 mL Schlenk flask was charged with a regioisomeric mixture of spirobifluorenes **17** and **18** in a ratio of 2:1 (160 mg, 204 μmol), $PdCl_2(PPh_3)_2$ (8 mg, 11 μmol), and CuI (4 mg, 22 μmol), and dry triethylamine (12 mL) was added. Then acetylene derivative **20** (28 g, 220 μmol) was added under argon, and the mixture was stirred at room temperature for 16 h. The completion of the reaction was checked by TLC (Hex:EtOAc = 10:1). The reaction mixture was treated with diethyl ether (60 mL) and the precipitate was filtered through a pad of silica gel (10 g, diethyl ether), and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (200 g, Hex:EtOAc equal to 20:1) to provide the symmetric isomer **21** (92 mg) as a white foamy solid and the isomer **22** (45 mg) as a white foamy solid in 86% yield (R_f = 0.29 for the isomer **21**; R_f = 0.36 for the isomer **22**, Hex:EtOAc = 10:1). For the isomer **21**: mp 99−100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.06 (s, 18H, CH_3), 0.99 (m, 4H, $C\underline{H}_2Si$), 3.03 (m, 4H, $SC\underline{H}_2$), 6.62 (d, J = 8 Hz, 2H, C$^{1'}$H, C$^{8'}$H), 6.87 (d, J = 2 Hz, 1H, C^{1}H), 6.89 (d, J = 1 Hz, 1H, C^{8}H), 7.06 (dd, J = 8 Hz, J = 1.5 Hz, 2H, C$^{2'}$H, C$^{7'}$H), 7.46 (dd, J = 7 Hz, J = 1.5 Hz, 2H, C$^{3''}$H, C$^{5''}$H), 7.49 (dd, J = 8 Hz, J = 1.5 Hz, 1H, C^{3}H), 7.53 (dd, J = 8 Hz, J = 1.5 Hz, 1H, C^{6}H), 7.55 (dd, J = 7 Hz, J = 1.5 Hz, 2H, C$^{2''}$H, C$^{6''}$H), 7.67 (d, J = 8 Hz, 1H, C^{4}H), 7.73 (d, J = 1.5 Hz, 2H, C$^{4'}$H, C$^{5'}$H), 7.78 (d, J = 8 Hz, 1H, C^{5}H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.5 (CH_3), 17.1 ($\underline{C}H_2Si$), 29.9 ($S\underline{C}H_2$), 65.2 (C^9), 88.7 (C$^{7''}$), 94.1 (C$^{8''}$), 111.7 (C$^{1''}$), 118.7 (CN), 120.4 (C$^{4'}$H, C$^{5'}$H, C^{5}H), 121.97 (C^7), 122.00 (C^2), 122.6 (C^{4}H), 124.6 (C$^{1'}$H, C$^{8'}$H), 127.7 (C^{1}H, C^{8}H), 128.2 (C$^{4''}$), 128.7 (C$^{2'}$H, C$^{7'}$H), 131.5 (C^{3}H), 132.07 (C^{6}H), 132.10 (C$^{3''}$H, C$^{5''}$H), 132.2 (C$^{2''}$H, C$^{6''}$H), 138.1 (C$^{3'}$, C$^{6'}$), 139.9 (C^{11}), 141.7 (C^{12}), 142.1 (C$^{11'}$, C$^{12'}$), 145.1 (C$^{10'}$, C$^{13'}$), 148.7 (C^{13}), 151.0 (C^{10}); IR (KBr) ν cm^{-1} 3050 (w, ν(=CH)), 2950 (m, $\nu_{as}(CH_2, CH_3)$), 2894 (w, $\nu_s(CH_2, CH_3)$), 2227 (m, ν(C≡N)), 2213 (m, ν(C≡C)), 1601 (s) and 1564 (w, ν(CC), Ph), 1509 (w), 1503 (m), 1467 (m), 1453 (s), 1416 (m), 1405 (m), 1259 (s), 1249 (vs, $\delta_s(CH_3)$, TMS), 1161 (m), 1124 (w), 1104 (w), 1083 (w), 1063 (m), 1006 (m), 956 (w), 858 (vs) and 838 (vs, $\delta_{as}(CH_3)$, TMS), 814 (vs), 749 (m), 724 (w), 694 (m, $\nu_{as}(SiC_3)$, TMS), 637 (m), 553 (m); EI MS m/z (%) 785 (2), 783 (2, M$^+$), 729 (5), 727 (5), 86 (90), 84 (100), 51 (60), 49 (96), 47 (27). Anal. Calcd for $C_{44}H_{42}BrNS_2Si_2$ (785.02): C, 67.32; H, 5.39; N, 1.78. Found: C, 67.48; H, 5.46; N, 1.71.

For the isomer **22**: mp 97−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm −0.15 (s, 9H, $CH_3^{(\rightarrow 1')}$), 0.04 (s, 9H, $CH_3^{(\rightarrow 6')}$), 0.37 (m, 2H, $C\underline{H}_2Si^{(\rightarrow 1')}$), 0.97 (m, 2H, $C\underline{H}_2Si^{(\rightarrow 6')}$), 2.45 (m, 2H, $SC\underline{H}_2^{(\rightarrow 1')}$), 3.00 (m, 2H, $SC\underline{H}_2^{(\rightarrow 6')}$), 6.48 (d, J = 8 Hz, 1H, C$^{8'}$H), 6.84 (d, J = 1.5 Hz, 1H, C^{1}H), 6.88 (d, J = 1 Hz, 1H, C^{8}H), 7.01 (dd, J = 8 Hz, J = 2 Hz, 1H, C$^{7'}$H), 7.14 (dd, J = 7.5 Hz, J = 0.5 Hz, 1H, C$^{4'}$H), 7.41 (td, J = 8 Hz, J = 0.5 Hz, 1H, C$^{3'}$H), 7.45 (dd, J = 7 Hz, J = 1.5 Hz, 2H, C$^{3''}$H, C$^{5''}$H), 7.49 (dd, J = 8 Hz, J = 2 Hz, 1H, C^{3}H), 7.54 (dd, J = 8 Hz, J = 1.5 Hz, 1H, C^{6}H), 7.55 (dd, J = 7 Hz, J = 2 Hz, 2H, C$^{2''}$H, C$^{6''}$H), 7.67 (dd, J = 8 Hz, J = 0.5 Hz, 1H, C$^{2'}$H), 7.69 (d, J = 8 Hz, 1H, C^{4}H), 7.71 (d, J = 1.5 Hz, 1H, C$^{5'}$H), 7.79 (d, J = 8 Hz, 1H, C^{5}H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.7 ($CH_3^{(\rightarrow 1')}$), −1.5 ($CH_3^{(\rightarrow 6')}$), 17.0 ($\underline{C}H_2Si^{(\rightarrow 1')}$), 17.2 ($\underline{C}H_2Si^{(\rightarrow 6')}$), 29.9 ($S\underline{C}H_2^{(\rightarrow 1')}$), 30.0 ($S\underline{C}H_2^{(\rightarrow 6')}$), 65.9 (C^9), 88.5 (C$^{7''}$), 94.5 (C$^{8''}$), 111.5 (C$^{1''}$), 117.8 (C$^{2'}$H), 118.7 (CN), 120.4 (C^{5}H), 120.7 (C$^{5'}$H), 121.6 (C^7), 122.0 (C^{4}H), 122.3 (C^2), 124.1 (C$^{8'}$H), 127.16 (C^{8}H), 127.19 (C^{1}H), 128.4 (C$^{4''}$), 128.8 (C$^{7'}$H), 129.3 (C$^{4'}$H), 129.5 (C$^{3'}$H), 131.2 (C^{3}H), 131.9 (C^{6}H), 132.1 (C$^{3''}$H, C$^{5''}$H), 132.2 (C$^{2''}$H, C$^{6''}$H), 135.2 (C$^{1'}$), 137.6 (C$^{6'}$), 141.1 (C^{11}), 141.7 (C$^{12'}$), 142.8 (C^{12}), 142.9 (C$^{11'}$), 145.6 (C$^{13'}$), 146.1 (C$^{10'}$), 147.5 (C^{13}), 149.8 (C^{10}); IR (KBr) ν cm^{-1} 3059 (w, ν(=CH)), 2950 (m, $\nu_{as}(CH_2, CH_3)$), 2894 (w, $\nu_s(CH_2, CH_3)$), 2228 (m, ν(C≡N)), 2213 (m, ν(C≡C)), 1726 (w), 1601 (s) and 1567 (w, ν(CC), Ph), 1503 (m), 1450 (s), 1419 (m), 1405 (m), 1389 (m), 1259 (m), 1249 (s, $\delta_s(CH_3)$, TMS), 1156 (m), 1126 (vw), 1104 (vw), 1080 (m), 1059 (w), 1006 (m), 954 (w), 858 (vs) and 839 (vs,

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$\delta_{as}(CH_3)$, TMS), 814 (s), 771 (m), 746 (m), 724 (w), 693 (w, $\nu_{as}(SiC_3)$, TMS), 638 (m), 554 (m).

*4-({2,3′,6′-Tris[2-(trimethylsilyl)ethylsulfanyl]-9,9′-spirobifluoren-7-yl}ethynyl)benzonitrile (**23**).* A dry 15 mL pressure tube was charged with spirobifluorene **21** (280 mg, 357 μmol), Xantphos (21 mg, 36 μmol), $Pd_2(dba)_3$ (19 mg, 18 μmol), and dry dioxane (8 mL). The tube was evacuated under a vacuum and refilled with argon three times. Then *N*,*N*-diisopropylethylamine (129 mg, 170 μL, 1 mmol), and 2-(trimethylsilyl)ethanethiol (73 mg, 540 μmol) were added under argon and the tube was quickly capped with a rubber septum. The reaction mixture was heated at 100 °C for 10 h. The completion of the reaction was checked by TLC (Hex:EtOAc = 10:1). After cooling, the reaction mixture was diluted with diethyl ether (60 mL), filtered through a pad of silica gel (10 g, diethyl ether), and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (300 g, hexane:ethyl acetate equal to 15:1) to provide the title compound **23** (285 mg) as a light yellow foamy solid in 95% yield (R_f = 0.35, Hex:EtOAc = 10:1): mp 72−73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm −0.10 (s, 9H, $CH_3^{(\rightarrow 2)}$), 0.06 (s, 18H, $CH_3^{(\rightarrow 3')}$, $CH_3^{(\rightarrow 6')}$), 0.75 (m, 2H, $C\underline{H}_2Si^{(\rightarrow 2)}$), 0.99 (m, 4H, $C\underline{H}_2Si^{(\rightarrow 3')}$, $C\underline{H}_2Si^{(\rightarrow 6')}$), 2.79 (m, 2H, $SC\underline{H}_2^{(\rightarrow 2)}$), 3.02 (m, 4H, $SC\underline{H}_2^{(\rightarrow 3')}$, $SC\underline{H}_2^{(\rightarrow 6')}$), 6.61 (d, *J* = 1 Hz, 1H, C^1H), 6.63 (d, *J* = 8 Hz, 2H, $C^{1'}H$, $C^{8'}H$), 6.87 (d, *J* = 1 Hz, 1H, C^8H), 7.05 (dd, *J* = 8 Hz, *J* = 1.5 Hz, 2H, $C^{2'}H$, $C^{7'}H$), 7.28 (dd, *J* = 8 Hz, *J* = 1.5 Hz, 1H, C^3H), 7.45 (dd, *J* = 8 Hz, *J* = 1.5 Hz, 2H, $C^{3''}H$, $C^{5''}H$), 7.51 (dd, *J* = 8 Hz, *J* = 1 Hz, 1H, C^6H), 7.54 (dd, *J* = 8 Hz, *J* = 1.5 Hz, 2H, $C^{2''}H$, $C^{6''}H$), 7.71 (d, *J* = 8 Hz, 1H, C^4H), 7.72 (d, *J* = 1.5 Hz, 2H, $C^{4'}H$, $C^{5'}H$), 7.75 (d, *J* = 8 Hz, 1H, C^5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ ppm −1.7 ($CH_3^{(\rightarrow 2)}$), −1.5 ($CH_3^{(\rightarrow 3')}$, $CH_3^{(\rightarrow 6')}$), 16.9 ($C\underline{H}_2Si^{(\rightarrow 2)}$), 17.1 ($C\underline{H}_2Si^{(\rightarrow 3')}$, $C\underline{H}_2Si^{(\rightarrow 6')}$), 29.3 ($SC\underline{H}_2^{(\rightarrow 2)}$), 30.0 ($SC\underline{H}_2^{(\rightarrow 3')}$, $SC\underline{H}_2^{(\rightarrow 6')}$), 65.2 ($C^9$), 88.4 ($C^{7''}$), 94.4 ($C^{8''}$), 111.5 ($C^{1''}$), 118.7 (CN), 120.1 ($C^5H$), 120.4 ($C^{4'}H$, $C^{5'}H$), 121.0 (C^4H), 121.2 (C^7), 124.1 (C^1H), 124.6 ($C^{1'}H$, $C^{8'}H$), 127.6 (C^8H), 128.3 ($C^{4''}$), 128.5 (C^3H), 128.8 ($C^{2'}H$, $C^{7'}H$), 132.0 (C^6H), 132.1 ($C^{3''}H$, $C^{5''}H$), 132.2 ($C^{2''}H$, $C^{6''}H$), 137.8 ($C^{3'}$, $C^{6'}$), 138.2 (C^2), 138.6 (C^{11}), 142.1 ($C^{11'}$, $C^{12'}$), 142.5 (C^{12}), 145.9 ($C^{10'}$, $C^{13'}$), 148.7 (C^{13}), 149.7 (C^{10}); IR (KBr) ν cm^{-1} 3054 (w, ν(=CH)), 2950 (m, $\nu_{as}(CH_2, CH_3)$), 2890 (w, $\nu_s(CH_2, CH_3)$), 2227 (w, ν(C≡N)), 2212 (w, ν(C≡C)), 1601 (m) and 1564 (w, ν(CC), Ph), 1502 (w), 1456 (w), 1414 (m), 1249 (s, $\delta_s(CH_3)$, TMS), 1162 (m), 1123 (w), 1104 (w), 1083 (w), 1073 (w), 1006 (m), 959 (vw), 858 (vs) and 838 (vs, $\delta_{as}(CH_3)$, TMS), 816 (s), 752 (m), 693 (m, $\nu_{as}(SiC_3)$, TMS), 637 (m), 553 (w); EI MS *m*/*z* (%) 837 (3, M^+), 753 (2), 648 (2), 73 (55), 44 (100). Anal. Calcd for $C_{49}H_{55}NS_3Si_3$ (838.42): C, 70.20; H, 6.61; N, 1.67. Found: C, 70.02; H, 6.55; N, 1.60.

*S,S′,S″-[7-(4-Cyanophenylethynyl)-9,9′-spirobifluorene-2,3′,6′-triyl] tris(thioacetate) (**24**).* In a 20 mL Schlenk flask, spirobifluorene **23** (110 mg, 131 μmol) was dissolved in the mixture of dry dichloromethane (8 mL) and acetyl chloride (0.8 mL), and put under argon. The solution was treated with $AgBF_4$ (160 mg, 33 mmol, 15% in hexane) and a light brown suspension was stirred at room temperature for 3 h. The completion of the reaction was checked by TLC (Hex:EtOAc = 3:1). The reaction mixture was diluted with dichloromethane (50 mL) and slowly poured into a saturated solution of $NaHCO_3$ (50 mL). The precipitate was filtered through a pad of Celite (CH_2Cl_2), and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (200 g, Hex:EtOAc equal to 4:1) to provide thioacetate **24** (69 mg) as a light yellow foamy solid in 79% yield (R_f = 0.19, Hexane:EtOAc = 3:1): mp > 400 °C (dec.); ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 2.31 (s, 3H, $CH_3^{(\rightarrow 2)}$), 2.45 (s, 6H, $CH_3^{(\rightarrow 3')}$, $CH_3^{(\rightarrow 6')}$), 6.81 (d, *J* = 8 Hz, 2H, $C^{1'}H$, $C^{8'}H$), 6.82 (d, *J* = 0.5 Hz, 1H, C^1H), 6.97 (d, *J* = 1 Hz, 1H, C^8H), 7.23 (dd, *J* = 8 Hz, *J* = 2 Hz, 2H, $C^{2'}H$, $C^{7'}H$), 7.49 (dd, *J* = 8 Hz, *J* = 2 Hz, 1H, C^3H), 7.51 (dd, *J* = 7 Hz, *J* = 1.5 Hz, 2H, $C^{3''}H$, $C^{5''}H$), 7.59 (dd, *J* = 7 Hz, *J* = 1.5 Hz, 2H, $C^{2''}H$, $C^{6''}H$), 7.63 (dd, *J* = 8 Hz, *J* = 1.5 Hz, 1H, C^6H), 7.92 (d, *J* = 8 Hz, 1H, C^5H), 7.94 (d, *J* = 2 Hz, 2H, $C^{4'}H$, $C^{5'}H$), 7.95 (d, *J* = 8 Hz, 1H, C^4H); ^{13}C NMR (125.8 MHz, CD_2Cl_2) δ ppm 30.5 ($CH_3^{(\rightarrow 2)}$), 30.7 ($CH_3^{(\rightarrow 3')}$, $CH_3^{(\rightarrow 6')}$), 65.9 (C^9), 89.3 ($C^{7''}$), 93.9 ($C^{8''}$), 112.1 ($C^{1''}$), 119.0 (CN), 121.5 (C^5H), 121.8 (C^4H), 122.9 (C^7), 125.2 ($C^{1'}H$, $C^{8'}H$), 127.2 ($C^{4'}H$, $C^{5'}H$), 127.9 (C^8H), 128.4 ($C^{4''}$), 129.11 (C^2), 129.13 ($C^{3'}$, $C^{6'}$), 130.3 (C^1H), 132.5 ($C^{3''}H$, $C^{5''}H$), 132.6 ($C^{2''}H$, $C^{6''}H$, C^6H), 135.0 ($C^{2'}H$, $C^{7'}H$), 135.5 (C^3H), 142.2 (C^{12}), 142.5 ($C^{11'}$, $C^{12'}$), 142.7 (C^{11}), 148.8 (C^{13}), 149.1 (C^{10}), 149.3 ($C^{10'}$, $C^{13'}$); IR (KBr) ν cm^{-1} 3055 (w, ν(=CH)), 2228 (m, ν(C≡N)), 2215 (m, ν(C≡C)), 1707 (vs, ν(C=O)), 1601 (m, ν(CC), Ph), 1503 (m), 1470 (w), 1459 (m), 1416 (m), 1404 (m), 1392 (m), 1351 (m), 1123 (bs), 1024 (w), 1004 (w), 950 (bm), 878 (w), 838 (m), 817 (s), 638 (m), 620 (s), 610 (s), 555 (w); EI MS *m*/*z* (%) 663 (6, M^+), 621 (27), 579 (16), 537 (20), 504 (16), 103 (57), 76 (43), 57 (46), 43 (100). Anal. Calcd for $C_{40}H_{25}NO_3S_3$ (663.82): C, 72.37; H, 3.80; N, 2.11. Found: C, 72.53; H, 3.89; N, 2.02.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **1**−**24** containing chemical structures and numbering used for the complete peak assignment. Crystallographic data (CIF) for **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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