DOI: 10.1002/ejoc.200700810

Redox-Active Catechol-Functionalized Molecular Rods: Suitable Protection Groups and Single-Molecule Transport Investigations

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Keywords: Molecular electronics / Protecting groups / Electrochemistry / Molecular rods / Catechol / Single-molecule conductance

The synthesis of molecular rod **1** comprising a central redox-active unit and two terminal acetyl-protected sulfur groups is reported. Various protecting groups for the catechol moiety were investigated and protected precursors **14**–**18** were synthesized. In particular, ethyl orthoformate **17** can be easily and selectively deprotected in mild acidic conditions ruling out the need for a strong Lewis acid like boron tribromide. The redox activity of **1** was confirmed by cyclic voltammetric investigations. Gold–molecule–gold junctions were formed with the dimethyl-protected rod **18**. Single-molecule transport investigations using this molecular rod revealed a set of three single-junction conductance values varying over two orders of magnitude.

Introduction

Molecular electronics, understood as the engineering of electronic properties by the integration of tailor-made molecules into electronic circuits, is of both fundamental and economic interest.[1–6] In particular, the combination of minute size and huge designable and synthesizable structural variety renders molecules promising functional units in electronic devices. Driven by the prospect of tiny electronically active building blocks at low cost, the field of molecular electronics has even made its way into the research portfolios of microelectronic companies. In the past decade, the investigation of single-molecule junctions has revealed not only interesting correlations between molecular structure and observed transport properties,[7–16] but also allowed the design and assembly of the first devices with electronic properties arising from integrated molecules, for example, a single-molecule rectifier.[17]

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Devices comprising molecular switches are currently of great interest. In order to alter the current through a molecular junction, compounds that possess structural bistability controlled by an external stimulus are required. Potential stimuli are electromagnetic radiation, electronic potential or chemical gradients. So far, several devices comprising single molecules as switches have been reported, for example, photoswitchable dithienylethene derivatives in a mechanically controlled break-junction (MCB)[18] or electrochemically addressable redox chromophores like viologens in an electrochemically addressable scanning tunnelling microscopy (STM) set-up.[19–21] A molecular rod comprising a central 6,6′-dinitro-2,2′-bipyridine subunit has been reported to display hysteretic transport properties in a variety of set-ups[22] ranging from a single-molecule MCB[23] to self-assembled monolayers (SAMs) in a crossed wire junction.[22] Hysteretic transport properties have been reported for junctions comprising SAMs of mechanically interlinked supermolecules like catenanes[24] and rotaxanes.[25,26] The observed bistability of these junctions presumably arises from structural rearrangements of the integrated supermolecules.[27] Laterally limited SAMs of nitro-functionalized molecular rods displayed a sudden collapse of the transport current at a threshold voltage referred to as the negative differential resistance (NDR).[28]

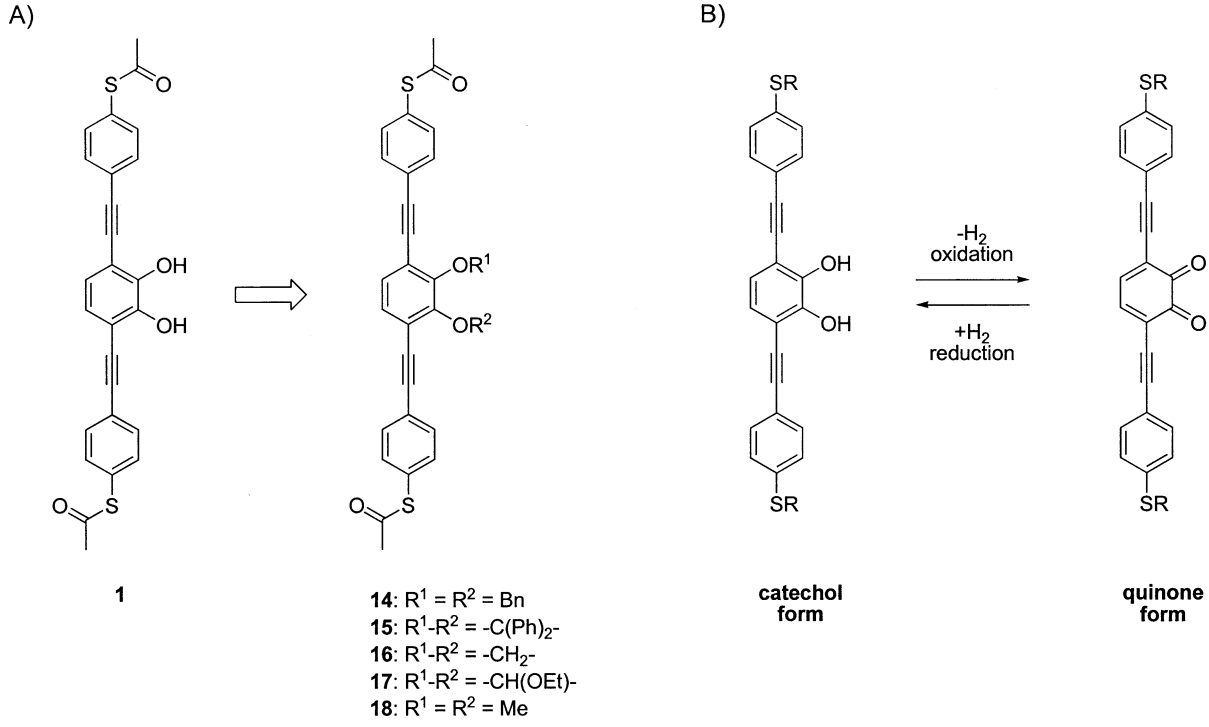
Under electrochemical control, junctions comprising single viologen derivatives show redox-state-dependent transport properties.[19–21] Furthermore, redox chromophores comprising substructures like an extended tetrathiafulvalene[29] or a quinone[30] have been proposed as their redox states are expected to control the extent of electronic delocalization and thus to strongly affect their electric trans-

parency. Indeed, molecular rods comprising quinone chromophores have been reported to display NDR properties in SAMs investigated by STM.[31,32]

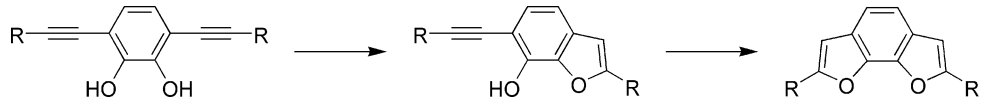
Our current interest is focused on catechol subunits as redox addressable chromophores in oligo(phenyleneethynylene) (OPE) rod systems. As depicted in Scheme 1, the extent of conjugation is not expected to be affected to a large degree by the redox state of the catechol subunit as both redox states provide a conjugated π system as alternating single and double bonds or as an aromatic unit. However, its ability to form hydrogen bonds will be altered considerably. Whereas the catechol subunit with its two hydroxy groups acts as a hydrogen donor, the quinone form after oxidation acts as a hydrogen acceptor as only the lone pairs of the two carbonyls are available to form hydrogen bonds. To be able to integrate this electrochemically addressable subunit into molecular architectures of increasing complexity comprising suitable functional groups as binding partners for hydrogen bonds, its chemical reactivity has to be controlled by suitable protecting groups. To investigate the feasibility of catechol-functionalized OPE rods, we targeted molecular rod **1** comprising terminal acetyl-protected sulfur groups with a view to immobilizing it between gold electrodes.

As depicted in Scheme 1, a series of potential precursors of the target structures masked with different protecting groups have been synthesized to investigate their tolerance towards the terminal acetylsulfanyl functions. Furthermore, the intrinsic lability of the target motif itself does not only point towards the importance of suitable protecting groups, but also further reduces the scope of applicable deprotection conditions. As displayed in Scheme 2, the free phenolic hydroxy groups *ortho* to the ethynyl groups tend to form five-membered heterocyclic benzofuran rings by reacting with the neighbouring alkyne. This intramolecular cyclization can be promoted by various reaction conditions, for example, mild bases,[33–35] palladium/copper catalytic systems,[36] TBAF[37] and UV irradiation.[38] The fact that the assembly of OPE rods depends on such conditions (e.g., in Sonogashira cross-coupling or TMS deprotection reactions) further motivated the search for a suitable catechol-protecting group.

Typically, catechol derivatives can be masked as diethers (including silyl ethers) or diesters similar to phenolic compounds. Cyclic acetals, ketals and esters allow selective protection of two adjacent hydroxy groups, as found in catechols, even in the presence of another isolated phenol function.[39] Methylene acetals are usually obtained by reaction



Scheme 1. A) Target molecular rod **1** and its various protected precursors **14**–**18**. B) Redox chemistry of the molecular rod **1**.



Scheme 2. Intermolecular cyclization to benzofuran derivatives.

with a methylene dihalide.[40,41] The resulting methylenedioxy group is relatively stable, but can be efficiently deprotected by use of a suitable Lewis acid such as a boron[42,43] or aluminium[44,45] halide. Acetone can be used to convert catechols into the corresponding acetonides[46] which are hydrolyzed in acidic conditions.[47,48] Cyclohexylidene ketals are prepared from cyclohexanone[49] and tolerate the use of butyllithium for metallation.[50] The reaction of dichlorodiphenylmethane[51] or dimethoxydiphenylmethane[52] with catechols leads to diphenylmethylene ketals. Deprotection of the latter is promoted by catalytic hydrogenation[53] or acidic hydrolysis.[54] The ethyl orthoformate protecting group is formed with triethyl orthoformate[54] and hydrolyzed in the presence of a catalytic amount of an acid such as TsOH.[55] Cyclic borates tolerate the basic conditions required for alkylation or acylation of a phenolic function, for example, and are easily removed in a dilute acid medium.[56] Lastly, the use of cyclic carbonates turns out to be rather limited owing to an enhanced sensitivity towards hydrolysis.[57]

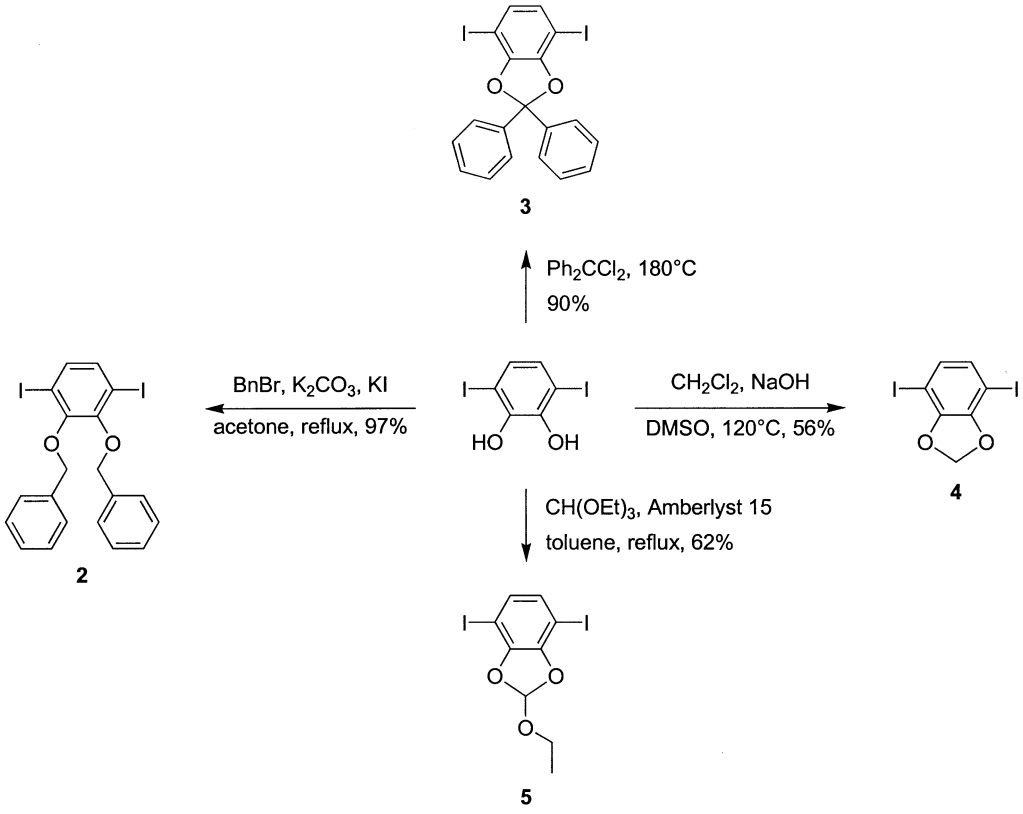
Herein we report the synthesis of the molecular rod **1** and the investigation of the suitability of several different protected precursors as potential building blocks not only for the target compound **1**, but also for further functionalized structures. In addition to the initial electrochemical investigations carried out on these compounds, the dimethyl-protected rod **18** was immobilized in Au–**18′**–Au junctions to demonstrate the suitability of the parent structure as a functional unit in a molecular device. In addition to the dimethoxy precursor **18**, various protecting groups for the catechol moiety, namely, benzyl ether **14**, diphenylmethylene ketal **15**, methylene acetal **16** and ethyl orthoformate **17**, have also been investigated (Scheme 1).

Results and Discussion

Suitable building blocks with a protected catechol subunit were synthesized and the molecular rods comprising these subunits assembled. Subsequently, the lability of the different protecting groups was investigated by applying a variety of deprotection protocols. Tentative cyclic voltammetry studies of these molecular rods have allowed us to demonstrate the redox activity of the integrated and deprotected catechol subunit. Finally, immobilization of one of these molecular rods in a molecular STM junction enabled preliminary single-molecule transport investigations to be undertaken.

Synthesis of the Protected Molecular Rods

The central building block, 2,3-dihydroxy-1,4-diiodobenzene, was obtained in four steps according to a previously reported procedure[58] starting with commercially available veratrole (1,2-dimethoxybenzene). A sequence of monolithiation followed by reaction with trimethylsilyl chloride allowed the stepwise introduction of two TMS groups onto the dimethoxybenzene ring. Iodo-desilylation

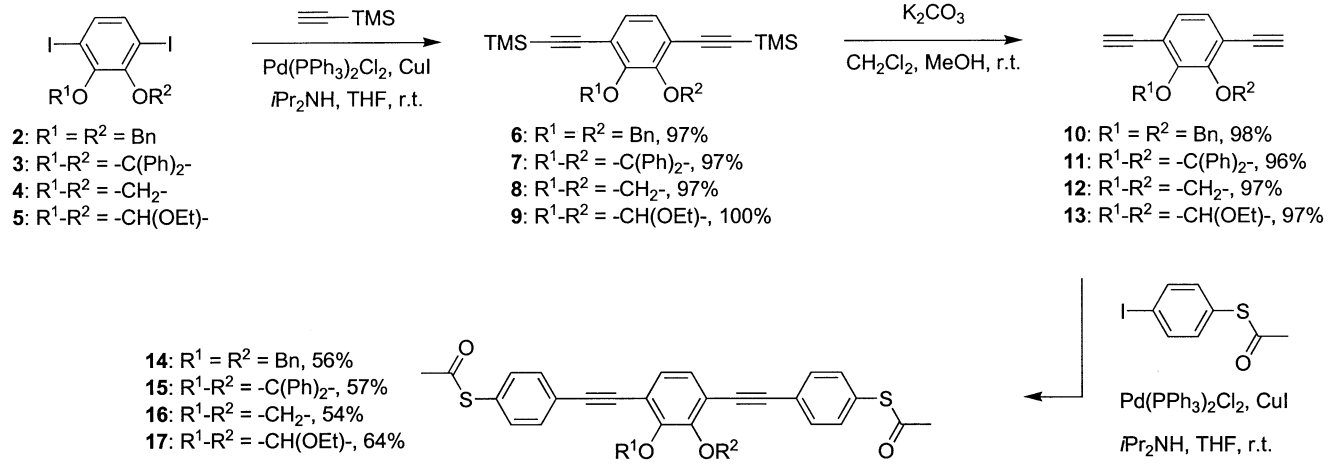


Scheme 3. Synthesis of protected diiodocatechol derivatives **2**–**5** using 2,3-dihydroxy-1,4-diiodobenzene as the central building block.

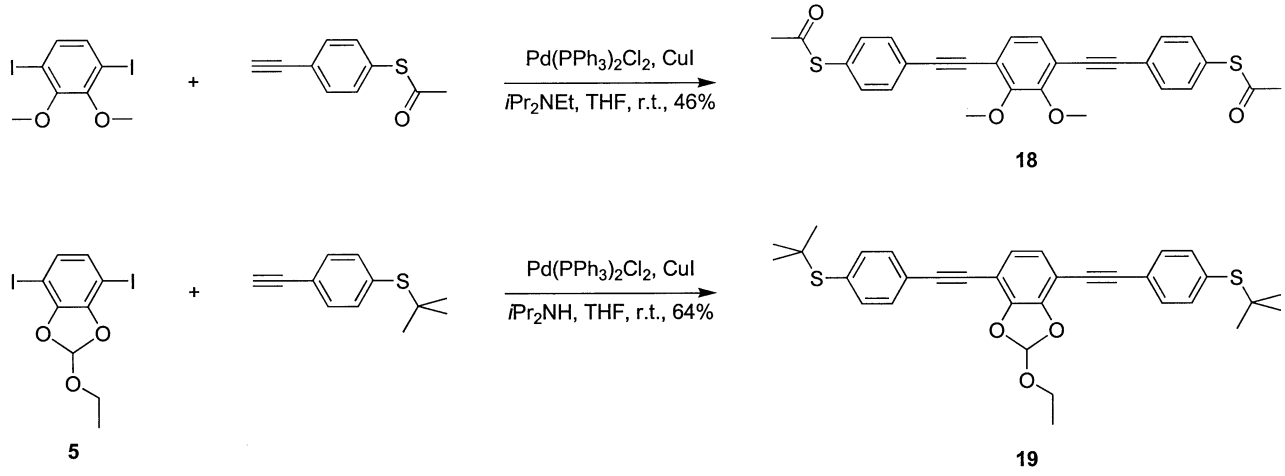
with iodine monochloride led to the diiodo intermediate which was finally converted into the desired 2,3-dihydroxy-1,4-diiodobenzene by demethylation with BBr_3. The corresponding benzyl-protected diiodocatechol **2** was readily obtained by alkylation of 2,3-dihydroxy-1,4-diiodobenzene with benzyl bromide in the presence of potassium carbonate and a catalytic amount of potassium iodide in refluxing acetone (Scheme 3). Heating 2,3-dihydroxy-1,4-diiodobenzene at 180 °C in neat dichlorodiphenylmethane gave the diphenylmethylene ketal **3** in 90% yield. The introduction of a methylene acetal as a catechol protecting group was achieved in hot DMSO containing dichloromethane and sodium hydroxide in excess, affording methylenedioxy derivative **4** (56% yield). Finally, the ethyl orthoformate intermediate **5** was isolated in 62% yield after condensing the free diiodocatechol with triethyl orthoformate in refluxing toluene in the presence of Amberlyst 15 resin as the acidic catalyst.

The four protected molecular rods **14**–**17** were assembled by comparable synthetic sequences (Scheme 4). Protected diiodocatechol derivatives **2**–**5** readily reacted with trimethylsilylacetylene in classical Sonogashira reaction conditions to give doubly TMS-protected diacetylenes **6**–**9** (97–100% yield). Potassium carbonate in a mixture of dichloromethane and methanol was then used to cleave almost quantitatively the two TMS protecting groups at room temperature, leading to intermediates **10**–**13**. The free diacetylenes **10**–**13** were subjected to a two-fold palladium- and copper-catalyzed cross-coupling reaction with 2.2 equivalents of 1-acetylsulfanyl-4-iodobenzene,[59,60] leading to the desired protected molecular rods **14**–**17** in reasonable yields (54–64%).

In an alternative synthetic strategy, these molecular rods can also be assembled in a one-step Sonogashira reaction, as displayed in Scheme 5 for molecular rods **18** and **19**. Rod **18**, comprising a dimethyl-protected catechol subunit, was obtained from 1,4-diiodo-2,3-dimethoxybenzene[58] and 1-acetylsulfanyl-4-ethynylbenzene[59,60] in 46% yield. Interestingly, 1,4-diiodo-2,3-dimethoxybenzene was previously obtained as an intermediate in the synthesis of the key building block 2,3-dihydroxy-1,4-diiodobenzene.[58] Finally, the orthoformate-protected diiodocatechol **5** and 1-*tert*-butylsulfanyl-4-ethynylbenzene[9,30] provided molecular rod **19** with more stable terminal *tert*-butylsulfanyl groups in 64% yield. The increased stability of the sulfur protecting groups



Scheme 4. Synthesis of protected molecular rods **14**–**17** from the corresponding protected diiodocatechol derivatives **2**–**5**.



Scheme 5. Synthesis of protected molecular rods **18** and **19** equipped with acetyl- and *tert*-butyl-protected sulfur groups, respectively.

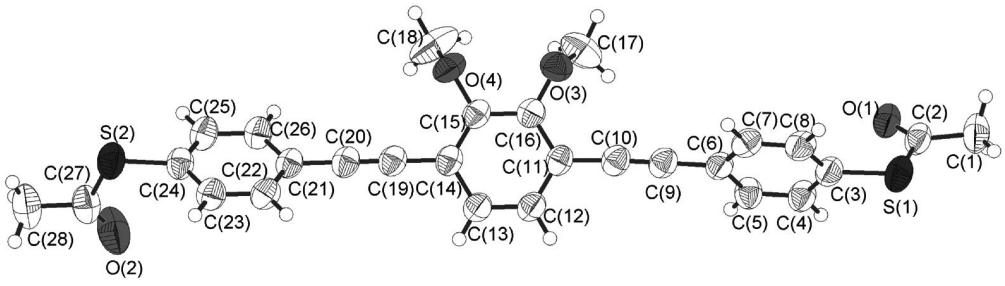


Figure 1. Molecular structure of **18** (ORTEP, thermal ellipsoids set at the 40% probability level). Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.495(4), C(2)–O(1) 1.203(4), C(2)–S(1) 1.788(4), S(1)–C(3) 1.771(3), C(27)–C(28) 1.510(5), C(27)–O(2) 1.191(4), C(27)–S(2) 1.770(4), S(2)–C(24) 1.775(3), O(3)–C(16) 1.361(4), O(3)–C(17) 1.405(5), O(4)–C(15) 1.377(3), O(4)–C(18) 1.349(5); C(2)–S(1)–C(3) 101.62(16), C(24)–S(2)–C(27) 103.16(15).

of **19** is of particular interest for electrochemical investigations.

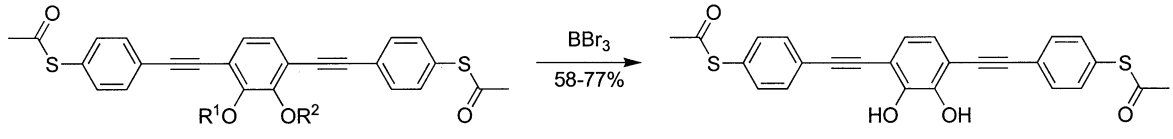
All the new compounds were fully characterized by conventional analytical and spectroscopic techniques, that is, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Furthermore, the purity of the compounds was confirmed by elemental analysis. In order to obtain additional structural details, numerous attempts to grow single crystals from these molecular rods were made. Finally, single crystals of compound **18** suitable for X-ray analysis were obtained. Molecular rod **18** crystallizes in the triclinic space group $P\bar{1}$ (Figure 1).[61] The intramolecular sulfur-to-sulfur distance is 20.02(25) Å and the average C–C bond length of the acetylene bridges is 1.201 Å. The two lateral phenyl rings are twisted with respect to the central one with torsion angles of 60.79(6)° [C(12)–C(11)–C(6)–C(5)] and 43.63(6)° [C(13)–C(14)–C(21)–C(22)].

Deprotection of the Catechol Core

Catechol deprotection was first attempted with boron tribromide (1 M in CH_2Cl_2) and was achieved with precursors **14**, **17** and **18**, leading to the formation of the acetylsulfanyl-functionalized molecular rod **1** (Scheme 6 and Table 1). With the dibenzyl- and orthoformate-protected rods **14** and **17**, protecting-group cleavage was conducted at room temperature in toluene containing acetyl chloride, ensuring in situ trapping of the sulfur end groups if ever cleaved (70 and 77% yields, respectively). Furthermore, the excess BBr_3 was added in several portions, depending on the evolution of the reaction which was easily monitored by TLC. The molecular rod **1** was also obtained from dimethyl-protected precursor **18** (58% yield). In this case, only CH_2Cl_2 was used as the solvent and the reaction was performed at a lower temperature (–7 °C). The slightly lower yield may partially arise from simultaneous deprotection of the acetylsulfanyl groups with BBr_3, highlighting the importance of using acetylating conditions (AcCl in toluene).

Precursor **15** could not be deprotected by reaction with BBr_3 as a Lewis acid or by standard catalytic hydrogenolysis (H_2, 10% Pd/C, Table 1). Compound **15**, comprising a diphenylmethylene ketal, promptly reacted in the presence of BBr_3, but the desired product **1** could neither be detected nor isolated after chromatography. Interestingly, the diphenyl ketal was hydrolyzed in acidic conditions (AcOH/EtOH/H_2O mixture at reflux).[54,62] However, as expected in such an acidic and aqueous medium, the thioacetyl functions were also cleaved. Generating the free catechol rod **1** from the methylenedioxy precursor **16** by the use of BBr_3 or in acidic conditions (HCOOH or TFA) failed as well. It is worth mentioning that the dibenzyl rod **14** was also found to be exceptionally inert towards catalytic hydrogenation or treatment with TFA.

The main drawback of the deprotection strategies so far discussed are the harsh reaction conditions, reducing the variety of potential functional groups in future macromolecules comprising catechol subunits. Of particular interest was the search for alternative routes to achieving orthogonal deprotection of the catechol core. Finding mild and se-



14: $R^1 = R^2$ = Bn
17: R^1-R^2 = -CH(OEt)-
18: $R^1 = R^2$ = Me

1

Scheme 6. Synthesis of target molecular rod **1** from protected precursors **14**, **17** and **18**.

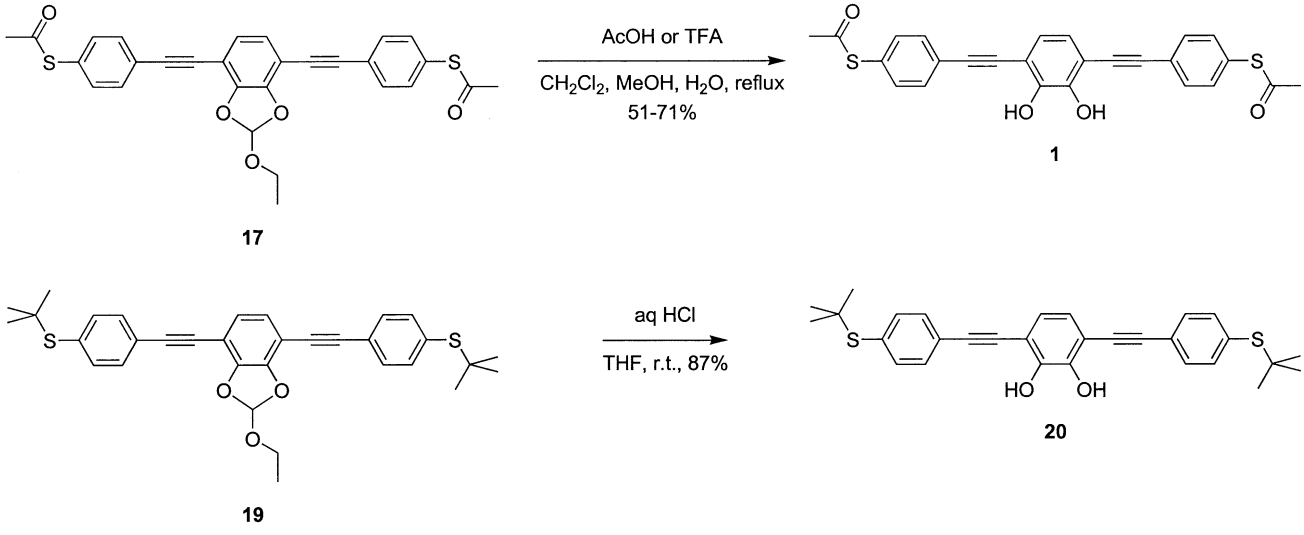
Table 1. Attempts at deprotection of catechols **14**–**19**.

Substrate	Protecting group	Conditions	Solvent	Temperature [°C]	Yield [%]
14	Bn	BBr_3	toluene, AcCl	r.t.	70
		H_2, 10% Pd/C	CH_2Cl_2, MeOH	r.t.	0[a]
		TFA	CH_2Cl_2, Ac_2O	r.t.	0[a]
15	$–C(Ph)_2–$	BBr_3	toluene, AcCl	r.t.	0[b]
		H_2, 10% Pd/C	THF	r.t.	0[a]
		TFA	CH_2Cl_2	r.t. to 45	0[a]
		aqueous HCl	EtOH	100	0[a]
		AcOH	EtOH, H_2O	115	0[b]
16	$–CH_2–$	BBr_3	CH_2Cl_2	–78 to r.t.	0[c]
		BBr_3	toluene, AcCl	r.t.	0[c]
		HCOOH	CH_2Cl_2	r.t. to 45	0[a]
		TFA	CH_2Cl_2	r.t. to 45	0[a]
17	–CH(OEt)–	BBr_3	toluene, AcCl	r.t.	77
		AcOH	CH_2Cl_2, MeOH, H_2O	50	71
		TFA	CH_2Cl_2, MeOH, H_2O	50	51
		TsOH	CH_2Cl_2, MeOH, H_2O	r.t. to 50	0[a]
18	Me	BBr_3	CH_2Cl_2	–7	58
19	–CH(OEt)–	aqueous HCl	THF	r.t.	87

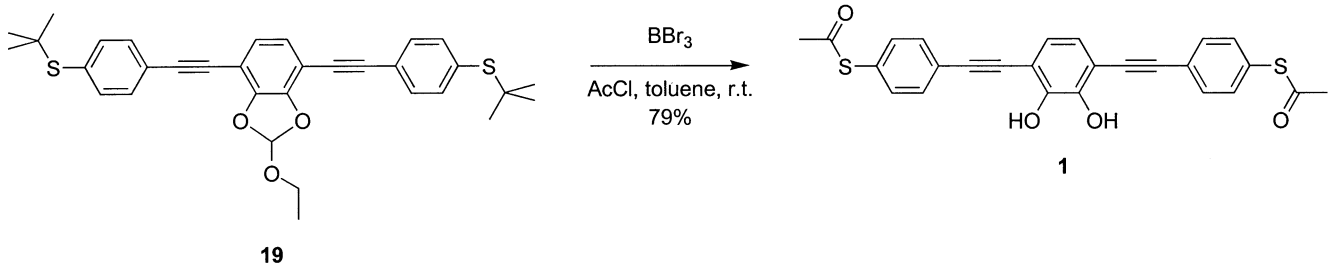
[a] No reaction. [b] Starting material consumed. [c] Starting material partially consumed.

lective conditions is crucial to expand this methodology to advanced architectures comprising a broader variety of chemical functions. Thus, **17** turned out to be a promising candidate owing to the more labile nature of the ethyl orthoformate protecting group, as already highlighted by its efficient cleavage with BBr_3 in 77% yield (Table 1). According to the literature,[55,63,64] the orthoester was expected to be readily hydrolyzed at room temp. in the presence of a catalytic amount of TsOH. Although the protected rod **17** exhibited surprising inertness towards TsOH, free catechol **1** could be obtained in 71% yield by using acetic acid in a boiling mixture of CH_2Cl_2, MeOH and H_2O (Scheme 7 and Table 1). TFA can also be used instead of AcOH (51% yield). Despite the presence of water in the reaction medium, these acidic conditions gently promoted the selective deprotection of the redox-active unit without affecting the acetylsulfanyl end groups. Finally, the *tert*-butylsulfanyl-terminated rod **19** permits the safe use of a stronger acid such as aqueous HCl[54] to cleave the orthoformate moiety at room temp., leading to product **20** in 87% yield (Scheme 7 and Table 1).

The BBr_3/AcCl/toluene system previously used to cleave the dibenzyl rod **14** and orthoester **17** with efficiency (70–77% yield) is also known to allow the trans-protection of *S*-*tert*-butyl groups into *S*-acetyl groups.[65–68] To our satisfaction, concomitant removal of the ethyl orthoformate protecting group and trans-protection of both terminal sulfur groups was successful with *tert*-butylsulfanyl orthoester **19**, giving the target acetylsulfanyl rod **1** in a good 79% yield (Scheme 8).



Scheme 7. Acidic deprotection of acetylsulfanyl- and *tert*-butylsulfanyl-functionalized orthoesters **17** and **19**, respectively.



Scheme 8. Simultaneous catechol deprotection and sulfur transprotection yielding acetylsulfanyl molecular rod **1** from *tert*-butylsulfanyl orthoester **19**.

Electrochemistry

In preliminary cyclic voltammetry experiments, the redox activity of the catechol subunit integrated into the molecular rod was investigated. Thus, the electrochemical properties of the free and orthoformate-protected catechol rods were investigated in methanol and in a 1:1 mixture of methanol and dichloromethane, respectively, containing 0.15 M sodium acetate as the supporting electrolyte using a glassy carbon electrode.

The acetylsulfanyl-terminated rod **1** reveals an anodic wave at +0.23 V assigned to the oxidation of the catechol core to the corresponding *ortho*-quinone (Figure 2, A). On the reverse scan, a cathodic peak appears at +0.03 V upon reduction of the newly formed *ortho*-quinone, leading to the regeneration of the initial catechol. Thus, a quasi-reversible redox process is found for the catechol/*ortho*-quinone couple. Interestingly, both the oxidation (0.21 V shift to negative potentials) and reduction (0.08 V shift to positive potentials) of **1** are more favourable than for catechol. The electron-donating phenylethynyl groups decorating the central catechol unit in **1** most likely facilitate its oxidation.[69–71] Owing to the orthoformate-protecting group masking the catechol moiety, **17** shows no redox activity in the same potential range.

In the case of rod **20** equipped with less labile *tert*-butylsulfanyl end groups, the behaviour of the catechol subunit is quite similar to that of **1**, with an oxidation wave at +0.19 V and a reduction wave at +0.09 V (Figure 2, B). Furthermore, a secondary cathodic peak appears at around –0.13 V. This feature is more pronounced at lower scan rates and is also visible as a shoulder in the voltammogram of catechol. This additional cathodic peak may be indicative of the reduction of a newly formed species during the course of the measurement. As already reported before, electro-methoxylation of the catechol unit is prone to occur by 1,4-addition of a solvent molecule to the *ortho*-quinone form.[72–74] Orthoester **19** remains electrochemically inert in the applied conditions.

Comparison of the electrochemical properties of the orthoformate-protected precursors (**17** and **19**) with those of the corresponding free catechol rods (**1** and **20**, respectively) demonstrates the deprotected catechol to be the origin of the observed redox activity (Figure 2A and B). Clearly, the integrated catechol subunit in these molecular rods provides a reversible two-electron two-proton process in a protic medium such as methanol even more easily than the parent unsubstituted catechol.

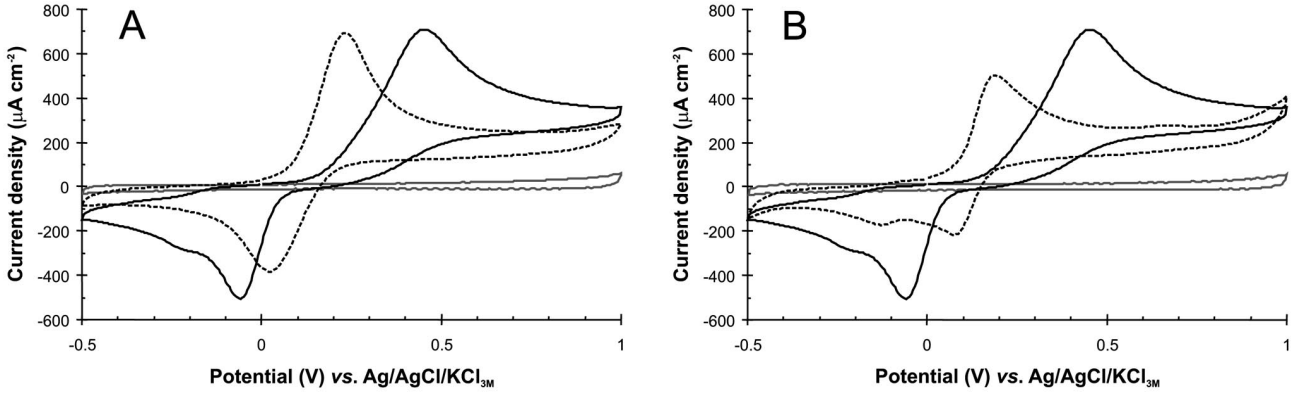


Figure 2. A) Cyclic voltammograms of 1 mM solutions of catechol (black) and the acetylsulfanyl rod **1** (dashed) in MeOH, and of the acetylsulfanyl orthoester **17** (grey) in MeOH/CH_2Cl_2 (1:1) at a glassy carbon electrode. B) Cyclic voltammograms of 1 mM solutions of catechol (black) and the *tert*-butylsulfanyl rod **20** (dashed) in MeOH, and of the *tert*-butylsulfanyl orthoester **19** (grey) in MeOH/CH_2Cl_2 (1:1) at a glassy carbon electrode. Supporting electrolyte: 0.15 M NaOAc. Scan rate: 300 mV s^{-1}.

Molecular Conductance Measurements

To investigate the suitability of these molecular rods for transport investigations, the molecular rod **18** comprising a dimethyl-protected central catechol subunit was exposed to preliminary conductance measurements. Therefore the rod **18** with terminal acetyl-protected sulfur anchor groups was studied in gold–molecule–gold junctions by using the STM-based stretching technique.[21,75,76] In conventional STM, the electrical potential (bias) is applied between a conductive probe (tip) and a bare or modified substrate surface. The tunnelling current, employed as a feedback signal, provides information on the surface topographic and electronic properties. The stretching experiment involves the formation and breaking of metal–molecule–metal junctions between the STM tip and an adsorbate-covered substrate surface.[19,20,75,76] The molecule under investigation bears thiol anchor groups after in situ deprotection with a drop of aqueous ammonia, enabling the formation of chemical bonds to both metal electrodes. As the tip approaches the adsorbate-modified substrate, molecular junctions are created with a certain probability. Subsequently, the current of the preformed metal–molecule–metal junctions is recorded upon retraction of the tip. Such current–distance traces are not exponential; they often exhibit characteristic plateaux and steps which are attributed to the breaking of individual or small groups of junctions. The statistical analysis of a large number of these retraction transients allows the evaluation of electrical properties of single-molecule junctions in a certain environment.

Figure 3 shows a set of individual current–distance retraction curves for the dimethyl-protected rod **18** in different current ranges recorded at E_{bias} = 0.1 V. The main panel reveals features within the high current range. The two insets illustrate details of the low current limits by employing a magnified *y* axis. Three sets of well-resolved plateaux are observed in the current range studied ($0 < I \leq 100$ nA). The values of the corresponding junction conductances are referred to as high (H), mid (M) and low (L) conductances. They vary over two orders of magnitude. The experimentally measured currents approach zero (<10 pA) after the low-current conductance plateau L.

A statistical analysis of the experimental current–distance traces was carried out to extract reliable values of the respective junction conductances. Plateaux in the current–distance traces were chosen as the criteria for the existence of a molecular junction. Plateaux were selected manually assuming a minimum length of 0.03 nm. The average length was 0.14 nm. The probability of forming a molecular junction is represented by 0.1–0.2 plateaux per curve.

The extracted vertical positions of plateaux (e.g., currents) were used to construct histograms (Figure 4). The *x* axis represents the plateau currents grouped in equidistant intervals (bins). The *y* axis represents the number of plateaux weighted with respect to their length in order to emphasize the contribution of the mechanically stable plateaux. The histograms constructed without weighting have less pronounced but essentially the same features.

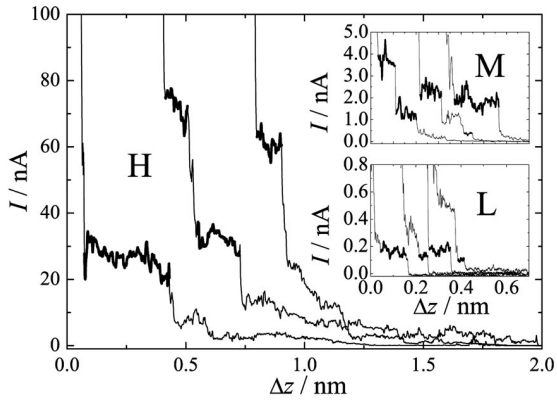


Figure 3. Current–distance retraction traces recorded for a 1 mM solution of **18** in mesitylene, E_{bias} = 0.1 V. The plateaux highlighted by thick lines represent stable configurations of metal–molecule–metal contacts. Plateaux corresponding to the highest conductance regime (H) are shown in the main plot. The two insets illustrate selected current traces in lower current ranges featuring plateaux corresponding to configurations with middle (M) and low (L) conductance junctions. Traces are displaced along the *x* axis for clarity.

Histograms constructed from experimental traces recorded in the current range up to 100 nA reveal two pronounced and equally separated peaks with maxima around 30 and 65 nA (Figure 4, A). These peaks are attributed to the single and double junctions of a high conductance state. The experimental data are represented by two Gaussian curves. Their centres were taken as the positions of the corresponding peaks and full-width-at-half-maximum (FWHM) values were taken as their errors giving 30 ± 5 and 66 ± 12 nA. The dependence of the peak current on the peak number is plotted in the inset. The average current through a high-conductance gold–molecule–gold junction was estimated as the slope of the linear fit with the intercept fixed to zero and values weighted by error. The corresponding current through the single junction and its conductance were found to be 31 ± 2 nA and 310 ± 20 nS (here and elsewhere, the error in the slope corresponds to the confidence limit of 95%, respectively). The initial part of the histogram in part A of Figure 4 exhibits a pronounced distribution tail if the bin width is chosen to be 2 nA. Magnification of this region ($I < 3$ nA) and reduction of the bin width to 0.1 nA reveals an additional set of conductance peaks (Figure 4, B). These data were analyzed in the same way as described above for high-conductance junctions. The corresponding mid-conductance junction is estimated to be 12 ± 1 nS. Further magnification of the current range ($I < 0.8$ nA) and reduction of the bin width to 0.01 nA still reveals structured histograms (Figure 4, C). However, the small number of low-conductance junctions does not lead to well-developed Gaussian-type peaks. A low-junction conductance of 1.4 ± 0.1 nS is obtained by grouping the maximum currents of the observed discrete features.

Three conductance values (1.4, 12 and 310 nS) were assigned to the gold–molecule–gold junctions formed in the present experiments. The ratio between the numbers of junctions exhibiting low (L), mid (M) and high (H) conduc-

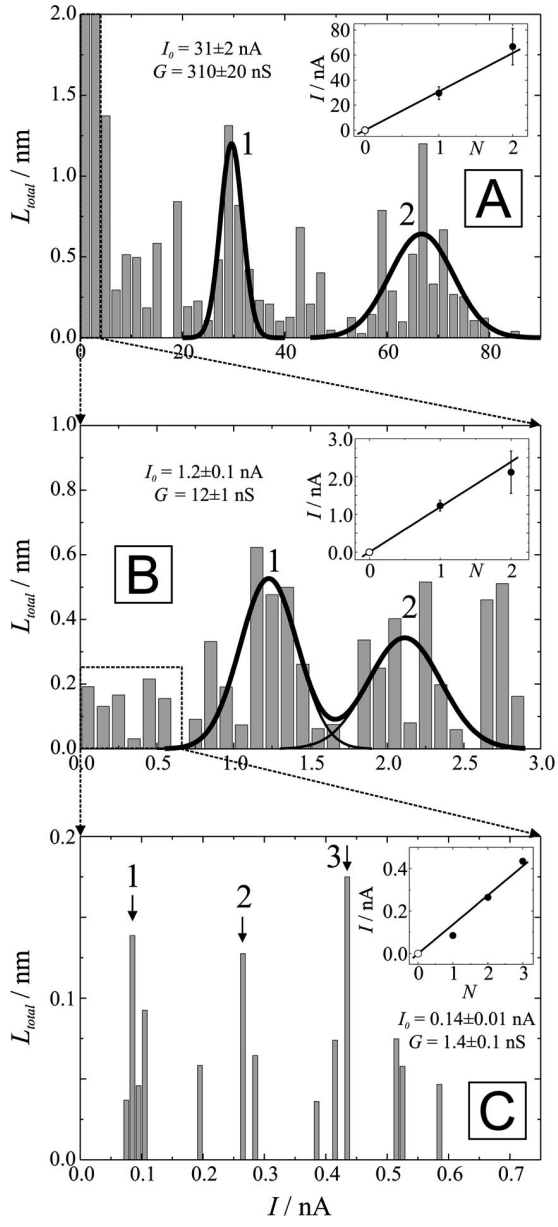


Figure 4. Length-weighted histograms of the plateau currents (E_{bias} = 0.1 V) for different current ranges and with sequentially decreasing bin widths. The insets illustrate plots of the peak position vs. peak number and the corresponding linear fits. A) 0–90 nA, bin width 2 nA; B) 0–3 nA, bin width 0.1 nA; C) 0–0.75 nA, bin width 0.01 nA.

tance values for the presented data is 9:38:53. The H and M junctions have rather similar formation probabilities. The number of low-conductance junctions is significantly smaller. Other experimental data support these observations as well. Metal–molecule–metal junctions exhibiting multiple values of single-junction conductance have already been found for a number of molecular systems.[23,76,77] Our current hypothesis is to assign these three different conductance values to different contact geometries between the molecule and the electrode. The estimated experimental ratio for the probability of plateau formation may give a clue to this point. However, this is a separate subject requiring high-level quantum chemical simulations of the junction conductance.[76] The gold–molecule–gold junction conductance of the dithiolated OPE lacking the two methoxy groups was found to be 13 nS.[78] Values of the single-junction conductances for various derivatives were of the same order of magnitude.[78,79] This value is close to the mid-conductance M found in our experiments and reflects the general trend that substituents only slightly affect the junction conductance as long as they do not possess low-lying energy levels. Interestingly, high and low conductances of rigid rod-like molecules have not been described in the literature before. STM-based conductance measurement of single-molecule junctions of compound **18** and related molecules are currently in progress in order to systematically study the effect of substituents on the conductance of molecular junctions and to evaluate the electrochemically triggered switching effect in OPEs with redox-active substituents such as the free catechol rod **1**.

Conclusions

The synthesis of a novel redox-active molecular rod derived from an OPE skeleton comprising a catechol subunit has been achieved. An ensemble of five protecting groups for the catechol unit was investigated; three of them afforded the target acetylsulfanyl-functionalized rod **1**. Notably, the ethyl orthoformate catechol protecting group turned out to be cleavable by BBr_3 as well as by mild acids like AcOH. These mild deprotection conditions, which are selective and take place readily, are paving the way to more complex molecular architectures comprising the redox-active catechol subunit. The residual redox activity of the catechol subunit integrated into the molecular rod has been demonstrated by cyclic voltammetry investigations. Furthermore, preliminary single-molecule transport investigations with the dimethyl-protected rod **18** have been presented. The molecular junctions were created mechanically in a STM-based set-up and analyzed statistically. Preliminary measurements revealed a set of three conductance values varying over two orders of magnitude. The current hypothesis is to attribute them to different binding geometries of the anchoring groups to the electrodes, providing an unprecedented insight into the molecule/electrode interface. Currently we are synthesizing larger macrocyclic structures of increasing complexity based on the catechol subunit that will undergo redox-state-dependent conformational changes.

Experimental Section

General Methods: Toluene and THF were dried by distillation over sodium/benzophenone. CH_2Cl_2 was dried by distillation over CaH_2. iPr_2NH and iPr_2NEt were dried by distillation over KOH. All other solvents and chemicals were of analytical grade and were used as supplied without further purification. Flash chromatography was performed on Fluka silica gel 60 (0.040–0.063 mm). ^1H (300 and 400 MHz) and ^{13}C (75 and 100 MHz) NMR spectra were recorded at room temperature with the residual proton resonances

in deuteriated solvents used as the internal references. Chemical shifts (δ) are reported in ppm. Mass spectra were obtained by electron-impact (EI) mass spectrometry. All mixtures of solvents are given in v/v ratio. The STM stretching experiments were carried out with a Molecular Imaging PicoSPM 2000 instrument. A thin gold film prepared by vapour deposition on a glass sheet followed by annealing in a hydrogen flame was used as the substrate. A cut and uncoated gold wire (0.25 mm diameter) served as the tip. All measurements were carried out on molecule **18** in a 1 mm solution of mesitylene after deprotection of the thiol groups. The bias voltage $E_{bias} = E_{tip} - E_{sample} = 0.1$ V was used throughout the experiment. The vertical movement of the tip was controlled by a dedicated LabView program. The current–distance traces were recorded by using a digital oscilloscope Yokogawa DL720 apparatus. The approach was stopped after reaching physical contact between gold tip and gold sample corresponding to a junction conductance of several G_0. The retraction rate of the tip varied between 25–30 nm s^{-1}.

2,3-Bis(benzyloxy)-1,4-diiodobenzene (2): A mixture of 2,3-dihydroxy-1,4-diiodobenzene (670 mg, 1.85 mmol), K_2CO_3 (769 mg, 5.56 mmol), KI (62 mg, 0.37 mmol) and benzyl bromide (485 μL, 4.08 mmol) in acetone (30 mL) was refluxed for 16 h. Solvents were evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 90:10 to 80:20) afforded **2** (969 mg, 97%) as a white solid, m.p. 98–103 °C. R_f = 0.53 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.07 (s, 4 H), 7.33 (s, 2 H), 7.37–7.46 (m, 6 H), 7.52–7.59 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.3, 93.6, 128.5 (1), 128.5 (4), 129.0, 135.9, 136.3, 152.3 ppm. $C_{20}H_{16}I_2O_2$ (542.15): calcd. C 44.31, H 2.97; found C 43.39, H 3.00. MS (EI): *m*/*z* (%) = 541.9 (0.4) $[M]^+$, 450.8 (4) $[M - C_7H_7]^+$, 288.1 (3) $[M - 2I]^+$, 181.1 (12) $[M - 2I - C_7H_7]^+$, 91.1 (100) $[C_7H_7]^+$.

1,4-Diiodo-2,3-(diphenylmethylenedioxy)benzene (3): A mixture of 2,3-dihydroxy-1,4-diiodobenzene (100 mg, 0.28 mmol) and dichlorodiphenylmethane (60 μL, 0.30 mmol) was heated at 180 °C for 10 min. Flash chromatography (SiO_2, hexane) afforded **3** (131 mg, 90%) as a white solid, m.p. 143–147 °C. R_f = 0.60 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (s, 2 H), 7.39–7.47 (m, 6 H), 7.63–7.68 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.1, 116.4, 126.5, 128.5, 129.6, 131.7, 139.2, 148.1 ppm. $C_{19}H_{12}I_2O_2$ (526.11): calcd. C 43.38, H 2.30; found C 43.51, H 2.28. MS (EI): *m*/*z* (%) = 525.8 (83) $[M]^+$, 448.8 (100) $[M - C_6H_5]^+$, 398.9 (12) $[M - I]^+$.

1,4-Diiodo-2,3-(methylenedioxy)benzene (4): A solution of 2,3-dihydroxy-1,4-diiodobenzene (923 mg, 2.55 mmol) and NaOH (675 mg, 16.9 mmol) in a mixture of dry CH_2Cl_2 (12 mL) and dry DMSO (34 mL) was heated at 120 °C for 19 h. After cooling to room temp., the solution was diluted with H_2O and extracted with AcOEt. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 100:0 to 95:5) afforded **4** (538 mg, 56%) as a white solid, m.p. 137–139 °C. R_f = 0.54 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.07 (s, 2 H), 6.89 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.8, 100.1, 131.8, 148.4 ppm. $C_7H_4I_2O_2$ (373.91): calcd. C 22.49, H 1.08; found C 22.75, H 1.17. MS (EI): *m*/*z* (%) = 373.8 (100) $[M]^+$.

2,3-(Ethoxymethylenedioxy)-1,4-diiodobenzene (5): A solution of 2,3-dihydroxy-1,4-diiodobenzene (858 mg, 2.37 mmol) and triethyl orthoformate (1.21 mL, 7.13 mmol) in toluene (25 mL) containing Amberlyst 15 (12 mg) was refluxed for 18 h. After cooling to room temp., the solution was filtered through Celite and the solvents evaporated. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 80:20) afforded **5** (610 mg, 62%) as a white solid, m.p. 58–59 °C. R_f = 0.52 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H), 3.76 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H), 6.93 (s, 2 H), 6.95 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 60.1, 70.4, 117.8, 131.8, 146.9 ppm. $C_9H_8I_2O_3$ (417.97): calcd. C 25.86, H 1.93; found C 26.02, H 1.86. MS (EI): *m*/*z* (%) = 417.8 (92) $[M]^+$, 372.8 (47) $[M - C_2H_5O]^+$, 361.8 (100) $[M - C_3H_6O + 2H]^+$.

2,3-Bis(benzyloxy)-1,4-bis(trimethylsilylethynyl)benzene (6): A solution of compound **2** (226 mg, 0.42 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg, 0.04 mmol) and CuI (10 mg, 0.05 mmol) in a mixture of dry THF (10 mL) and dry *i*Pr_2NH (2 mL) was degassed with argon for 30 min. Trimethylsilylacetylene (135 μL, 0.93 mmol) was added and the solution was stirred at room temp. for 65 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 80:20) afforded **6** (195 mg, 97%) as a yellow oil. R_f = 0.57 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 18 H), 5.13 (s, 4 H), 7.17 (s, 2 H), 7.41–7.50 (m, 6 H), 7.59–7.64 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0, 75.8, 100.7, 100.9, 119.7, 128.3, 128.5, 128.6(9), 128.7(1), 137.3, 153.7 ppm. $C_{30}H_{34}O_2Si_2 \cdot 0.3H_2O$ (488.17): calcd. C 73.81, H 7.14; found C 73.94, H 7.06. MS (EI): *m*/*z* (%) = 482.3 (42) $[M]^+$, 391.2 (9) $[M - C_7H_7]^+$, 376.2 (9) $[M - C_7H_7 - CH_3]^+$, 361.1 (9) $[M - C_7H_7 - 2CH_3]^+$, 91.1 (100) $[C_7H_7]^+$.

2,3-(Diphenylmethylenedioxy)-1,4-bis(trimethylsilylethynyl)benzene (7): A solution of compound **3** (262 mg, 0.33 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 0.02 mmol) and CuI (9 mg, 0.05 mmol) in a mixture of dry THF (12 mL) and dry *i*Pr_2NH (2 mL) was degassed with argon for 30 min. Trimethylsilylacetylene (160 μL, 1.10 mmol) was added and the solution was stirred at room temp. for 3 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 90:10) afforded **7** (225 mg, 97%) as a white solid, m.p. 159–160 °C. R_f = 0.68 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.31 (s, 18 H), 6.86 (s, 2 H), 7.39–7.47 (m, 6 H), 7.62–7.67 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.1, 98.9, 100.5, 105.2, 118.1, 125.1, 126.7, 128.4, 129.5, 139.7, 148.5 ppm. $C_{29}H_{30}O_2Si_2$ (466.72): calcd. C 74.63, H 6.48; found C 74.33, H 6.80. MS (EI): *m*/*z* (%) = 466.1 (89) $[M]^+$, 451.0 (21) $[M - CH_3]^+$, 389.2 (100) $[M - C_6H_5]^+$.

2,3-(Methylenedioxy)-1,4-bis(trimethylsilylethynyl)benzene (8): A solution of compound **4** (506 mg, 1.35 mmol), $Pd(PPh_3)_2Cl_2$ (47 mg, 0.07 mmol) and CuI (27 mg, 0.14 mmol) in a mixture of dry THF (32 mL) and dry *i*Pr_2NH (6 mL) was degassed with argon for 30 min. Trimethylsilylacetylene (435 μL, 2.99 mmol) was added and the solution was stirred at room temp. for 17 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 100:0 to 80:20) afforded **8** (412 mg, 97%) as a white solid, m.p. 137–139 °C. R_f = 0.61 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 18 H), 6.08 (s, 2 H), 6.82 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 0.0, 98.3, 100.8, 102.1, 105.2, 125.1, 148.8 ppm. $C_{17}H_{22}O_2Si_2$ (314.53): calcd. C 64.92, H 7.05; found C 64.80, H 6.98. MS (EI): *m/z* (%) = 314.1 (100) $[M]^+$, 299.1 (25) $[M - CH_3]^+$.

2,3-(Ethoxymethylenedioxy)-1,4-bis(trimethylsilylethynyl)benzene (9): A solution of compound **5** (485 mg, 1.16 mmol), $Pd(PPh_3)_2Cl_2$ (41 mg, 0.06 mmol) and CuI (22 mg, 0.12 mmol) in a mixture of dry THF (28 mL) and dry *i*Pr_2NH (5 mL) was degassed with argon for 30 min. Trimethylsilylacetylene (370 μL, 2.55 mmol) was added and the solution was stirred at room temp. for 3 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/AcOEt, 95:5) afforded **9** (415 mg, 100%) as a yellowish solid, m.p. 118–121 °C. R_f = 0.58 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 18 H), 1.29 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H), 3.76 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H), 6.85 (s, 2 H), 6.97 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0, 14.9, 59.8, 98.2, 100.9, 104.9, 119.8, 125.2, 147.1 ppm. $C_{19}H_{26}O_3Si_2$ (358.58): calcd. C 63.64, H 7.31; found C 63.64, H 7.37. MS (EI): *m/z* (%) = 358.1 (81) $[M]^+$, 313.1 (25) $[M - C_2H_5O]^+$, 287.1 (28) $[M - C_3H_9Si + 2H]^+$, 73.3 (100) $[C_3H_9Si]^+$.

2,3-Bis(benzyloxy)-1,4-diethynylbenzene (10): K_2CO_3 (333 mg, 2.41 mmol) was added to a solution of compound **6** (194 mg, 0.40 mmol) in a degassed mixture of CH_2Cl_2 (30 mL) and MeOH (30 mL). After stirring at room temp. for 17 h, the solvents were evaporated. CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 50:50) afforded **10** (133 mg, 98%) as a yellow oil. R_f = 0.38 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 2 H), 5.18 (s, 4 H), 7.22 (s, 2 H), 7.34–7.44 (m, 6 H), 7.50–7.57 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.7, 83.0, 104.4, 118.6, 125.2, 126.6, 128.4, 129.6, 139.3, 149.0 ppm. $C_{24}H_{18}O_2 \cdot 0.2H_2O$ (342.00): calcd. C 84.29, H 5.42; found C 84.46, H 5.69. MS (EI): *m/z* (%) = 338.1 (3) $[M]^+$, 247.1 (13) $[M - C_7H_7]^+$, 91.1 (100) $[C_7H_7]^+$.

1,4-Diethynyl-2,3-(diphenylmethylenedioxy)benzene (11): K_2CO_3 (407 mg, 2.92 mmol) was added to a solution of compound **7** (227 mg, 0.49 mmol) in a degassed mixture of CH_2Cl_2 (10 mL) and MeOH (10 mL). After stirring at room temp. for 30 min, the solvents were evaporated. CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 80:20) afforded **11** (150 mg, 96%) as a white solid, m.p. 134–135 °C. R_f = 0.50 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.38 (s, 2 H), 6.90 (s, 2 H), 7.36–7.46 (m, 6 H), 7.60–7.69 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.7, 83.0, 104.4, 118.6, 125.2, 126.6, 128.4, 129.6, 139.3, 149.0 ppm. $C_{23}H_{14}O_2 \cdot 0.1H_2O$ (324.16): calcd. C 85.22, H 4.42; found C 85.23, H 4.51. MS (EI): *m/z* (%) = 322.0 (48) $[M]^+$, 245.0 (100) $[M - C_6H_5]^+$.

1,4-Diethynyl-2,3-(methylenedioxy)benzene (12): K_2CO_3 (1.07 g, 7.63 mmol) was added to a solution of compound **8** (400 mg, 1.27 mmol) in a degassed mixture of CH_2Cl_2 (90 mL) and MeOH (90 mL). After stirring at room temp. for 1.5 h, the solvents were evaporated. CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 80:20) afforded **12** (209 mg, 97%) as a light-brown solid, m.p. 101–103 °C. R_f = 0.41 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.34 (s, 2 H), 6.11 (s, 2 H), 6.86 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.3, 83.0, 102.3, 104.4, 125.1, 149.3 ppm. $C_{11}H_6O_2 \cdot 0.1H_2O$ (171.97): calcd. C 76.83, H 3.63; found C 76.75, H 3.58. MS (EI): *m/z* (%) = 170.1 (100) $[M]^+$.

2,3-(Ethoxymethylenedioxy)-1,4-diethynylbenzene (13): K_2CO_3 (969 mg, 6.94 mmol) was added to a solution of compound **9** (415 mg, 1.16 mmol) in a degassed mixture of CH_2Cl_2 (25 mL) and MeOH (25 mL). After stirring at room temp. for 30 min, the solvents were evaporated. CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/AcOEt, 90:10) afforded **13** (240 mg, 97%) as a yellowish oil. R_f = 0.53 (SiO_2, hexane/CH_2Cl_2, 50:50). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H), 3.35 (s, 2 H), 3.77 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H), 6.90 (s, 2 H), 6.99 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 59.9, 77.16, 83.2, 104.1, 120.0, 125.2, 147.6 ppm. $C_{13}H_{10}O_3$ (214.22): calcd. C 72.89, H 4.70; found C 72.79, H 4.74. MS (EI): *m/z* (%) = 214.1 (75) $[M]^+$, 169.1 (100) $[M - C_2H_5O]^+$, 158.1 (51) $[M - C_3H_6O + 2H]^+$.

1,4-Bis[(4-acetylsulfanylphenyl)ethynyl]-2,3-bis(benzyloxy)benzene (14): A solution of compound **10** (133 mg, 0.39 mmol) and 1-acetylsulfanyl-4-iodobenzene (240 mg, 0.86 mmol) in a mixture of dry THF (12 mL) and dry *i*Pr_2NH (2 mL) was degassed with argon for 30 min. $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) and CuI (8 mg, 0.04 mmol) were added and the solution was stirred at room temp. for 21 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 50:50 to 30:70) afforded **14** (141 mg, 56%) as a yellow solid, m.p. 148–150 °C. R_f = 0.54 (SiO_2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 6 H), 5.22 (s, 4 H), 7.27 (s, 2 H), 7.33–7.39 (m, 6 H), 7.40 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.49 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.51–7.57 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.4, 76.1, 87.4, 94.7, 119.6, 124.4, 128.4, 128.5, 128.5(8), 128.6(4), 128.9, 132.3, 134.3, 137.1, 153.5, 193.5 ppm. $C_{40}H_{30}O_4S_2$ (638.79): calcd. C 75.21, H 4.73; found C 75.23, H 4.72. MS (EI): *m/z* (%) = 638.2 (5) $[M]^+$, 596.2 (18) $[M - C_2H_3O + H]^+$, 554.1 (58) $[M - 2C_2H_3O + 2H]^+$, 505.1 (9) $[M - C_2H_3O - C_7H_7 + H]^+$, 463.1 (23) $[M - 2C_2H_3O - C_7H_7 + 2H]^+$, 91.1 (100) $[C_7H_7]^+$.

1,4-Bis[(4-acetylsulfanylphenyl)ethynyl]-2,3-(diphenylmethylenedioxy)benzene (15): A solution of compound **11** (66 mg, 0.20 mmol) and 1-acetylsulfanyl-4-iodobenzene (125 mg, 0.45 mmol) in a mixture of dry THF (5 mL) and dry *i*Pr_2NH (1 mL) was degassed with argon for 30 min. $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) were added and the solution was stirred at room temp. for 68 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 50:50 to 40:60) afforded **15** (73 mg, 57%) as a yellow solid, m.p. 166–168 °C. R_f = 0.64 (SiO_2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 6 H), 6.96 (s, 2 H), 7.38–7.47 (m, 10 H), 7.62 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H), 7.65–7.71 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.4, 85.3, 94.2, 105.1, 118.4, 124.3, 124.8, 126.6, 128.4, 128.5, 129.5, 132.4, 134.3, 139.5, 148.3, 193.5 ppm. $C_{39}H_{26}O_4S_2$ (622.75):

calcd. C 75.22, H 4.21; found C 75.38, H 4.17. MS (EI): *m*/*z* (%) = 622.2 (28) $[M]^+$, 580.1 (47) $[M - C_2H_3O]^+$, 538.1 (100) $[M - 2C_2H_3O]^+$, 461.1 (33) $[M - 2C_2H_3O - C_6H_5]^+$.

1,4-Bis[(4-acetylsulfanylphenyl)ethynyl]-2,3-(methylenedioxy)-benzene (16): A solution of compound **12** (103 mg, 0.61 mmol) and 1-acetylsulfanyl-4-iodobenzene (370 mg, 1.33 mmol) in a mixture of dry THF (7 mL) and dry *i*Pr_2NH (1 mL) was degassed with argon for 30 min. $Pd(PPh_3)_2Cl_2$ (28 mg, 0.02 mmol) and CuI (9 mg, 0.05 mmol) were added and the solution was stirred at room temp. for 19 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. The crude product was purified by flash chromatography (SiO_2, hexane/CH_2Cl_2, 50:50 to 40:60). Crystallization from a $CHCl_3$/hexane mixture afforded **16** (155 mg, 54%) as a yellow solid, m.p. 171–172 °C. R_f = 0.50 (SiO_2, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 6 H), 6.15 (s, 2 H), 6.95 (s, 2 H), 7.40 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H), 7.57 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.4, 84.4, 94.3, 102.2, 105.1, 124.0, 124.9, 128.7, 132.4, 134.3, 148.6, 193.5 ppm. $C_{27}H_{18}O_4S_2$ (470.56): calcd. C 68.92, H 3.86; found C 68.71, H 3.97. MS (EI): *m*/*z* (%) = 470.0 (55) $[M]^+$, 427.9 (39) $[M - C_2H_3O + H]^+$, 386.1 (100) $[M - 2C_2H_3O + 2H]^+$.

1,4-Bis[(4-acetylsulfanylphenyl)ethynyl]-2,3-(ethoxymethylenedioxy)benzene (17): A solution of compound **13** (240 mg, 1.12 mmol) and 1-acetylsulfanyl-4-iodobenzene (685 mg, 2.46 mmol) in a mixture of dry THF (28 mL) and dry *i*Pr_2NH (5 mL) was degassed with argon for 30 min. $Pd(PPh_3)_2Cl_2$ (39 mg, 0.06 mmol) and CuI (21 mg, 0.11 mmol) were added and the solution was stirred at room temp. for 5 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 50:50 to 20:80) afforded **17** (367 mg, 64%) as a yellow solid, m.p. 169–171 °C. R_f = 0.55 (SiO_2, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H), 2.43 (s, 6 H), 3.83 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H), 6.99 (s, 2 H), 7.04 (s, 1 H), 7.40 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H), 7.58 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 30.4, 59.9, 84.8, 94.5, 104.8, 119.9, 124.0, 124.9, 128.7, 132.4, 134.3, 146.9, 193.3 ppm. $C_{29}H_{22}O_5S_2$ (514.61): calcd. C 67.68, H 4.31; found C 67.53, H 4.47. MS (EI): *m*/*z* (%) = 514.1 (100) $[M]^+$, 472.1 (83) $[M - C_2H_3O + H]^+$, 430.1 (66) $[M - 2C_2H_3O + 2H]^+$, 374.0 (34) $[M - 2C_2H_3O - C_3H_6O + 4H]^+$.

1,4-Bis[(4-acetylsulfanylphenyl)ethynyl]-2,3-dimethoxybenzene (18): 1,4-Diiodo-2,3-dimethoxybenzene (800 mg, 2.05 mmol), $Pd(PPh_3)_2Cl_2$ (88 mg, 0.13 mmol) and CuI (48 mg, 0.25 mmol) were dissolved in dry and degassed THF (12 mL). Dry and degassed *i*Pr_2NEt (6 mL) was added, followed by addition of 1-acetylsulfanyl-4-ethynylbenzene (796 mg, 4.52 mmol). The reaction mixture was stirred at room temp. for 16 h, then H_2O was added and the product was extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, toluene/AcOEt, 95:5) afforded **18** (460 mg, 46%) as a yellow solid, m.p. 128–129 °C. R_f = 0.50 (SiO_2, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 6 H), 4.04 (s, 6 H), 7.21 (s, 2 H), 7.43 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H), 7.58 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.4, 61.5, 86.9, 94.5, 119.0, 124.4, 128.1, 128.5, 132.3, 134.3, 154.3, 193.5 ppm. $C_{28}H_{22}O_4S_2$ (486.60): calcd. C 69.11, H 4.56; found C 68.81, H 4.39. MS (EI): *m*/*z* (%) = 486.1 (70) $[M]^+$, 444.0 (53) $[M - C_2H_3O + H]^+$, 402.0 (100) $[M - 2C_2H_3O + 2H]^+$.

1,4-Bis[(4-*tert*-butylsulfanylphenyl)ethynyl]-2,3-(ethoxymethylenedioxy)benzene (19): A solution of compound **5** (578 mg, 1.38 mmol) and 1-*tert*-butylsulfanyl-4-ethynylbenzene (581 mg, 3.05 mmol) in a mixture of dry THF (33 mL) and dry *i*Pr_2NH (6 mL) was degassed with argon for 30 min. $Pd(PPh_3)_2Cl_2$ (48 mg, 0.07 mmol) and CuI (26 mg, 0.14 mmol) were added and the solution was stirred at room temp. for 19 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, hexane/CH_2Cl_2, 100:0 to 60:40) afforded **19** (367 mg, 64%) as a yellow solid, m.p. 131–134 °C. R_f = 0.75 (SiO_2, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26–1.33 (m, 21 H), 3.81 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H), 6.98 (s, 2 H), 7.03 (s, 1 H), 7.51 (s, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 31.1, 46.6, 59.8, 84.6, 94.7, 104.8, 119.8, 123.1, 124.8, 131.7, 133.9, 137.3, 146.9 ppm. $C_{33}H_{34}O_3S_2$ (542.75): calcd. C 73.03, H 6.31; found C 72.76, H 6.41. MS (EI): *m*/*z* (%) = 542.1 (59) $[M]^+$, 497.1 (9) $[M - C_2H_5O]^+$, 486.0 (13) $[M - C_4H_9 + H]^+$, 430.0 (100) $[M - 2C_4H_9 + 2H]^+$.

1,4-Bis[(4-acetylsulfanylphenyl)ethynyl]-2,3-dihydroxybenzene (1): M.p. 193–196 °C. R_f = 0.25 (SiO_2, CH_2Cl_2/MeOH, 99:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 6 H), 5.80 (br. s, 2 H), 7.00 (s, 2 H), 7.42 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H), 7.58 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.4, 85.3, 96.1, 110.7, 123.7, 123.8, 128.9, 132.3, 134.4, 144.6, 193.5 ppm. $C_{26}H_{18}O_4S_2 \cdot 0.6H_2O$ (469.36): calcd. C 66.53, H 4.12; found C 66.44, H 3.99. MS (EI): *m*/*z* (%) = 458.1 (25) $[M]^+$, 416.1 (41) $[M - C_2H_3O + H]^+$, 374.1 (100) $[M - 2C_2H_3O + 2H]^+$, 342.1 (25) $[M - C_2H_3O - C_2H_3OS + 2H]^+$.

Synthesis of 1 from 14: A solution of compound **14** (92 mg, 0.14 mmol) in a mixture of dry toluene (24 mL) and acetyl chloride (6 mL) was stirred at room temp. and then BBr_3 (1 M in CH_2Cl_2, 290 µL, 0.29 mmol) was added. More BBr_3 (1 M in CH_2Cl_2, 290 µL, 0.29 mmol) was added after 30 min and 1 h. The solution was cooled to 0 °C, H_2O was added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2/MeOH, 100:0 to 99:1) followed by filtration through SiO_2 with $CHCl_3$ afforded **1** (46 mg, 70%) as a yellow solid.

Synthesis of 1 from 17 (BBr_3 Deprotection): A solution of compound **17** (66 mg, 0.13 mmol) in a mixture of dry toluene (21 mL) and acetyl chloride (5 mL) was stirred at room temp. and then BBr_3 (1 M in CH_2Cl_2, 290 µL, 0.29 mmol) was added. More BBr_3 (1 M in CH_2Cl_2, 290 µL, 0.29 mmol) was added after 30 min. The solution was cooled to 0 °C, H_2O was added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2/MeOH, 100:0 to 99:1) afforded **1** (45 mg, 77%) as a yellow solid.

Synthesis of 1 from 17 (AcOH Deprotection): A solution of compound **17** (44 mg, 0.09 mmol) and AcOH (1 mL) in a mixture of CH_2Cl_2 (8 mL), MeOH (10 mL) and H_2O (0.25 mL) was refluxed for a week. After evaporation of the solvents, flash chromatography (SiO_2, CH_2Cl_2/MeOH, 100:0 to 99:1) afforded **1** (28 mg, 71%) as a yellow solid.

Synthesis of 1 from 17 (TFA Deprotection): A solution of compound **17** (94 mg, 0.18 mmol) and TFA (14 µL, 0.19 mmol) in a mixture of CH_2Cl_2 (10 mL), MeOH (9.5 mL) and H_2O (0.5 mL) was refluxed for a week. After evaporation of the solvents, flash

chromatography (SiO_2, CH_2Cl_2/MeOH, 100:0 to 99:1) afforded **1** (43 mg, 51%) as a yellow solid.

Synthesis of 1 from 18: Compound **18** (206 mg, 0.42 mmol) was dissolved in dry CH_2Cl_2 (25 mL), then BBr_3 (1 M in CH_2Cl_2, 1.7 mL, 1.70 mmol) was added dropwise over 5 min at –7 °C. The reaction mixture was stirred at –7 °C for 25 min, then poured onto ice and the product was extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, toluene/AcOEt, 85:15 to 80:20) afforded **1** (112 mg, 58%) as a yellow solid.

Synthesis of 1 from 19: A solution of compound **19** (200 mg, 0.37 mmol) in a mixture of dry toluene (60 mL) and acetyl chloride (13 mL) was stirred at room temp. and then BBr_3 (1 M in CH_2Cl_2, 740 μL, 0.74 mmol) was added. More BBr_3 (1 M in CH_2Cl_2, 740 μL, 0.74 mmol) was added after 1, 2, 3 and 4 h. The solution was cooled to 0 °C, H_2O was added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2/MeOH, 100:0 to 99:1) followed by filtration through SiO_2 with $CHCl_3$ afforded **1** (134 mg, 79%) as a yellow solid.

1,4-Bis[(4-*tert*-butylsulfanylphenyl)ethynyl]-2,3-dihydroxybenzene (20): A solution of compound **19** (106 mg, 0.20 mmol) in a mixture of THF (9.5 mL) and aqueous 37% HCl (0.5 mL) was stirred at room temp. for 19 h. The solution was evaporated, CH_2Cl_2 and H_2O were added, the organic phase was separated and the aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered and the solvents evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2) afforded **20** (83 mg, 87%) as a yellow solid, m.p. 198–201 °C. R_f = 0.31 (SiO_2, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 18 H), 5.78 (br. s, 2 H), 7.00 (s, 2 H), 7.48–7.56 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.1, 46.8, 85.0, 96.4, 110.8, 122.9, 123.6, 131.7, 134.2, 137.4, 144.4 ppm. $C_{30}H_{30}O_2S_2 \cdot 0.3H_2O$ (492.09): calcd. C 73.22, H 6.27; found C 73.20, H 6.28. MS (EI): *m/z* (%) = 486.1 (39) $[M]^+$, 430.1 (7) $[M - C_4H_9 + H]^+$, 374.0 (100) $[M - 2C_4H_9 + 2H]^+$.

Acknowledgments

The authors acknowledge the Volkswagen Foundation and the Helmholtz Foundation (Project "Integrated Molecular Switches") for supporting this work. I. P. also acknowledges support through a Ph. D. fellowship sponsored by Deutscher Akademischer Austauschdienst (DAAD). We are grateful to Dr. Elaine Medlycott for carefully reading this manuscript.

[1] N. Weibel, S. Grunder, M. Mayor, *Org. Biomol. Chem.* **2007**, *5*, 2343–2353.
[2] R. L. Carroll, C. B. Gorman, *Angew. Chem. Int. Ed.* **2002**, *41*, 4378–4400.
[3] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541–548.
[4] N. J. Tao, *Nat. Nanotechnol.* **2006**, *1*, 173–181.
[5] J. R. Heath, M. A. Ratner, *Phys. Today* **2003**, *56*, 43–49.
[6] C. Joachim, M. A. Ratner, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 8801–8808.
[7] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Löhneysen, *Phys. Rev. Lett.* **2002**, *88*, 176804/1–176804/4.
[8] M. Mayor, C. von Hänisch, H. B. Weber, J. Reichert, D. Beckmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1183–1186.
[9] M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann, M. Fischer, *Angew. Chem. Int. Ed.* **2003**, *42*, 5834–5838.
[10] R. E. Holmlin, R. F. Ismagilov, R. Haag, V. Mujica, M. A. Ratner, M. A. Rampi, G. M. Whitesides, *Angew. Chem. Int. Ed.* **2001**, *40*, 2316–2320.
[11] J. G. Kushmerick, D. B. Holt, J. C. Yang, J. Naciri, M. H. Moore, R. Shashidhar, *Phys. Rev. Lett.* **2002**, *89*, 086802/1–086802/4.
[12] J. G. Kushmerick, D. B. Holt, S. K. Pollack, M. A. Ratner, J. C. Yang, T. L. Schull, J. Naciri, M. H. Moore, R. Shashidhar, *J. Am. Chem. Soc.* **2002**, *124*, 10654–10655.
[13] J. G. Kushmerick, A. S. Blum, D. P. Long, *Anal. Chim. Acta* **2006**, *568*, 20–27.
[14] N. Tao, *J. Mater. Chem.* **2005**, *15*, 3260–3263.
[15] X. Li, B. Xu, X. Xiao, X. Yang, L. Zang, N. Tao, *J. Chem. Soc. Faraday Trans.* **2006**, *131*, 111–120.
[16] J. He, O. Sankey, M. Lee, N. Tao, X. Li, S. Lindsay, *J. Chem. Soc. Faraday Trans.* **2006**, *131*, 145–154.
[17] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 8815–8820.
[18] D. Dulic, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees, *Phys. Rev. Lett.* **2003**, *91*, 207402/1–207402/4.
[19] Z. Li, I. Pobelov, B. Han, T. Wandlowski, A. Błaszczyk, M. Mayor, *Nanotechnology* **2007**, *18*, 044018/1–044018/8.
[20] W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Höbenreich, D. J. Schiffrin, R. J. Nichols, *J. Am. Chem. Soc.* **2003**, *125*, 15294–15295.
[21] Z. Li, B. Han, G. Meszaros, I. Pobelov, T. Wandlowski, A. Błaszczyk, M. Mayor, *J. Chem. Soc. Faraday Trans.* **2006**, *131*, 121–143.
[22] A. S. Blum, J. G. Kushmerick, D. P. Long, C. H. Patterson, J. C. Yang, J. C. Henderson, Y. Yao, J. M. Tour, R. Shashidhar, B. R. Ratna, *Nat. Mater.* **2005**, *4*, 167–172.
[23] E. Lörtscher, J. W. Ciszek, J. Tour, H. Riel, *Small* **2006**, *2*, 973–977.
[24] C. P. Collier, G. Matterstei, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172–1175.
[25] Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. DeIonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2002**, *3*, 519–525.
[26] C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **2001**, *123*, 12632–12641.
[27] J. O. Jeppesen, K. A. Nielsen, J. Perkins, S. A. Vignon, A. Di Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani, J. Becher, J. F. Stoddart, *Chem. Eur. J.* **2003**, *9*, 2982–3007.
[28] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, *286*, 1550–1552.
[29] J. K. Sørensen, M. Vestergaard, A. Kadziola, K. Kils, M. B. Nielsen, *Org. Lett.* **2006**, *8*, 1173–1176.
[30] E. H. van Dijk, D. J. T. Myles, M. H. van der Veen, J. C. Hummelen, *Org. Lett.* **2006**, *8*, 2333–2336.
[31] F.-R. F. Fan, J. Yang, L. Cai, D. W. Price Jr, S. M. Dirk, D. V. Kosynkin, Y. Yao, A. M. Rawlett, J. M. Tour, A. J. Bard, *J. Am. Chem. Soc.* **2002**, *124*, 5550–5560.
[32] F.-R. F. Fan, J. Yang, S. M. Dirk, D. W. Price, D. Kosynkin, J. M. Tour, A. J. Bard, *J. Am. Chem. Soc.* **2001**, *123*, 2454–2455.
[33] R. W. Bates, C. J. Gabel, J. Ji, T. Rama-Devi, *Tetrahedron* **1995**, *51*, 8199–8212.
[34] C. Koradin, W. Dohle, A. L. Rodriguez, B. Schmid, P. Knochel, *Tetrahedron* **2003**, *59*, 1571–1587.
[35] S. Anderson, P. N. Taylor, G. L. B. Verschoor, *Chem. Eur. J.* **2004**, *10*, 518–527.
[36] N. G. Kundu, M. Pal, J. S. Mahanty, S. K. Dasgupta, *J. Chem. Soc. Chem. Commun.* **1992**, 41–42.
[37] K. Hiroya, N. Suzuki, A. Yasuhara, Y. Egawa, A. Kasano, T. Sakamoto, *J. Chem. Soc. Perkin Trans. 1* **2000**, 4339–4346.
[38] J. P. Ferris, F. R. Antonucci, *J. Chem. Soc. Chem. Commun.* **1972**, 126–127.

[39] T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd Ed., Wiley, New York, **1999**.
[40] Y. Fukazawa, H. Kitayama, K. Yasuhara, K. Yoshimura, S. Usui, *J. Org. Chem.* **1995**, *60*, 1696–1703.
[41] A. H. McManus, M. J. Fleming, M. Lautens, *Angew. Chem. Int. Ed.* **2007**, *46*, 433–436.
[42] S. Kamisuki, S. Takahashi, Y. Mizushina, S. Hanashima, K. Kuramochi, S. Kobayashi, K. Sakaguchi, T. Nakata, F. Sugawara, *Tetrahedron* **2004**, *60*, 5695–5700.
[43] S.-Y. Sit, K. Xie, S. Jacutin-Porte, K. M. Boy, J. Seanz, M. T. Taber, A. G. Gulwadi, C. D. Korpinen, K. D. Burris, T. F. Molski, E. Ryan, C. Xu, T. Verdoorn, G. Johnson, D. E. Nichols, R. B. Mailman, *Bioorg. Med. Chem.* **2004**, *12*, 715–734.
[44] M. Node, K. Nishide, K. Fuji, E. Fujita, *J. Org. Chem.* **1980**, *45*, 4275–4277.
[45] Y.-Z. Hu, D. L. J. Clive, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1421–1424.
[46] A. Bernet, K. Seifert, *Helv. Chim. Acta* **2006**, *89*, 784–796.
[47] M. Kodama, Y. Shiobara, H. Sumitomo, K. Matsumura, M. Tsukamoto, C. Harada, *J. Org. Chem.* **1988**, *53*, 72–77.
[48] D. L. Andersen, T. G. Back, L. Janzen, K. Michalak, R. P. Pharis, G. C. Y. Sung, *J. Org. Chem.* **2001**, *66*, 7129–7141.
[49] P. R. Weider, L. S. Hegedus, H. Asada, *J. Org. Chem.* **1985**, *50*, 4276–4281.
[50] G. Schill, K. Murjahn, *Chem. Ber.* **1971**, *104*, 3587–3593.
[51] M. Kawase, A. K. Sinhababu, E. M. McGhee, T. Milby, R. T. Borchardt, *J. Med. Chem.* **1990**, *33*, 2204–2211.
[52] M. D. Shair, T. Y. Yoon, K. K. Mosny, T. C. Chou, S. J. Danishefsky, *J. Am. Chem. Soc.* **1996**, *118*, 9509–9525.
[53] B. Alluis, O. Dangles, *Helv. Chim. Acta* **2001**, *84*, 1133–1156.
[54] A. Alam, Y. Takaguchi, H. Ito, T. Yoshida, S. Tsuboi, *Tetrahedron* **2005**, *61*, 1909–1918.
[55] A. Merz, M. Rauschel, *Synthesis* **1993**, 797–802.
[56] R. R. Scheline, *Acta Chem. Scand.* **1966**, *20*, 1182.
[57] H. Hillemann, *Ber. Dtsch. Chem. Ges. B* **1938**, *71*, 34–41.
[58] Z. Zhu, T. M. Swager, *Org. Lett.* **2001**, *3*, 3471–3474.
[59] D. L. Pearson, J. M. Tour, *J. Org. Chem.* **1997**, *62*, 1376–1387.
[60] D. T. Gryko, C. Clausen, K. M. Roth, N. Dontha, D. F. Bocian, W. G. Kuhr, J. S. Lindsey, *J. Org. Chem.* **2000**, *65*, 7345–7355.
[61] Crystal data for **18**: $C_{28}H_{22}O_4S_2$, a = 915.15(18), b = 1266.3(3), c = 1315.2(3) pm, α = 108.78(3), β = 106.98(3), γ = 105.74(3)°, $V = 1262.7(4) \times 10^6$ pm^3; triclinic $P\bar{1}$, Z = 2, $\rho_{calcd.}$ = 1.2803 g cm^{-1}, μ(Mo-K_α) = 0.242 mm^{-1}, STOE IPDS2, Mo-K_α radiation, λ = 0.71073 Å, T = 200 K, $2\theta_{max}$ = 52°, 5573 reflections measured, 3988 independent reflections (R_{int} = 0.0323), 2268 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-square techniques against F^2, 307 parameters (S, O, C were refined anisotropically, H atoms calculated at ideal positions). R_1 = 0.0488, wR_2 = 0.1433 (all data), GOF 0.946, maximum peak 0.156 e Å^{-3}. CCDC-662155 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[62] M. Bouktaib, S. Lebrun, A. Atmani, C. Rolando, *Tetrahedron* **2002**, *58*, 10001–10009.
[63] F. Dietl, G. Gierer, A. Merz, *Synthesis* **1985**, 626–631.
[64] S. Danishefsky, J. Y. Lee, *J. Am. Chem. Soc.* **1989**, *111*, 4829–4837.
[65] N. Stuhr-Hansen, *Synth. Commun.* **2003**, *33*, 641–646.
[66] N. Stuhr-Hansen, J. B. Christensen, N. Harrit, T. Bjørnholm, *J. Org. Chem.* **2003**, *68*, 1275–1282.
[67] N. Stuhr-Hansen, J. K. Sørensen, K. Moth-Poulsen, J. B. Christensen, T. Bjørnholm, M. B. Nielsen, *Tetrahedron* **2005**, *61*, 12288–12295.
[68] A. Błaszczyk, M. Chadim, C. von Hänisch, M. Mayor, *Eur. J. Org. Chem.* **2006**, 3809–3825.
[69] S. M. Golabi, D. Nematollahi, *J. Electroanal. Chem.* **1997**, *420*, 127–134.
[70] N. J. Simmons, K. O. A. Chin, J. A. Harnisch, B. Vaidya, W. S. Trahanovsky, M. D. Porter, R. J. Angelici, *J. Electroanal. Chem.* **2000**, *482*, 178–187.
[71] A. R. Fakhari, D. Nematollahi, A. B. Moghaddam, *J. Electroanal. Chem.* **2005**, *577*, 205–210.
[72] D. Nematollahi, S. M. Golabi, *J. Electroanal. Chem.* **1996**, *405*, 133–140.
[73] D. Nematollahi, S. M. Golabi, *J. Electroanal. Chem.* **2000**, *481*, 208–214.
[74] D. Nematollahi, S. M. Golabi, *Electroanalysis* **2001**, *13*, 1008–1015.
[75] B. Xu, N. J. Tao, *Science* **2003**, *301*, 1221–1223.
[76] C. Li, I. Pobelov, T. Wandlowski, A. Bagrets, A. Arnold, F. Evers, *J. Am. Chem. Soc.* **2007**, submitted for publication.
[77] X. Li, J. He, J. Hihath, B. Xu, S. M. Lindsay, N. Tao, *J. Am. Chem. Soc.* **2006**, *128*, 2135–2141.
[78] X. Xiao, L. A. Nagahara, A. M. Rawlett, N. Tao, *J. Am. Chem. Soc.* **2005**, *127*, 9235–9240.
[79] W. Haiss, C. Wang, I. Grace, A. S. Batsanov, D. J. Schiffrin, S. J. Higgins, M. R. Bryce, C. J. Lambert, R. J. Nichols, *Nat. Mater.* **2006**, *5*, 995–1002.

Received: August 31, 2007
Published Online: November 21, 2007

