A divergent synthesis of oligoarylalkanethiols with Lewis-basic N-donor termini

Björn Schüpbach and Andreas Terfort*

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Araliphatic thiols are key molecules for the formation of self-assembled monolayers with high long-range order. If these monolayers shall act as bases for the attachment of other molecules, the respective thiols need to carry suitable functional groups, such as the amino or the pyridine group. Due to their Lewis-basicity, these groups are not compatible with the thiol group under most reaction conditions. Here, an entry into this versatile class of compounds is presented, by using fundamental building blocks in which the thiol groups are protected as triisopropylsilyl sulfides making them compatible with many reagents including Grignard reagents and palladium catalysts. With this strategy at hand, six thiols with bi- and terphenyl backbones, one to three methylene groups, and amino or pyridine head groups became accessible in short reaction sequences.

Introduction

The attachment of functional groups to the surface of solids is the basis of numerous techniques, such as adsorption control,[1] sensing,[2] or solid phase synthesis.[3] While many of these applications require only a more or less dense distribution of these functional groups, the most advanced ones such as microelectronics or nano-architectures require also a very high density as well as excellent lateral order.[4] A typical approach for this kind of surface functionalisation is the deposition of self-assembled monolayers (SAMs), which are formed by the self-terminating reaction of suitable molecules with the solid surfaces. For the archetypical example, the thiolate-on-gold system, it has been established already 25 years ago that even flexible alkane chains become densely packed in an ordered fashion within these surface layers.[5] Unfortunately, the introduction of any donor group at the topmost position (therefore called the 'head group' by many authors), almost always results in disorder in the respective SAM due to significant and often directed interactions, such as hydrogen bonding.[6] These interactions primarily lead to the bending of the alkyl chains under formation of so-called 'gauche defects' (in a well-ordered monolayer the alkyl chains adopt an *all-trans* conformation), leading to a diminished packing density accompanied by translational disorder. In the past, we[7] and others[8] could show that the use of stiff backbones, which cannot be bent by the head group interactions, is a suitable strategy to suppress this disorder mechanism. Advantageous backbones for these applications, both from the viewpoint of accessibility as well as conformational stiffness, are *para*-oligophenyls, such as *p*-terphenyl. These moieties are not only rod-shaped themselves, but can be co-axially extended in the respective 4-(4′-, 4″-, …)positions – this is with the binding groups for the surface attachment as well as with the desired head groups – permitting the rational design of a plethora of molecules with different lengths and substitution patterns and predictable SAM-forming properties.[9] This approach was recently extended by the introduction of short alkyl chains in between the *p*-oligophenyl units and the binding groups. The alkyl chains on one hand are flexible enough to permit an adjustment between the adsorption site and the preferred packing of the oligophenyl moieties, and on the other hand are stiff enough to communicate the binding situation at the anchoring group up to the head group due to their preference of the *all-trans* conformation.[10] This ultimately results in monolayers with exceptional long range order and a pronounced odd-even effect on the tilt angle of the oligophenyl unit. The latter also affects the thickness of the monolayers as well as the orientation of any functional group attached to the oligophenyl unit.

We wanted to extend this principle to SAM-forming molecules carrying Lewis-basic head groups, which shall permit the attachment of further groups after SAM formation, either by coordination (metals) or formation of covalent bonds (amides *etc.*). For this, we chose the pyridine and the primary amino group, since they are well-established in coordination chemistry as well as organic chemistry, and should fit well into densely packed aromatic monolayers due to their small size. Both of these groups have been used successfully for a large bandwidth of applications. Some very basic studies on the monolayer-forming properties of pyridine-terminated thiols show that only under special precautions highly ordered monolayers can be obtained.[11] Some of these monolayers show a pronounced dependency of their structure on the pH value.[12] The typical use, as stated above, is the attachment of metal ions by coordination, either for analytical purposes[13] or for the formation of thin metal films.[14] Pyridine-terminated monolayers have also been used for the tight attachment of redox-active proteins to investigate their electrochemical behaviour.[15] Even two 4-pyridylbenzene thiols with[16] and without[17] alkylchain have been reported. The latter have been used as a template for the directed growth of glycine crystals.[18] For amino-terminated monolayers, the focus of interest is clearly on the covalent attachment of biological entities.[19] While for the latter application mostly aliphatic thiols have been employed, a few reports describe the use of aminothiophenols with the basic

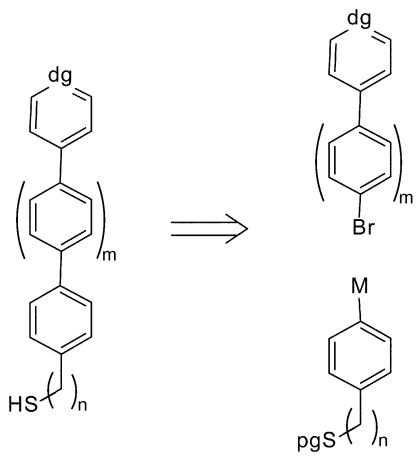
Institut für Anorganische und Analytische Chemie, Universität Frankfurt, Max-von-Laue-Straße 7, 60438, Frankfurt, Germany. E-mail: aterfort@chemie.uni-frankfurt.de; Fax: +49 (0)69 798 29188

idea to provide a better electronic coupling. The redox-active probes then have been either attached covalently[20] or electrostatically.[21]

Due to the numerous applications, we figured it necessary to develop a family of molecules, which provides the access to highly ordered amino- and pyridyl-terminated monolayers on gold. The major challenge for the synthesis of thiols bearing Lewis-basic groups is that the thiol groups become very air-sensitive under basic conditions, making their handling difficult, in particular during the purification or the deposition of the molecules. This is especially true for molecules carrying primary alkylamino groups, the corresponding ammonium ions of which have comparable pK_a values as alkanethiol groups (about 10–11). If these groups are present in the same molecule, most of the thiol groups will become deprotonated, thus being not only less suited for the formation of SAMs[22] but also becoming almost instantly oxidized upon contact with air. It is therefore viable to use a suitable protecting group chemistry for the thiol groups during the construction of the molecule framework, setting the sensitive combination only free at the very end of the synthesis.

Results and discussion

Several strategies for the synthesis of 4-substituted bi- and terphenyl derivatives have been employed in the past.[23] Since in most cases only one or two compounds were targeted, the development of divergent synthetic strategies mostly was not necessary. In contrast to this, our extended study on the behaviour of substituted oligophenylalkanethiols in SAMs required fast and efficient access to a variety of molecules not only with different head groups but also with different lengths of the alkyl chains. We therefore decided to develop a building block approach in which benzene or biphenyl derivatives, which already carry the required head group, become attached to more or less universal synthons (**1**) that permit the introduction of (protected) ω-mercaptoalkyl groups of different lengths (Scheme 1).

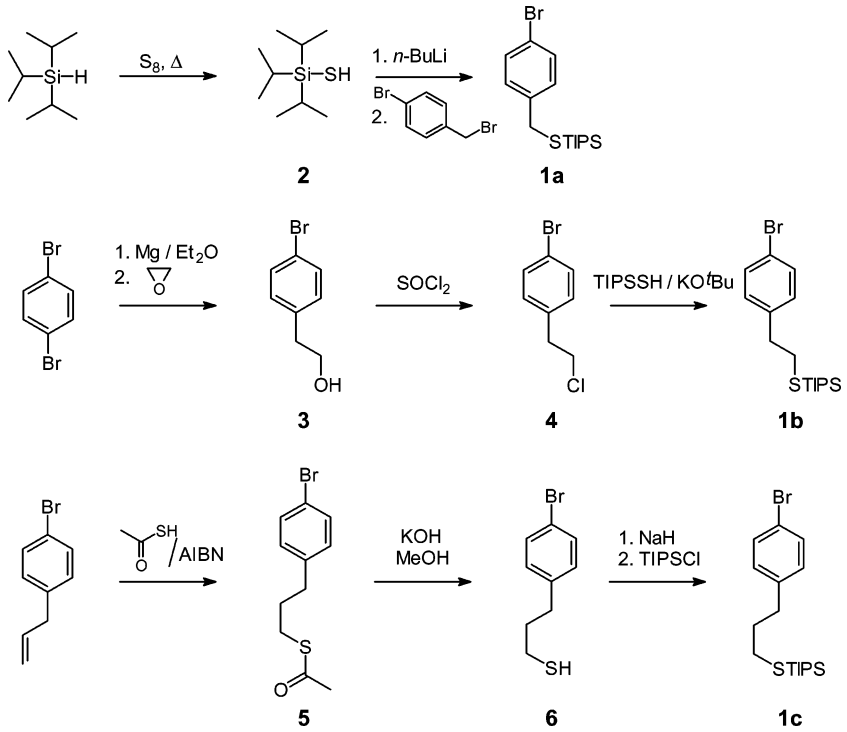


Scheme 1 Retrosynthetic approach to the N-terminated oligophenyls. 'dg' signifies the donor group (N or C-NH_2), 'M' is a metal–organic group, and 'pg' represents a suitable protective group for the coupling chemistry. m and n are 0–1 and 1–3 in this manuscript, respectively.

The synthons also already carry a phenyl group, since C–C coupling reactions between arenes are well established and can proceed under mild conditions. A general problem is that most of these coupling reactions are catalyzed by metals, typically palladium, which become poisoned by thiols. Therefore many attempts have been made to render thiol chemistry and Pd(0) catalysed cross coupling compatible.[24] The most obvious strategy is to protect the thiol group during the coupling step (pg in Scheme 1) and remove the protecting group as a last step in the synthetic sequence. Frequently the *t*-butyl group has been employed, but its removal requires harsh or inconvenient (Hg(II), H_2S) conditions giving only low yields.[17,25] Because of that, we were looking for another sterically hindered protecting group which is easy to introduce and which is also easily cleaved under mild conditions. Soderquist *et al.* have introduced the triisopropylsilyl (TIPS) group as protecting group for thiols, which even is compatible with Grignard conditions, as the authors demonstrated for a protected bromoalkanethiol,[26] by hydrolysing the respective organometallic compound with deuterium oxide to obtain the deuterated alkylsilanethiol. We could recently extend this approach by demonstrating that the Grignard reagent obtained from 4-BrC_6H_4STIPS can be employed in Pd catalyzed cross coupling reactions either directly or after transformation in the corresponding organozinc reagent.[27] The deprotection of the thiol group can then be accomplished with acids or with tetrabutylammonium fluoride.[26,28]

For the access to (substituted) oligophenylalkanethiols, we needed to prepare the analogous 4-bromophenylalkyl TIPS-thioethers **1a–c** with varying chain length. As has been shown in ref. 26, triisopropylsilanethiol (TIPSSH, **2**) is a suitable reagent not only for the introduction of the TIPS group but the sulfur atom as well. We simplified the synthesis of **2** by the direct reaction of triisopropylsilane with elemental sulfur[29] (Scheme 2). Deprotonation with n-butyllithium or potassium-*t*-butoxide activates this material for the reaction with alkyl halides. For the synthesis of the synthon with only one methylene group (**1a**), 91% yield could be obtained by using commercially available 4-bromobenzyl bromide. For the synthesis of the respective homolog with an ethylene group, first the carbon backbone had to be assembled, starting from 1,4-dibromobenzene. This was converted to the mono-Grignard reagent in ether (in THF the reaction does not proceed selectively), before being reacted with oxirane in THF. The presence of catalytic amounts of Cu(I) salts helped the ring-opening addition to give 2-(4-bromophenyl)ethanol **3** in 64% yield. Treatment of **3** with thionyl chloride yielded the respective chloride (**4**, 68%), which then was reacted with the aforementioned lithium salt of **2** under formation of 67% of **1b**. As an alternative route, the photo-induced addition of thiols to alkenes, which due to its cleanliness and high yields now is considered to be a 'click' reaction,[30] has been tested. Nevertheless, the addition of **2** to 4-bromostyrene proceeded sluggish and yielded only about 50% of **1b** in an impure state. We therefore prefer the multistep process, in spite of its overall yield of only 29%, since this method utilizes much cheaper reagents (permitting its performance on a multi-gram scale) and yields pure products.

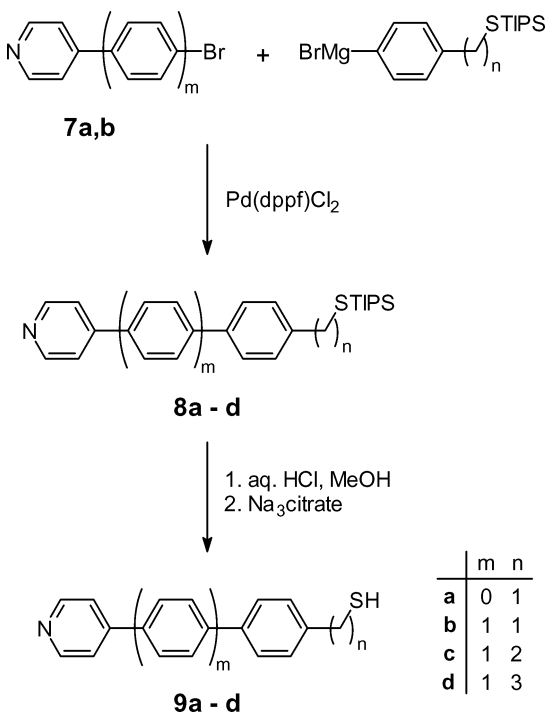
For the synthesis of the third synthon (**1c**, with three methylene groups), 4-bromo(prop-2-enyl)benzene was used as starting material, which itself can be obtained from 1,4-dibromobenzene according to a literature procedure.[31] The attempted addition of **2** using AIBN or light as initiators proceeded even more sluggish than in case of the respective styrene. In contrast to



Scheme 2 Syntheses of the building blocks **1a–c** with different lengths of the alkyl chain between the phenyl rings and the sulfur atoms. The latter are already protected for the coupling chemistry (TIPS = triisopropylsilyl).

this, the addition of thioacetic acid to **1c** proceeded smoothly to give *S*-3-(4-bromophenyl)propyl thioacetate **5** in 80% yield. Surprisingly, this reaction even started in the absence of AIBN when the reaction is carried out in air. The resulting thioacetate **5** was saponificated with KOH to the respective thiol **6** in almost quantitative yield (Scheme 2). This was converted to the TIPS thioether by the action of triisopropylsilylchloride (TIPSCl). For the success of the reaction the choice of the right base turned out to be essential: While for the silylation of thiophenols with trimethylsilylchloride (TMSCl) triethylamine was reported to be useful,[32] the reaction of **6** with TIPSCl in presence of this base proceeded unsatisfactorily (50% conversion after one week at reflux temperature). The use of n-BuLi, as has been successful for the inverse etherification steps above, gave full conversion after 24 h at room temperature, but undesired byproducts were formed, most likely due to halogen-lithium exchange in **6**. In this case we therefore could only isolate **1c** in a yield of 52%. Because both methods were unsatisfactory, we were looking for an alternative strong base which is non-nucleophilic and does not undergo halogen/metal exchange. We found that sodium hydride is the base of choice for the deprotonation of **6**. The resulting sodium thiolate reacted very smoothly with TIPSCl permitting the isolation of the third synthon **1c** in a yield of 83%.

With the synthons **1a–c** at hand, the synthesis of the donor-substituted oligophenylalkanethiols could be approached. For the attachment of the 4-pyridyl head groups, either the commercially available 4-bromopyridine (**7a**, as hydrochloride) or 4-(4-bromophenyl)pyridine (**7b**, ref. [33]) have been used. These were reacted with the Grignard reagents of **1a–c** in the presence of $Pd(dppf)Cl_2$ (Kumada reaction) to form the coupling products **8a–d** in 34–74% yield (Scheme 3). In case of **7a**, the deprotonation



Scheme 3 Assembly of the 4-pyridyl-terminated oligophenylalkanethiols using the Kumada coupling with the Grignard reagents of **1a–c**, followed by the deprotection of the thiol group.

of the hydrochloride was achieved by the action of one equivalent of ethylmagnesium chloride before the other reagents were added. In the final step, the TIPS group was removed protolytically using

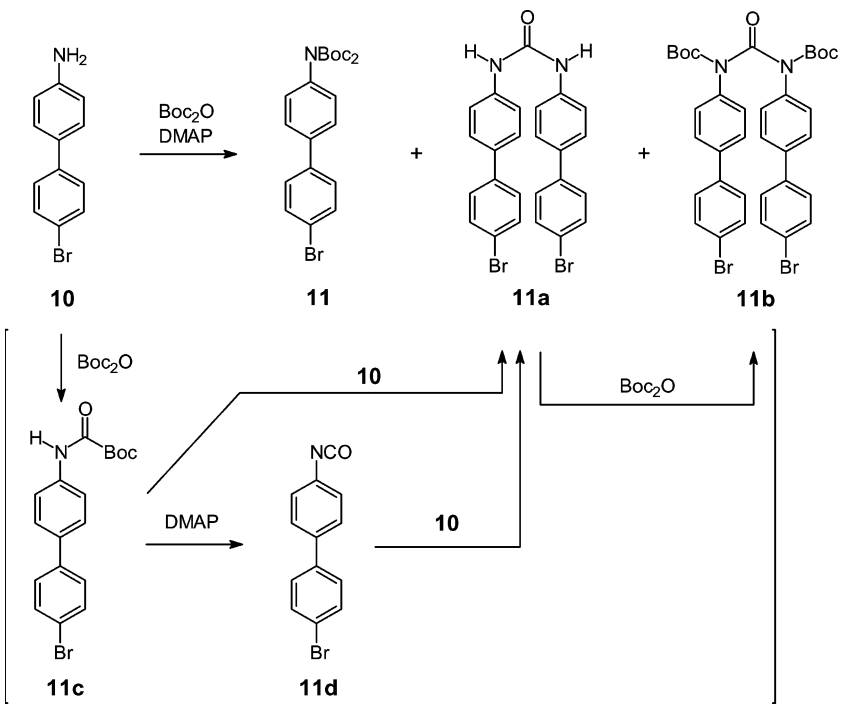
HCl. The free molecules **9a–d** were obtained by adjusting the pH to about 8 to deprotonate the pyridyl ring but not the thiol group. The pyridinethiols are air-stable as crystalline compounds but become easily oxidized in solution.

For the extension of this approach to the amino-terminated thiols, suitable building blocks had to be found. The amino group is inherently not compatible with most metal–organic reagents, typically leading to the protonation of the reagents. It is therefore necessary to introduce protective groups which are compatible with the coupling chemistry. For this, we decided to switch from the magnesium-based coupling chemistry (Kumada coupling) to the respective zinc-based chemistry (Negishi coupling) known to be compatible with carbonyl groups so we could use the *t*-butyloxycarbonyl (Boc) group for the protection of the amino group. This well-established group has the advantage – among others – to be removable under acidic conditions, that is, the same conditions under which the TIPS group can be removed. Since the simple Boc amides are even more acidic than the corresponding amines, we decided to rather use the diBoc imides instead.

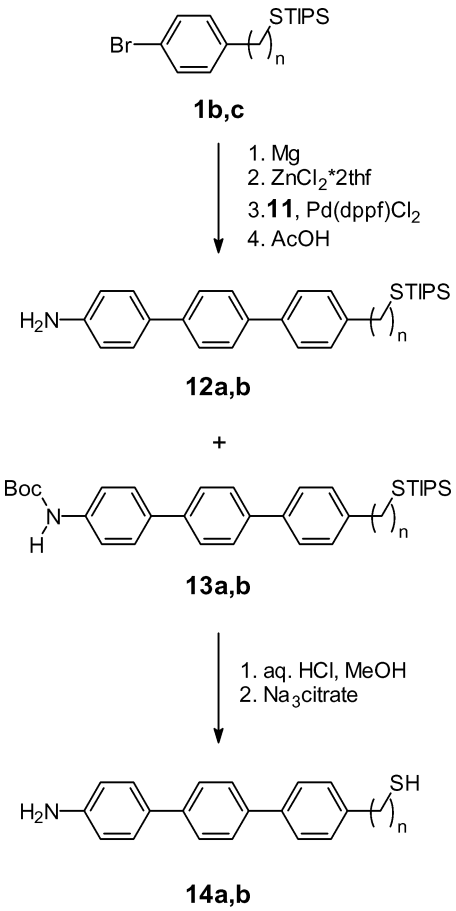
To obtain the building block for the synthesis of the amino-terminated terphenyl thiols, we treated 4-amino-4′-bromobiphenyl **10**[34] with an excess of di-*tert*-butyl dicarbonate (Boc_2O) in the presence of Steglich's catalyst[35] (4-dimethylaminopyridine, DMAP). It turned out that, if the catalyst was added right from the beginning of the reaction, three products were obtained, with a yield of the desired imide **10** of only 16%. The other two products were identified to be *N*,*N*′-bis-(4′-bromobiphenyl-4-yl)urea **11a** and *N*,*N*′-diBoc-*N*,*N*′-bis(4′-bromobiphenyl-4-yl)urea **11b**. It has been suggested that these ureas either form from an intermediate carbamic-carbonic anhydride **11c** directly or *via* the respective isocyanate **11d**, by the action of unaltered **10**.[36] By reaction of **11a** with excess Boc_2O, **11b** is obtained (Scheme 4). The respective mono-Boc compound could not be isolated. To improve the yield of **11**, we attempted to protect **10** with Boc_2O in the presence of sodium hydride but without Steglich's catalyst. Surprisingly, the sodium hydride itself could not push the reaction directly to the di-Boc compound **11**, but when DMAP was added, we finally were able to obtain **11** in a more acceptable yield of 51% with **11b** as only by-product (34%).

The thus protected amine **11** was then used for the Negishi cross coupling in the presence of $Pd(dppf)Cl_2$ as catalyst (Scheme 5). Presumably due to the formation of Lewis-acidic zinc salts, no coupling products still carrying the diBoc imido group could be isolated but rather the terphenyl derivatives with no (**12a**,**b**) or one Boc group (**13a**,**b**) remaining. The two classes of compounds, which formed in a ratio of ~ 2 : 3 (**12**:**13**), could be easily separated by chromatography giving total yields of 68% (**12a**,**13a**) and 66% (**12b**,**13b**), respectively. For the removal of the protective groups, acidic conditions similar to the ones used for the pyridine-terminated thiols have been chosen, regardless on whether the materials with or without Boc group have been used. The final amino thiols **14a**,**b** could be obtained with good to excellent yields, if some precautionary measures were taken, since the amino-terminated thiols are even more air sensitive than the pyridine thiols, in particular in solution.

To obtain the amino thiols **14a**,**b** with very high purity, gradient sublimation in high vacuum is recommended. The resulting colourless solids can be stored under exclusion of air for months, but they slowly turn yellowish upon exposure to oxygen.



Scheme 4 The synthesis of the amino-terminated oligophenylalkanethiols requires a complete protection of the amino-group during the coupling step to avoid protolysis of the metal–organic reagent. The di-Boc group is compatible with the zinc-organic reagent and can be removed under the same conditions as the TIPS group, but its introduction is accompanied by the formation of the two ureas **11a** and **11b**. The formation of **11a** can be suppressed by the presence of NaH during the protection, resulting in an improved yield of **11**. See text for details.



Scheme 5 The couplings of the diBoc imide **11** with the zinc reagents of **1b**,**c** yield the terphenyls **12a**,**b** and **13a**,**b** under loss of one or both Boc groups. The deprotection of either yields the amino thiols **14a**,**b** in good to excellent yields.

Conclusions

As could be demonstrated here, the careful choice of protective group chemistry opens the door to the synthesis of arylalkanethiols carrying Lewis-basic head groups, which can be used for the formation of densely functionalized surfaces. The triisopropylsilyl (TIPS) group turned out to be the protective group of choice for the thiol groups, since the respective silylthioether is compatible with the metal–organic reagents and the conditions under which the molecular backbones are constructed. For the protection of amino groups, the diBoc imide proved to be useful, since it is not only stable under the coupling conditions but can be removed using the same reagents as for the removal of the TIPS group (that is, acidic methanol). By pre-forming the TIPS thioethers with small 4-bromophenylalkyl residues, central building blocks became accessible, which permit the fast and efficient synthesis of all the Lewis-basic molecules in this study. We believe that this divergent approach can easily be extended to many other oligophenylalkanethiols bearing all kinds of head groups.

Experimental section

General

All chemicals were purchased from commercial sources and used without further purification except for TIPSCl and thioacetic acid, which were distilled prior to use. Unless otherwise stated, all reactions were carried out using standard Schlenk procedures and anhydrous and oxygen-free solvents. THF and diethyl ether were destilled from Na/K alloy. DMF was distilled from CaH_2. 'Oxygen-free', but not dry solvents were liberated of oxygen by passing a stream of nitrogen through the respective solvent for at least one hour. 4-(4-Bromophenyl)pyridine,[33] 4-bromo(prop-2-enyl)benzene,[31] 4-amino-4′-bromobiphenyl,[34] and Pd(dppf)Cl_2[37] were prepared according to literature procedures. The synthesis of triisopropylsilanethiol (**2**) was carried out in analogy to a literature known synthesis of triphenylsilanethiol.[29] Melting points were determined with an apparatus according to Dr Tottoli and are uncorrected. The following NMR spectrometers were used: Bruker Avance 300, Bruker DRX 400, Bruker Avance 400, Bruker ARX 200, and Varian Gemini 2000. IR spectra were recorded on a Bruker Vertex or a Nicolet 6700 Fourier-transform IR spectrometer using a diamond ATR cell. Mass spectra were recorded on a MAT 95 from Finnigan or a Finnigan LTQ-FT from Thermo Fischer Scientific. For elemental analysis we used a vario micro cube from elementar. GCMS analysis was carried out using a Trace GC 2000 Series in combination with a Finnigan Trace mass spectrometer from ThermoQuest CE Instruments.

4-Bromobenzyl(triisopropylsilyl)sulfide (1a)

To a solution of **2** (9.22 g, 48.4 mmol) in 100 mL of THF, n-BuLi (30 ml of a 1.6 mol L^{-1} solution in hexanes, 48 mmol) was added under external cooling with ice. Cooling was maintained and 4-bromobenzyl bromide (10.54 g, 42.17 mmol) dissolved in 50 mL of THF was added slowly. After the reaction mixture was stirred for 20 h at room temperature, 25 mL of water were added and the THF was evaporated under reduced pressure. Further 100 mL of water were added. The aqueous suspension was extracted once with methylcyclohexane and three times with CH_2Cl_2. Acidification with HOAc helped the separation of the phases. The organic phases were collected, the solvent was evaporated and the remaining oil distilled under reduced pressure (oil pump vacuum). Collection of the fraction boiling at 142 °C yielded the product as colourless liquid. 13.77 g (38.31 mmol), 91%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.45–7.37 (m, 2H, CH-ar), 7.26–7.19 (m, 2H, CH-ar), 3.70 (s, 2H, CH_2), 1.40–1.20 (m, 3H, CH), 1.20–1.10 (m, 18H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 139.8, 131.5, 130.1, 120.6, 29.5, 18.5, 12.7 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 2943 (CH-alk), 2889 (CH-alk), 2865 (CH-alk), 1486, 1461, 1071, 1012, 881 cm^{-1}. MS (EI): m/z (%) = 358 (22) [M^+], 315 (89), 273 (22), 90 (27). $C_{16}H_{27}BrSSi$ (359.44): calcd. C 53.46, H 7.57, S 8.92; found C 53.31, H 7.47, S 9.10.

2-(4-Bromophenyl)ethyl-1-*S*-triisopropylsilylsulfide (1b) from 4-bromostyrene

A mixture of 4-bromostyrene (5.87 g, 32.0 mmol), **2** (12 mL, 11 g, 56 mmol), and some crystals of AIBN was heated to 120–130 °C (no solvent) for 7 days with daily additions of AIBN. After this time, no further conversion could be observed by GLC. The crude mixture containing the product was separated by distillation using a kugelrohr apparatus. First, volatile materials were distilled off at 75 °C/10 mbar. After that, distillation was continued in oil pump vacuum. Collection of the fraction boiling at an

oven temperature of 175 °C yielded the product as colourless liquid. 5.97 g (16.0 mmol), 50%. The product still contained some impurities but was of sufficient purity for further transformations.

2-(4-Bromophenyl)ethyl-1-*S*-triisopropylsilylsulfide (1b) from 1-bromo-4-(2-chloroethyl)benzene (4)

KO*t*Bu (8.45 g, 75.3 mmol) was dissolved in 50 mL of dry DMF. **2** (15.34 g, 80.69 mmol) was added under external cooling with an ice bath. 1-Bromo-4-(2-chloroethyl)benzene **4** (14.85 g, 67.65 mmol) was added directly to the cooled mixture. After being stirred for 48 h at room temperature, the solution was acidified by addition of glacial acetic acid. The DMF and excess acetic acid were removed in vacuum. The remainder was dissolved in a mixture of water and light petroleum. The organic phase was separated and washed with water once. After evaporation of the light petroleum, the remaining liquid was distilled in oil pump vacuum. Collection of the fraction boiling at 146 °C yielded the product as colourless liquid. 17.07 g (45.71 mmol), 67%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.43–7.37$ (m, 2H, CH-ar), 7.10–7.04 (m, 2H, CH-ar), 2.89–2.69 (m, 4H, CH_2), 1.32–1.17 (m, 3H, CH), 1.15–1.06 (m, 18H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 137.8, 129.6, 128.4, 118.3, 37.1, 25.3, 16.7, 10.8$ ppm. IR (ATR): $\tilde{\nu}_{max} = 2943$ (CH-alk), 2889 (CH-alk), 2864 (CH-alk), 1488, 1462, 1072, 1012, 881 cm^{-1}. MS (APCI$^-$): m/z (%) = 215 (100) [$BrPh(CH_2)_2S^-$]. $C_{17}H_{29}BrSSi$ (373.47): calcd. C 54.67, H 7.83, S 8.59; found C 54.50, H 7.64, S 8.56.

3-(4-Bromophenyl)propyl-1-*S*-triisopropylsilyl sulfide (1c), deprotonation with NEt_3

3-(4-Bromophenyl)propane thiol (**6**) (55.66 g, 240.8 mmol) and triisopropylsilyl chloride (54.62 g, 283.3 mmol) and triethylamine (34.61 g, 342.0 mmol) were dissolved in 150 mL of THF. The reaction mixture turned turbid, but no significant evolution of heat was observed. After heating the mixture under reflux for 24 h, only low conversion was observed. After refluxing for further 96 h the solvent mixture was removed under reduced pressure. The remainder was distributed between water and light petroleum. The organic phase was separated and washed with water once. After evaporation of the petrol ether, the remaining liquid was fractionated in oil pump vacuum by means of a 40 cm vigreux column. Collection of the fraction boiling at 140–160 °C yielded the product as a slightly yellowish liquid. 43.22 g (111.5 mmol) 46% of **1c**, with 24.83 g (107.4 mmol) of **6** being recovered.

3-(4-Bromophenyl)propyl-1-*S*-triisopropylsilyl sulfide (1c), deprotonation with n-BuLi

To a solution of **6** (25.08 g, 108.5 mmol) in 170 mL of dry THF, n-BuLi (104 mmol, 65 mL of a 1.6 mol L^{-1} solution in hexanes) was added at an internal temperature between –60 and -50 °C. The reaction mixture was allowed to warm to 0 °C. After that, TIPSCl (22.93 g, 11.89 mmol) was added and the mixture was stirred for 24 h at room temperature. Addition of water and evaporation of the THF followed. The aqueous suspension was extracted twice with light petroleum. The organic extracts were evaporated under reduced pressure. Final distillation *via* a 30 cm Vigreux column yielded pure **1c** as a colourless oil. 22.04 g (56.88 mmol), 52%.

3-(4-Bromophenyl)propane-1-*S*-triisopropylsilyl sulfide (1c), deprotonation with NaH

Sodium hydride (2.33 g, 97.1 mmol) was suspended in 50 mL of dry THF. To this, a solution of **6** (17.75 g, 76.79 mmol) in 50 mL of dry THF was added slowly. After the formation of gas and heat ceased, TIPSCl (21.75 g, 112.8 mmol) was added to the mixture. Stirring became impossible due to formation of precipitates. Because of that, further 50 mL of THF were added. The mixture was refluxed for 3 h and stirred at room temperature for 14 h. Acetic acid (50 mL), water (200 mL), and light petroleum (100 mL) were added. The organic phase was separated off and washed with water. The organic solvents were evaporated and the remaining liquid was distilled at 10^{-5} mbar. Some lower boiling impurities had to be separated. Distillation of the fraction boiling at a temperature of 140–145 °C yielded the product as colourless liquid. 24.69 g (63.72 mmol), 83%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41–7.36$ (m, 2H, CH-ar), 7.09–7.04 (m, 2H, CH-ar), 2.70 (t, 2H, $^3J = 7.6$ Hz, CH_2), 2.52 (t, 2H, $^3J = 7.1$ Hz, CH_2), 1.95–1.84 (m, 2H, CH_2), 1.28–1.15 (m, 3H, CH), 1.12–1.06 (m, 18H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 140.6, 131.3, 130.2, 119.6, 34.3, 34.0, 25.1, 18.6, 12.7$ ppm. IR (ATR): $\tilde{\nu}_{max} = 2942$ (CH-alk), 2864 (CH-alk), 2858 (CH-alk), 1488, 1462, 1072, 1012, 882 cm^{-1}. MS (APCI$^-$): m/z (%) = 229 (100) [$BrPh(CH_2)_3S^-$]. $C_{18}H_{31}BrSSi$ (387.49): calcd. C 55.79, H 8.06, S, 8.27; found C 55.85, H 7.93, S 8.50.

2-(4-Bromophenyl)ethanol (3)

Caution: The reaction is highly exothermic and might start surprisingly after an induction period. During the addition of the oxirane, the reaction mixture often solidifies. It is essential to use a powerful mechanical stirrer and to have a cooling bath of liquid nitrogen at hand. The mono-Grignard reagent of 1,4-dibromobenzene was obtained by careful addition of a solution of the dibromobenzene (140.33 g, 596.7 mmol) in 300 mL of dry Et_2O to magnesium turnings (17.78 g, 731.4 mmol) activated with 1,2-dibromoethane. The reaction was completed by heating under reflux for 1h. Then the solution of the Grignard reagent was decanted from remaining magnesium. Upon addition of CuBr (7.15 g, 49.8 mmol) the solution turned black. Oxirane (~100 mL, ~90 g, ~2 mol) was dissolved in 150 mL of dry THF. The reaction flask was cooled with ethanol/N_2 and the first 100 mL of the oxirane solution were added in such rate that the internal temperature was maintained between –10 and + 5 °C. After that, the reaction mixture solidified and stirring became impossible even if mechanical stirring was used. To regain a stirrable reaction mixture, 100 mL of anhydrous THF were added to the reaction mixture. At a temperature between 5 and 10 °C, the next 100 mL of the solution of ethylene oxide in THF were slowly added. After that the cooling bath was removed and the remaining 50 mL of the oxirane solution were added. Stirring was continued for 30 min until an analytical sample taken from the mixture and hydrolyzed did not show significant amounts of bromobenzene by GC-MS analysis. Acetic acid (100 mL) was added followed by addition of 200 mL of water. The organic phase was separated off and ether (200 mL) was added to the aqueous phase. The mixture was filtered through a pad of Celite™ and the ethereal phase was separated off. The combined organic

phases were evaporated and the remaining liquid was distilled in vacuum at 2 mbar using a 1.5 m spinning band column. First, some more volatile impurities (*e.g.* bromobenzene) distilled. Collection of the fraction boiling at 105 °C/2 mbar yielded the product as colourless liquid. 77.07 g (383.3 mmol), 64%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.45–7.39 (m, 2H, CH-ar), 7.12–7.06 (m, 2H, CH-ar), 3.80 (t, 2H, ^3J = 6.6 Hz, CH_2), 2.79 (t, 2H, ^3J = 6.5 Hz, CH_2), 1.83 (s, 1H, OH) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 137.5, 131.5, 130.7, 120.2, 63.2, 38.4 ppm. MS (EI): *m*/*z* (%) = 202 (39) [M^+], 171 (100), 121 (15), 91 (94). IR (ATR): $\tilde{\nu}_{max}$ = 3320 (OH), 2940 (CH-alk), 2874 (CH-alk), 1487, 1403, 1072, 1043, 1009, 833, 804 cm^{-1}. C_8H_9BrO (201.06): calcd. C 47.79, H 4.51; found C 47.52, H 4.39.

1-Bromo-4-(2-chloroethyl)benzene (4)

No Schlenk technique was used for this preparation. **3** (76.45 g, 380.2 mmol) was dissolved in 50 mL of CH_2Cl_2. To this solution, thionyl chloride (60 mL, 98 g, 0.82 mol) was added. The mixture was stirred at room temperature for 30 min and heated under reflux for 1 h. The solvent and excess thionyl chloride was removed. The intermediate chlorosulfinyl ester was transformed to the chloride **4** by pyrolysis. When heating to 140 °C evolution of gas was observed. The mixture was further heated to 170 °C for 2 h. After cooling to room temperature, the product was distilled through a 1.5 m spinning band column. Collection of the fraction boiling at 85 °C at 2 mbar yielded the product as colourless liquid. 56.54 g (257.6 mmol), 68%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47–7.43 (m, 2H, CH-ar), 7.12–7.09 (m, 2H, CH-ar), 3.70 (t, 2H, ^3J = 7.2 Hz, CH_2), 3.02 (t, 2H, ^3J = 7.2 Hz, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.0, 131.6, 130.5, 120.8, 44.6, 38.4 ppm. MS (ESI^-): *m*/*z* (%) = 219 (100), [M – H^+]. IR (ATR): $\tilde{\nu}_{max}$ = 2957 (CH-alk), 1487, 1071, 1010, 901, 800, 739 cm^{-1}. C_8H_8BrCl (219.51): calcd. C 43.77, H 3.67; found C 43.79, H 3.64.

S-3-(4-Bromophenyl)propyl thioacetate (5)

No Schlenk technique was used for this preparation. Thioacetic acid (44.84 g, 589.1 mmol) was added to 4-bromo(prop-2-enyl)benzene (56.84 g, 296.0 mmol) under stirring. When about half of the quantity of thioacetic acid was added, a vigorous reaction started spontaneously, which generated copious amounts of heat. After all of the thioacetic acid was added, a small amount of AIBN was added to the still hot reaction mixture. Stirring at room temperature was continued for further 14 h. The excess thioacetic acid was evaporated at 2 mbar at room temperature. The remaining product was distilled through a 40 cm vigreux column. Collection of the fraction boiling at 116 °C at 0.4 mbar yielded the product as a slightly yellowish liquid. 64.49 g (236.1 mmol), 80%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.45–7.35 (m, 2H, CH-ar), 7.10–7.00 (m, 2H, CH-ar), 2.86 (t, 2H, ^3J = 7.3 Hz, CH_2), 2.63 (t, 2H, ^3J = 7.6 Hz, CH_2), 2.33 (s, 3H, CH_3), 1.92–1.82 (m, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.7, 140.1, 131.6, 130.2, 119.8, 34.2, 31.0, 30.7, 28.4 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3023 (CH-ar), 2935 (CH-ar), 2858 (CH-alk), 1687 (C=O), 1487, 1133, 1011 cm^{-1}. HRMS ($C_{11}H_{14}BrOS$, $[HM]^+$): calcd. for 272.9943; found 272.9938. $C_{11}H_{13}BrOS$ (273.19): calcd. C 48.36, H 4.80, S 11.74; found C 48.25, H 4.72, S 12.00.

3-(4-Bromophenyl)propyl thiol (6)

To a solution of potassium hydroxide (32.06 g, 571.4 mmol) in 300 mL of oxygen-free methanol, *S*-3-(4-bromophenyl)propyl thioacetate (**5**) (64.49 g, 236.1 mmol) was added under nitrogen. After the slightly exothermic reaction ceased, the reaction mixture was heated under reflux for 1h, and stirred for 14 h at room temperature. The mixture was acidified with 20% H_2SO_4 which resulted in precipitation of copious amounts of salt. The mixture was extracted twice with CH_2Cl_2 and once with light petroleum. The organic extracts were washed with water once and evaporated. Distillation of the remainder and collection of the fraction boiling at 110 °C (3 mbar) yielded the product as a yellowish liquid. 52.45 g (226.9 mmol), 96%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.42–7.36 (m, 2H, CH-ar), 7.07–7.01 (m, 2H, CH-ar), 2.70 (t, 2H, ^3J = 7.5 Hz, CH_2), 2.63 (dt, 2H, ^3J = 7.4 Hz, CH_2), 1.89 (q, 2H, ^3J = 7.3 Hz, CH_2), 1.35 (t, 1H, ^3J = 7.8 Hz, SH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 140.1, 131.4, 130.1, 119.6, 35.1, 33.6, 23.8 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3022 (CH-ar), 2931 (CH-alk), 2956 (CH-alk), 1486, 1072, 1010, 806 cm^{-1}. MS (ESI^-): *m*/*z* (%) = 263 (100), [M + CH_3O^-]. $C_9H_{11}BrS$ (231.15): calcd. C 46.76, H 4.80, S 13.87; found C 46.49, H 4.63, S 14.04.

4-(4′-((Triisopropylsilylthio)methyl)phenyl)pyridine (8a)

4-Bromopyridine hydrochloride (3.43 g, 17.6 mmol) was suspended in 10 mL of THF. Ethylmagnesium chloride (18 mmol, 9.0 ml of a 2 mol L^{-1} solution in THF) was added, resulting in warming of the solution and the appearance of a slight red colour. Pd(dppf)Cl_2 (0.27 g, 0.37 mmol) was added, followed by addition of the Grignard reagent prepared from **1a**. After stirring at room temperature for 2 h, water was added to the deep violet solution. Most of the THF was removed *in vacuo* and the remainder was extracted with diethyl ether. The organic solvents were evaporated and the residual oil was coevaporated with CH_2Cl_2 to remove water. The product was column filtrated through a pad of silica using ethyl acetate (some fast moving, non-polar impurities had to be removed) to obtain a yellowish oil. 3.27 g (9.14 mmol), 52%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.70–8.61 (m, 2H, CH-ar), 7.61–7.55 (m, 2H, CH-ar), 7.54–7.44 (m, 4H, CH-ar), 3.80 (s, 2H, CH_2), 1.41–1.20 (m, 3H, CH), 1.19 (m, 18H, CH_3) ppm. IR (ATR): $\tilde{\nu}_{max}$ = 2944 (CH-ar), 2863 (CH-alk), 1595, 1461, 1400, 1019, 986, 882, 812, 794 cm^{-1}. MS (EI): *m*/*z* (%) = 357 (2) [M^+], 336 (6), 314 (15), 169 (100).

Coupling of 1-(4-bromophenyl)alkane-ω-*S*-triisopropylsilyl sulfides with 4-bromophenylpyridine. Typical procedure

A solution of the Grignard reagent was prepared from 13.2 mmol of the respective 1-(4-bromophenyl)alkyl-ω-*S*-triisopropylsilyl sulfide, 1.00 g (41.2 mmol) of magnesium and 25 mL of THF. This solution was added to 2.50 g (10.5 mmol) of 4-(4-bromophenyl)pyridine and 0.16 g (0.22 mmol) Pd(dppf)Cl_2 in 50 mL of THF. After the reaction mixture was stirred for 16 h at room temperature, water was added. The THF was removed and the aqueous slurry was extracted with CH_2Cl_2. The CH_2Cl_2 was evaporated. The remaining material was dissolved in ethyl acetate and filtered through a plug of alumina. After evaporation of the ethyl acetate, the remaining solid was crystallised from methylcyclohexane.

4-(4′-((Triisopropylsilylthio)methyl)biphenyl-4-yl)pyridine (8b)

Colourless solid, yield 2.71 g, 47%, m.p. 118–121 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ = 8.67–8.63 (m, 2H, CH-ar), 7.50–7.34 (m, 8H, CH-ar), 7.12–7.09 (m, 2H, CH-ar), 3.74 (s, 2H, CH_2), 1.27–1.03 (m, 21H, $CH(CH_3)_2$) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 150.9, 147.4, 141.8, 140.9, 139.3, 137.3, 129.5, 127.9, 127.6, 127.5, 121.4, 30.2, 18.8, 13.1 ppm. MS (APCI$^+$): m/z (%) = 434 (100) [HM$^+$]. $C_{27}H_{35}NSSi$ (433.72): calcd. C 74.77, H 8.13, N 3.23, S 7.39; found C 74.74, H 7.99, N 3.09, S 7.43.

4-(4′-(2-(Triisopropylsilylthio)ethyl)biphenyl-4-yl)pyridine (8c)

Colourless solid, yield 2.03 g (34%), m.p. 108–109 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ = 8.67–8.62 (m, 2H, CH-ar), 7.50–7.43 (m, 4H, CH-ar), 7.37–7.33 (m, 2H, CH-ar), 7.19–7.14 ((m, 2H, CH-ar), 7.11–7.07 (m, 2H, CH-ar), 2.97–2.90 (m, 2H, CH_2), 2.83–2.75 (m, 2H, CH_2), 1.22–1.03 (m, 21H, $CH(CH_3)_2$) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 150.9, 147.4, 142.0, 140.8, 138.9, 137.3, 129.5, 127.8, 127.6, 127.5, 121.4, 39.7, 27.9, 18.8, 13.0 ppm. HRMS ($C_{28}H_{38}NSSi$, [HM]$^+$): calcd. 448.2489; found 438.2473. $C_{28}H_{37}NSSi$ (447.75): calcd. C 75.11, H 8.33, N 3.13, S 7.16; found C 75.06, H 8.29, N 2.99, S 6.96.

4-(4′-(3-(Triisopropylsilylthio)propyl)biphenyl-4-yl)pyridine (8d)

Brownish solid, yield 3.63 g (74%) m.p. 119–120 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.67–8.60 (m, 2H, CH-ar), 7.53–7.49 (m, 2H, CH-ar), 7.49–7.45 (m, 2H, CH-ar), 7.39–7.33 (m, 2H, CH-ar), 7.20–7.15 (m, 2H, CH-ar), 7.12–7.07 (m, 2H, CH-ar), 2.73 (mt, 2H, ^3J = 7.5 Hz, CH_2), 2.51 (t, 2H, ^3J = 7.0 Hz, CH_2), 1.95 (m, 2H, CH_2), 1.22–1.04 (m, 21H, $CH(CH_3)_2$) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 150.9, 147.5, 142.1, 141.6, 138.4, 137.2, 129.5, 127.8, 127.6, 127.4, 121.4, 34.9, 34.5, 25.5, 18.8, 13.1, ppm. HRMS ($C_{29}H_{40}NSSi$, [HM]$^+$): calcd. 462.2645; found 462.2628. $C_{29}H_{39}NSSi$ (461.78): calcd. C 75.43, H 8.51, N 3.03, S 6.94; found C 75.61, H 8.66, N 2.80, S 6.44.

Deprotection of the oligoarylalkanethiols. Typical procedure

The silyl sulfide (**8a–d** or **12/13a,b**, 2.40 mmol) was dissolved in a boiling mixture of 50 mL of oxygen-free methanol and 10 mL of oxygen-free 20% HCl. The mixture was heated under reflux for 20 h and allowed to cool to room temperature. In the case of the pyridine thiols, 50 mL of a mixture of water and methanol 1 : 1$_{vol}$ was added resulting in clear solutions of the pyridinium salts. This mixture was washed three times with light petroleum to remove non-polar impurities before the methanol was removed. This procedure could not be applied for the amino thiols because of the lower solubility of their ammonium salts compared to the pyridinium salts.

The following steps had to be performed under strict exclusion of oxygen: The pH of the remaining aqueous phase was adjusted to about 8 by addition of trisodium citrate. The slurry was extracted with CH_2Cl_2 immediately. The extract was evaporated to dryness.

In case of the pyridine-terminated thiols **9a–d**, the remaining solid was dissolved in 250 mL of boiling, oxygen-free methylcyclohexane, filtered hot through a Schlenk frit, and left for crystallisation. The crystals were filtered by suction, washed with light petroleum, and dried. The products could be further purified by vacuum gradient sublimation at a pressure of about 10^{-3} Pa.

The amino-terminated thiols **14a,b** were sublimed in the gradient apparatus without previous crystallisation.

(4-(Pyridin-4-yl)phenyl)methanethiol (9a)

Colourless solid, yield 3.27 g (62%, m.p. 64–66 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ = 8.63–8.58 (m, 2H, CH-ar), 7.24–7.18 (m, 2H, CH-ar), 7.07–7.04 (m, 2H, CH-ar), 7.04–7.01 (m, 2H, CH-ar), 3.29 (d, 2H, ^3J = 7.6 Hz, CH_2), 1.51 (t, 1H, ^3J = 7.6 Hz, SH) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 150.9, 147.4, 142.3, 137.1, 128.9, 127.3, 121.4, 28.5 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3026 (CH-ar), 2907 (CH-alk), 2568 (SH), 1594, 1485, 721 cm^{-1}. MS (EI): m/z (%) = 201 (27) [M$^+$], 168 (100). $C_{12}H_{11}NS$ (201.29): calcd. C 71.60, H 5.51, N 6.96, S 15.93; found C 71.85, H 5.73, N 6.99, S 15.96.

(4′-(Pyridin-4-yl)biphenyl-4-yl)methanethiol (9b)

Colourless solid, yield 0.55 g (82%) m.p. 254–256 °C (decomp.). ^{1}H NMR (C_6D_6, 400 MHz): δ = 8.67–8.62 (m, 2H, CH-ar), 7.48–7.44 (m, 2H, CH-ar), 7.43–7.39 (m, 2H, CH-ar), 7.38–7.33 (m, 2H, CH-ar), 7.15–7.11 (m, 2H, CH-ar), 7.11–7.08 (m, 2H, CH-ar), 3.34 (d, 2H, ^3J = 7.5 Hz, CH_2), 1.50 (t, 1H, ^3J = 7.5 Hz, SH) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 150.9, 147.4, 141.7, 141.2, 139.4, 137.5, 130.0, 128.9, 127.9, 127.5, 121.4, 28.6 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3035 (CH-ar), 2924 (CH-alk), 1591, 1562, 1399, cm^{-1}. HRMS ($C_{18}H_{16}NS$, [HM]$^+$): calcd. 278.0998; found 278.0992. $C_{18}H_{15}NS$, (277.38): calcd. C 77.94, H 5.45, N 5.05, S 11.56; found C 77.80, H 5.60, N 4.89, S 11.83.

2-(4′-(Pyridin-4-yl)biphenyl-4-yl)ethane-1-thiol (9c)

Colourless solid, yield 0.90 g (72%) m.p. 162–164 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.66–8.62 (m, 2H, CH-ar), 7.52–7.47 (m, 2H, CH-ar), 7.47–7.42 (m, 2H, CH-ar), 7.38–7.34 (m, 2H, CH-ar), 7.11–7.07 (m, 2H, CH-ar), 7.02–6.98 (m, 2H, CH-ar), 2.62 (t, 2H, ^3J = 7.3 Hz, CH_2), 2.58–2.49 (m, 2H, CH_2), 1.17 (t, 1H, ^3J = 7.9 Hz, SH) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 150.9, 147.4, 141.9, 139.9, 138.9, 137.4, 129.5, 127.8, 127.6, 127.4, 121.4, 40.1, 26.0 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3031 (CH-ar), 2929 (CH-alk), 2900 (CH-alk), 2837 (CH-alk), 1590, 1398 cm^{-1}. MS (ESI$^+$): m/z (%) = 292 (100), [HM]$^+$. $C_{19}H_{17}NS$ (291.41): calcd. C 78.31, H 5.88, N 4.81, S 11.00; found C 78.08, H 6.15, N 4.78, S 10.79.

3-(4′-(Pyridin-4-yl)biphenyl-4-yl)propane-1-thiol (9d)

Colourless solid, yield 0.86 g (55%), m.p. 159–161 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.66–8.62 (m, 2H, CH-ar), 7.54–7.50 (m, 2H, CH-ar), 7.50–7.45 (m, 2H, CH-ar), 7.39–7.34 (m, 2H, CH-ar), 7.11–7.08 (m, 2H, CH-ar), 7.08–7.04 (m, 2H, CH-ar), 2.47 (t, 2H, ^3J = 7.5 Hz, CH_2), 2.15 (dt, 2H, ^3J = 7.0 Hz, ^3J = 7.9 Hz, CH_2), 2.59–2.48 (m, 2H, CH_2), 0.97 (t, 1H, ^3J = 7.9 Hz, SH) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 150.9, 147.4, 142.0, 141.3, 138.5, 137.3, 129.3, 127.8, 127.7, 127.4, 121.4, 35.7, 34.1, 26.0 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3029 (CH-ar), 2934 (CH-alk), 2848 (CH-alk), 1587, 1484, 1399, 1002 cm^{-1}. HRMS ($C_{20}H_{20}NS$, [HM]$^+$): calcd. 306.1311; found 306.1303. $C_{20}H_{19}NS$ (305.44): calcd. C 78.65, H 6.27, N 4.59, S 10.50; found C 78.94, H 6.47, N 4.50, S 10.76.

4′-Bromo-4-(di-*N*-Boc)-aminobiphenyl (11) and *N*,*N*′-di-Boc-*N*,*N*′-bis(4′-bromobiphenyl-4-yl)urea (11b)

Sodium hydride (1.86 g, 77.5 mmol) was suspended in THF (20 mL) and di-*tert*-butyldicarbonate (6.75 g, 30.9 mmol) was added. To this, a solution of 4′-bromo-4-aminobiphenyl (2.92 g, 11.8 mmol) in THF (40 mL) was slowly added, but no formation of gas or heat was observed. Stirring was continued for 100 h at room temperature. After that, TLC indicated that the free amine was consumed. A catalytic amount of DMAP was added and stirring was continued for further 70 h. The sodium hydride was filtered from the solution and the solvent was removed. The remaining oil was filtered over silica using dichloromethane as eluent. The solvent of the eluate was removed and the remaining oil was chromatographed over silica using CH_2Cl_2. First, the di-Boc-urea was eluted. Elution of the di-Boc-derivative followed. Evaporation of the solvent afforded the still impure products which were crystallised from methylcyclohexane to yield the pure products as colourless crystals.

4′-Bromo-4-(*N*,*N*-di-Boc-imido)biphenyl (11)

Colourless solid, yield 2.69 g (51%), m.p. 150–152 °C. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.60–7.50 (m, 4H, CH-ar), 7.49–7.41 (m, 2H, CH-ar), 7.26–7.18 (m, 2H, CH-ar), 1.45 (s, 18H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 63 MHz): 152.0, 139.3, 139.0, 138.9, 131.9, 128.7, 128.3, 127.2, 121.7, 82.9, 27.9 ppm. IR (ATR): ν_{max} = 3093 (CH-ar), 3041 (CH-ar), 2971 (CH-alk), 2929 (CH-alk), 1781 (C=O), 1703, 1486, 1367, 1282, 1246, 1147, 1096, 1004, 856, 817, 777 cm^{-1}. HRMS ($C_{22}H_{26}NO_4$, [HM]$^+$): calcd. 448.1118; found 448.1113. $C_{22}H_{26}NO_4$ (448.35): calcd. C 58.94, H 5.85, N 3.12; found C 59.16, H 6.08, N 3.01.

N,*N*′-Di-Boc-*N*,*N*′-bis(4′-bromobiphenyl-4-yl)urea (11b)

Colourless solid, yield 1.45 g (2.00 mmol) (34%), m.p. 175 °C (dec). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.61–7.51 (m, 4H, CH-ar), 7.50–7.42 (m, 2H, CH-ar), 7.40–7.33 (m, 2H, CH-ar), 1.48 (s, 9H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 63 MHz): 154.6, 152.0, 139.4, 139.3, 138.4, 131.9, 128.7, 128.3, 127.3, 121.8, 83.6, 28.0 ppm. IR (ATR): ν_{max} = 3085 (CH-ar), 3041 (CH-ar), 2980 (CH-alk), 2943 (CH-alk), 1736 (C=O), 1708 (C=O), 1480, 1320, 1296, 1248, 1138, 1075, 1003, 837, 810, 797 cm^{-1}. MS (APCI$^+$): *m*/*z* (%) = 524 (100) [M – 2Boc]$^+$, 567 (37). $C_{35}H_{34}Br_2N_2O_5$ (722.46): calcd. C 58.19, H 4.74, N 3.88; found C 58.28, H 4.62, N 3.74.

4-(ω-(Triisopropylsilylthio)alkyl)-4″-*N*-Boc-aminoterphenyls (12a,b) and 4-(ω-(triisopropylsilylthio)alkyl)-4″-aminoterphenyls (13a,b), typical procedure

A solution of the Grignard compound prepared from **1b**,**c** (6 mmol) and magnesium (0.30 g, 13 mmol) in THF (15 mL) was added to $ZnCl_2$·2thf (3.62 g, 12.9 mmol). Further 40 mL of THF were added, followed by the addition of Pd(dppf)Cl_2 (0.10 g 0.14 mmol) and **11** (2.21 g, 4.93 mmol). After the mixture was stirred at room temperature for 16 h, the THF was removed and water was added. During addition the formation of a gas was observed. The suspension was acidified by addition of glacial acetic acid and extracted with CH_2Cl_2. The organic phase was washed with water and saturated $NaHCO_3$ and evaporated to dryness. Polar impurities were removed by filtration through a plug of silica using CH_2Cl_2 as eluent. Final purification and separation of the products was done by column chromatography over silica with light petroleum/CH_2Cl_2 gradient from 1 : 1 as eluent. Evaporation of the solvent yielded the products as solids. Analytical samples could be obtained by crystallisation from methylcyclohexane.

4-(2-(Triisopropylsilylthio)ethyl)-4″-aminoterphenyl (12a)

Yellowish solid, yield 1.46 g (27%), slightly impure, m.p. 125–129 °C.^{1}H-NMR (C_6D_6, 250 MHz): δ = 7.55 (s, 4H, CH-ar), 7.55–7.50 (m, 2H, CH-ar), 7.45–7.39 (m, 2H, CH-ar), 7.20–7.10 (m, 2H, CH-ar), 6.43–6.35 (m, 2H, CH-ar), 2.89–2.99 (m, 2H, CH_2), 2.84 (brd. s, 2H, NH_2),2.85–2.73 (m, 2H, CH_2), 1.22–1.05 (m, 21H, -$CH(CH_3)_2$) ppm. ^{13}C-NMR (C_6D_6, 63 MHz): 146.7, 140.7, 140.0, 139.6, 139.2, 129.3, 128.2, 127.4, 127.1, 115.4, 39.9, 28.0, 18.8, 13.0 ppm. IR (ATR): ν_{max} = 3451, 3358, 2942 (CH-alk), 2889 (CH-alk), 2864 (CH-alk), 1618, 1492, 1462, 1277, 881, 804 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 462 (100) [HM]$^+$. $C_{29}H_{39}NSSi$ (461.78): calcd. C 75.43, H 8.51, N 3.03, S 6.94; found C 74.01, H 7.86, N 3.04, S 6.64.

4-(3-(Triisopropylsilylthio)propyl)-4″-aminoterphenyl (12b)

Slightly yellowish solid, yield 0.65 g (28%), m.p. 138 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.62–7.55 (m, 4H, CH-ar), 7.55–7.50 (m, 2H, CH-ar), 7.45–7.39 (m, 2H, CH-ar), 7.27–7.21 (m, 2H, CH-ar), 6.72–6.66 (m, 2H, CH-ar), 3.63 (brd. s, 2H, NH_2), 2.81–2.72 (m, 2H, CH_2), 2.56 (t, 2H, ^3J = 7.9 Hz, CH_2), 2.02–1.89 (m, 2H, CH_2), 1.36–1.15 (m, 3H, CH), 1.15–1.00 (m, 18H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 145.8, 140.5, 139.7, 138.7, 138.3, 130.8, 128.8, 127.7, 127.1, 126.7, 126.5, 115.3, 34.4, 34.2, 25.2, 18.5, 12.6 ppm. IR (ATR): ν_{max} = 3479, 3370, 2940 (CH-alk), 2889 (CH-alk), 2863 (CH-alk), 1618, 1491, 1460, 1283, 881, 812, 678 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 477 (100) [HM]$^+$. $C_{30}H_{41}NSSi$ (475.27): calcd. C 75.73, H 8.69, N 2.94, S 6.74; found C 75.85, H 8.76, N 2.69, S 6.96.

4-(2-(Triisopropylsilylthio)ethyl-4″-*N*-Boc-aminoterphenyl (13a)

Slightly yellowish solid, yield 2.67 g (41%), m.p. 134–135 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.64 (s, 4H, CH-ar), 7.60–7.57 (m, 2H, CH-ar), 7.57–7.55 (m, 2H, CH-ar), 7.48–7.43 (m, 2H, CH-ar), 7.31–7.27 (m, 2H, CH-ar), 6.54 (brd. s, 1H, NH), 2.99–2.92 (m, 2H, CH_2), 2.85–2.78 (m, 2H, CH_2), 1.55 (s, 9H, CH_3) 1.35–1.21 (m, 3H, -CH), 1.15–1.10 (m, 18H, -CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): 152.7, 140.0, 139.6, 139.4, 138.9, 137.8, 135.4, 129.0, 127.5, 127.4, 127.1, 127.1, 118.9, 80.7, 39.5, 28.4, 27.5, 18.6, 12.8 ppm. IR (ATR): ν_{max} = 3423 (NH), 2942 (CH–Al), 2865 (CH–Al), 1727 (C=O), 1504, 1156, 808 cm^{-1}. MS (APCI$^+$): *m*/*z* (%) = 463 (100) [H(H_2N-(C_6H_4)$_3$-(CH_2)$_2$-STIPS]$^+$, 503 (85), 567 (65). $C_{34}H_{47}NO_2SSi$ (561.89): calcd. C 72.68, H 8.43, N 2.49, S 5.69; found C 72.52, H 8.26, N 2.45, S 5.65.

4-(3-(Triisopropylsilylthio)propyl-4″-*N*-Boc-aminoterphenyl (13b)

Slightly yellowish solid, yield 1.09 g (38%), m.p. 154–155 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.64–7.56 (m, 4H, CH-ar), 7.53–7.46 (m, 2H, CH-ar), 7.46–7.37 (m, 2H, CH-ar), 7.46–7.39 (m, 2H, CH-ar), 7.28–7.22 (m, 2H, CH-ar), 6.65 (brd. s, 1H, NH),

2.82–2.78 (m, 2H, CH_2), 2.56 (t, 2H, ^3J = 7.1 Hz, CH_2), 2.20–1.90 (m, 2H, CH_2), 1.53 (s, 9H, -$C(CH_3)_3$) 1.33–1.15 (m, 3H, -CH), 1.14–1.00 (m, 18H, -CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 152.7, 140.7, 139.5, 139.1, 138.2, 137.7, 135.3, 128.9, 127.3, 127.2, 126.9, 126.8, 118.8, 80.5, 34.4, 34.2, 28.3, 25.2, 18.5, 12.7 ppm. IR (ATR): ν_{max} = 3421 (NH), 3021 (CH-Ar), 2929 (CH–Al), 2865 (CH–Al), 1723 (C=O), 1505, 1156, 810 cm^{-1}. MS ($APCI^+$): m/z (%) = 478 (100) [$H(H_2N$-$(C_6H_4)_3$-$(CH_2)_3$-STIPS$^+$], 517 (90), 557 (25). $C_{35}H_{49}NO_2SSi$ (575.33): calcd. C 72.99, H 8.58, N 2.43, S 5.57; found C 73.09, H 8.77, N 2.27, S 5.71.

(4-Aminoterphenyl-4″yl)ethane-2-thiol (14a)

colourless solid, yield 0.39 g (65%), m.p. 227–230 °C. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.54 (s, 4H, CH-ar), 7.53–7.47 (m, 2H, CH-ar), 7.43–7.34 (m, 2H, CH-ar), 7.25–7.16 (m, 2H, CH-ar), 6.75–6.65 (m, 2H, CH-ar), 3.67 (brd. s, 2H, NH_2), 2.97–2.83 (m, 2H, CH_2), 2.83–2.69 (m, 2H, CH_2), 1.36 (t, 1H, ^3J = 7.6 Hz, SH) ppm. ^{13}C-NMR ($CDCl_3$, 63 MHz): 145.9, 140.0, 139.2, 138.8, 138.7, 131.0, 129.1, 127.9, 127.2, 127.0, 126.7, 115.4, 39.9, 26.0 ppm. IR (ATR): ν_{max} = 3397, 3320, 3208, 3030 (CH-ar), 2930 (CH-alk), 2849 (CH-alk), 1601, 1491, 1442, 1400, 1257, 1149, 804 cm^{-1}. MS (ESI^+): m/z (%) = 306 (100) $[HM]^+$. $C_{20}H_{19}NS$ (305.44): calcd. C 78.65, H 6.27, N 4.59, S 10.50; found C 78.42, H 6.50, N 4.40, S 10.42.

(4-Aminoterphenyl-4″yl)propane-3-thiol (14b)

colourless solid, from **12b**: yield 0.18 g (76%), from **13b**: yield 0.17 g (100%), m.p. 240 °C (dec). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.54 (s, 4H, CH-ar), 7.51–7.45 (m, 2H, CH-ar), 7.42–7.36 (m, 2H, CH-ar), 7.22–7.15 (m, 2H, CH-ar), 6.74–6.66 (m, 2H, CH-ar), 3.67 (brd. s, 2H, NH_2), 2.81–2.72 (t, 2H,^3J = 7.5 Hz, CH_2), 2.51 (dt, 2H, $^3J_1$=$^3J_2$=7.3 Hz, CH_2), 1.91 (tt, 2H,$^3J_1$=$^3J_2$=7.3 Hz, CH_2), 1.31 (t, 1H,^3J = 7.9 Hz, SH) ppm. ^{13}C-NMR ($CDCl_3$, 63 MHz): 145.9, 140.3, 139.9, 138.8, 138.6, 131.0, 128.9, 127.9, 127.2, 126.9, 126.6, 115.4, 35.4, 34.0, 24.0 ppm. IR (ATR): ν_{max} = 3325 (NH), 3029 (CH-ar), 2919 (CH-al), 1605, 1491, 1399, 1256, 1144, 807 cm^{-1}. MS (ESI^+): m/z (%) = 320 (100) $[HM]^+$. $C_{21}H_{21}NS$ (319.46): calcd. C 78.95, H 6.63, N 4.38, S 10.04; found C 78.95, H 6.77, N 4.28, S 10.11.

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