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# Synthesis of molecular chains: phenylene thioether and sulfoxide oligomers

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ABSTRACT

The application of a general synthetic approach to prepare molecular chains is reported. It is based on a step-by-step method each consisting first in a Pd-catalyzed reaction between ArI and HXAr′Br (Ar=aryl, Ar′=arylene) to give ArXAr′Br followed by a Cu-catalyzed replacement of Br by I to give ArXAr′I that can be reacted with HXAr′Br in the following step. The application of this method is here illustrated to prepare phenylene sulfide oligomers (X=S). Starting from $RC_6H_4I$-4 (R=H, MeO, $NO_2$, $NH_2$) and $HSC_6H_4Br$-*x* (*x*=2, 4) it is possible to grow chains in one direction to give $X(C_6H_4S$-*m*$)_nC_6H_4R$-4 (*n*=1, X=Br, *m*=4, R=H, MeO, $NO_2$, $NH_2$, SMe and *m*=2, R=H, MeO, $NO_2$; *n*=1, X=I, *m*=2 or 4, R=H, MeO, $NO_2$; *n*=2, X=Br, *m*=2 or 4, R=H, MeO, $NO_2$; *n*=2, X=I, *m*=4, R=MeO, $NO_2$; *n*=3, X=Br, *m*=4, R=MeO, $NO_2$; *n*=3, X=I, *m*=4, R=$NO_2$ and *n*=4, X=Br or I, *m*=4, R=$NO_2$). From $HSC_6H_4Br$-*x* and $IC_6H_4I$-4 the chains can grow in two directions to give $X(C_6H_4S$-4$)_nC_6H_4X$-4 (*n*=2 or 4, X=Br or I), 2-$XC_6H_4(SC_6H_4$-4$)_nSC_6H_4X$-2 (*n*=3 or 5, X=Br). Using diiodomesitylene the dithioethers $C_6HMe_3$-2,4,6-$(SC_6H_4X$-4$)_2$-1,3 (X=Br, I) have been prepared. The series of sulfoxides $X(C_6H_4S(O)$-4$)_nC_6H_4R$-4 (X=Br, *n*=1, R=MeO, *n*=3, R=$NO_2$, *n*=4, R=Br; X=R=I, *n*=2) has been obtained from the corresponding thioethers and $PhICl_2$.



## 1. Introduction

The synthesis of linear chains[1–3] or branched[3–7] molecules is receiving considerable attention because they can be important in different key research areas (pharmaceuticals,[1,5,8] sensors,[9] opto-electronic, non-linear optical and photonic devices,[6,10] gene delivery,[11] catalysis,[7,12] chiral recognition,[13] ion-selective electrodes or membranes,[14] etc.[3,15]). To prepare such molecules, a variety of repeating step-by-step coupling methods have been used.[4c,16–18]

The main objective of this paper is to report the application of the general synthetic approach we have preliminarly reported to prepare oligomers or molecular chains.[17] This method involves (i) a Pd-catalyzed C–X coupling between ArI and HXAr′Br (Ar=aryl, Ar′=arylene, X=O, S, NH, C≡C, etc.) to give ArXAr′Br and (ii) a Cu-catalyzed replacement of bromide by iodide to give ArXAr′I that can be used for the next step.

We have chosen the synthesis of oligomeric phenylene thioethers for the first illustration of our synthetic method because these compounds are of great interest. Thus, polyarylene thioethers are thermoplastics having excellent thermal and dimensional stabilities, hydrophobicity, good fire retardant and mechanical properties, and high refractive index.[19] Poly(1,4-phenylene sulfide), which is commercially produced by polycondensation of 1,4-dichlorobenzene with sodium sulfide at high temperature and pressure,[20] is increasingly used in electronic/electric, aircraft, and aerospace industries.[21] Some of their oligomeric analogs are used as ion-selective electrodes.[22] In this paper we illustrate our synthetic approach by synthesizing thioether chains (X=S) containing 1–6 sulfur atoms. The synthesis of a few *para*-phenylene thioethers has been the subject of a preliminary publication.[17] With respect to this communication, this full paper reports that this method can be used (1) for preparing new chains grown in one direction $X(C_6H_4S$-*m*$)_nC_6H_4R$-4 with new R=H, $NH_2$, SMe or with other phenylene groups (*ortho*, *m*=2); (2) to grow chains in two directions using two different methods allowing to build longer chains (six sulfur atoms vs four) and to include in the chain *ortho*- and *meta*-substituted phenylene groups, and (3) to prepare oligomeric sulfoxides after oxidation of the thioether chains.

The most general method for the synthesis of non-symmetrical diaryl thioethers is based on transition metal-catalyzed substitution of aryl halides or triflates by arene thiolates.[23] Thus, Co,[24] Ni,[25] Pd,[26,27] or Cu[28–30] complexes have been used as catalysts to prepare diaryl thioethers with good to excellent yields. These and other methods have been used to prepare oligomeric thioethers.[17–19,29,31–34]

Some polysulfoxides in which a sulfoxide group is part of the backbone have been prepared by oxygenation of the corresponding alkyl aryl[35] or vinyl aryl[36] polysulfides, using different oxidizing agents. Conversely, poly(arylene ether sulfoxide)s have been prepared, via nucleophilic substitution polycondensation of bis(4-fluorophenyl) sulfoxide and potassium salts of bisphenols, for

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converting them to the corresponding sulfides via a reduction reaction of the sulfoxide. Under various conditions mixtures of cyclic or linear oligomers have been prepared.[21]

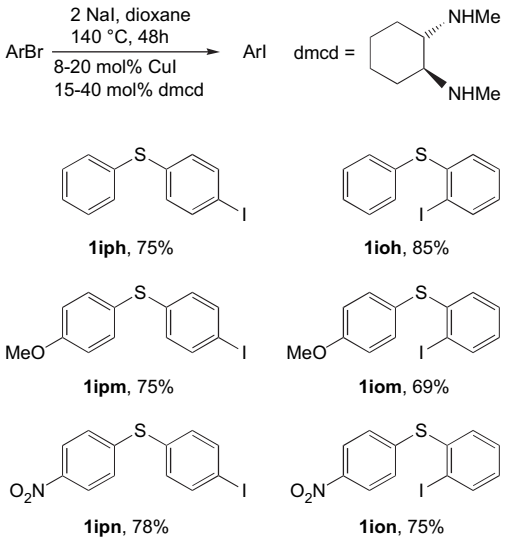
## 2. Results and discussion

### 2.1. Synthesis of phenylene thioether chains

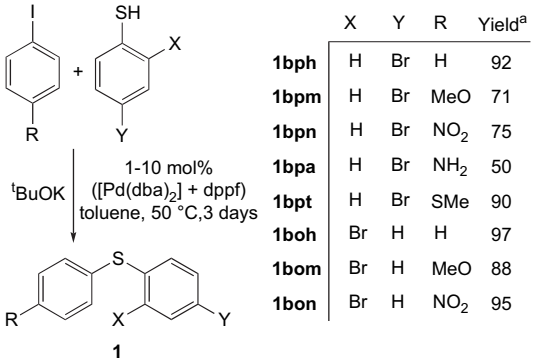
The synthesis of these thioethers was carried out by reacting iodoarenes and bromoaryl thiols, by a modification of the palladium-catalyzed method reported by Schopfer.[27] The name of the reported compounds is formed by (1) the number of sulfur atoms bridging the aryl groups, (2) a letter showing if the halogen is bromine (**b**) or iodine (**i**), (3) another letter showing if sulfur and the halogen are in *para* (**p**) or *ortho* (**o**) position, and (4) a letter showing the nature of the R group: H (**h**), MeO (**m**), $NO_2$ (**n**), $NH_2$ (**a**) SMe (**t**). Scheme 1 shows the diaryl thioethers prepared from equimolecular amounts of $BrC_6H_4SH$-4 or $BrC_6H_4SH$-2 and K($O^tBu$), 1–1.38 equiv of $RC_6H_4I$-4 (R=H, MeO, $NO_2$) and using as catalyst 1 mol% (10 mol% for **1bpa**) of an equimolecular mixture of $[Pd_2(dba)_3]\cdot dba$ ('Pd(dba)$_2$'; dba=dibenzylideneacetone) and 1,1′-bis(diphenylphosphino)ferrocene (dppf), instead of bis[2-(diphenylphosphino)phenyl]ether used as ligand in the Schopfer's method.[27] Because the oxidative addition reaction of the bromoarene must be prevented, the reaction was carried out at lower temperatures and during more time than in the original work (50 °C vs 100 °C; 3 days vs 2 h). If the reaction time is shortened (1 day) the amount of catalyst must be increased (5 mol%).

The bromoarene **1bph**, **1bpm**, or **1bpn**, does not react with $BrC_6H_4SH$-4 (100 °C, 10 mol% of catalyst). Higher temperatures were not attempted because mixtures of polymers would form. Therefore, the next C–S coupling process required the substitution of bromine by iodine in compounds **1**. This process was carried out by using a slightly modified version of the copper-catalyzed halogen exchange reaction reported by Buchwald that uses 5 mol% of CuI, 10 mol% of racemic *trans*-*N*,*N*′-dimethyl-1,2-cyclohexane diamine (dmcd), and 2 equiv of NaI in dioxane at 110 °C during 22–24 h.[37] Our best results (Scheme 2) were obtained by using a greater proportion of catalyst,[37] higher temperatures, and longer reaction times (see Section 4).

Following the same two-step method we have prepared bromide and iodide oligothioethers with 2–4 sulfur atoms (Scheme 3). The amounts of the catalyst used in the halogen exchange step must be notably increased as the number of sulfur atoms increases. Thus, the amounts (mol%) of CuI/dmcd used were 20/40 (**2ipm**, **2ipn**) or 40/80 (**3ipn**, **4ipn**). The *ortho*-substituted dithioethers **2boh**, **2bom**, **2bon** were also prepared from the corresponding monothioethers (Scheme 4) but all attempts to prepare the iodo derivatives **2ioh**, **2iom**, **2ion**, led to mixtures with the corresponding bromides even when the amount of CuI/dmcd was 40/80 mol%. For the C–S coupling step we have preferred to use a shorter reaction time (1 day vs 3 days) by increasing the amount of the catalyst (5 vs 1 mol%).

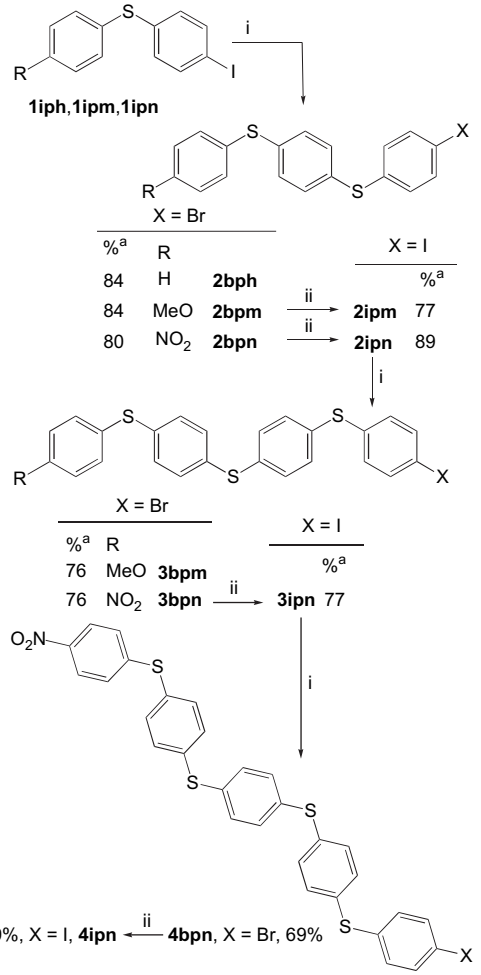



**Scheme 2.** Synthesis of iodo monothioethers.

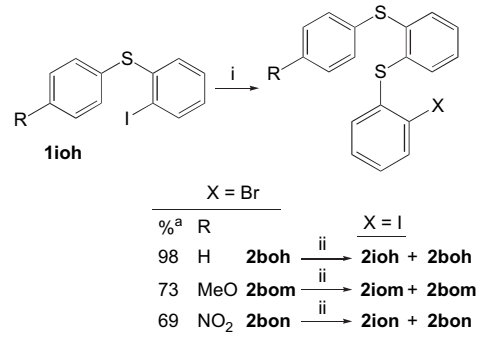



| | X | Y | R | Yield[a] |
|---|---|---|---|---|
| **1bph** | H | Br | H | 92 |
| **1bpm** | H | Br | MeO | 71 |
| **1bpn** | H | Br | $NO_2$ | 75 |
| **1bpa** | H | Br | $NH_2$ | 50 |
| **1bpt** | H | Br | SMe | 90 |
| **1boh** | Br | H | H | 97 |
| **1bom** | Br | H | MeO | 88 |
| **1bon** | Br | H | $NO_2$ | 95 |

**Scheme 1.** Synthesis of bromo monothioethers. [a]Isolated yields.




**Scheme 3.** Synthesis of thioethers with 2–4 sulfur atoms. [a]Isolated yields. (i) $BrC_6H_4SH$-4+K$O^tBu$+cat. (Pd)=[Pd(dba)$_2$+dppf] (5 mol%); (ii) 2NaI+cat. (Cu)=[CuI+2dmcd] (20–40 mol%).




**Scheme 4.** Synthesis of thioethers with two sulfur atoms in *ortho* positions. [a]Isolated yields. (i) $BrC_6H_4SH$-2+$KO^tBu$+cat. (Pd)=[$Pd(dba)_2$+dppf] (5 mol %); (ii) 2NaI+cat. (Cu)=[CuI+2dmcd] (20–40 mol %).

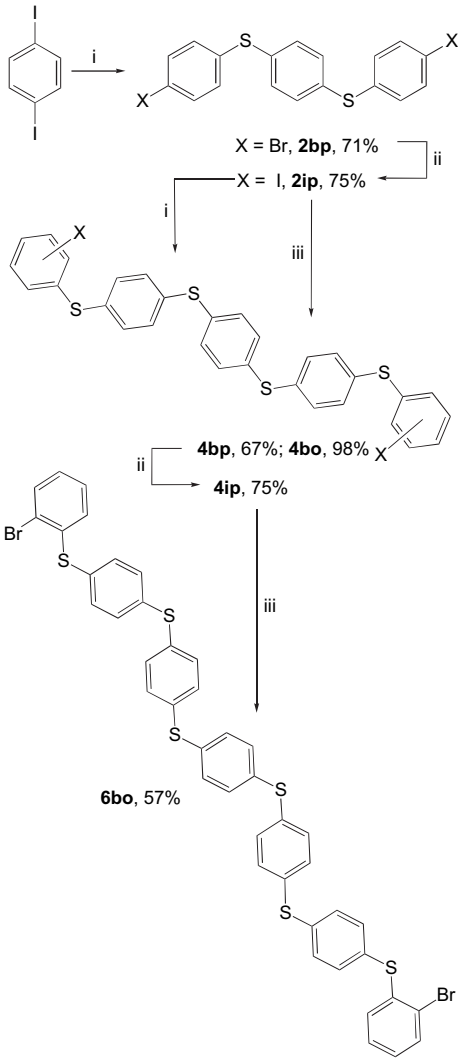
The *para*-substituted thioethers are similar to those reported by Gingras.[29] These were prepared through a three-step process: (i) *para*-bromination of a thiomethyl arene to give Br–Ar–SMe, (ii) Pd- or Cu-catalyzed coupling of the bromoarenes with a thiophenol R–Ar′–SH to give R–Ar′–S–Ar–SMe, and (iii) dealkylation of the SMe group to give R–Ar′–S–Ar–SH. With respect to our two-step method, the reported yields are similar or lower, and the end groups are limited to H or a group with +M effect (MeO, $^i$PrO, MeS, HS, Br) while our method has been shown to be compatible with both +M (OMe, Br, I, $NH_2$) and −M groups ($NO_2$). Unfortunately, thioethers with more than four sulfur atoms could not be prepared using ArX and $BrC_6H_4SH$ because their insolubility prevents recrystallization. Thus, in our case, the iodide **4ipn** could not be isolated analytically pure and the three iodides **2io** could not be separated from the starting bromides. Probably, introducing suitable substituents could improve the solubility of the chains and the length could be increased. However, we have not attempted this possibility because, as mentioned in Section 1, this was not our objective. The synthesis of a few linear or cyclic oligo(*para*-phenylene)thioethers 4-$XC_6H_4(SC_6H_4$-4)$_n$X ($n$=2, X=H; $n$=4, X=Br, I)[33] or $(SC_6H_4$-4)$_n$ ($n$=4, 5, 6)[38] has also been reported.

To grow longer chains faster we attempted to prepare $Br(C_6H_4S$-4)$C_6H_4SH$-4 with the objective of using it instead of $BrC_6H_4SH$-4. However, the dealkylation of the thiomethyl group in **1bpt**, using $NaS^tBu$ in DMF at 150–160 °C,[29,32] or diazotization of **1pba** followed by reaction with potassium thioacetate,[39] was unsuccessful.

Two different strategies, using as starting materials diiodo derivatives, diiodomesitylene or $IC_6H_4$I-4, or a dithiol, $HSC_6H_4SH$-4, were followed for applying our method to grow longer molecular chains in two directions.

## 2.2. Synthesis of phenylene thioether chains from 1,4-diiodobenzene or diiodomesitylene

The reaction between equimolecular amounts of $BrC_6H_4SH$-4 and $KO^tBu$ with half an equivalent of $IC_6H_4$I-4 in the presence of 5 mol % of the catalytic mixture of $Pd(dba)_2$ and dppf (toluene, 50 °C, 24 h) gives $Br(C_6H_4S$-4)$_2C_6H_4$Br-4 (**2bp**). Bromide by iodide exchange to give **2ip** (dioxane, 140 °C, 48 h), C–S coupling with $BrC_6H_4SH$-4 to give **4bp** and a new bromide by iodide exchange to give **4ip** (Scheme 5) allowed to prepare the chain up to the solubility limit of these compounds. In fact, compounds **4bp** and **4ip** were too insoluble (in $CDCl_3$, $CD_2Cl_2$, $(CD_3)_2CO$, $(CD_3)_2SO$) to allow the recording of their NMR spectra. However, new four- and six-sulfur-chains could be isolated by reacting **2ip** or **4ip** with $BrC_6H_4SH$-2 to give 2-$BrC_6H_4(SC_6H_4$-4)$_3SC_6H_4$Br-2 (**4bo**) or 2-$BrC_6H_4(SC_6H_4$-4)$_5SC_6H_4$Br-2 (**6bo**) which are soluble enough to allow NMR studies. However, all atempts to prepare the corresponding iodides gave mixtures containing the starting bromide compounds.

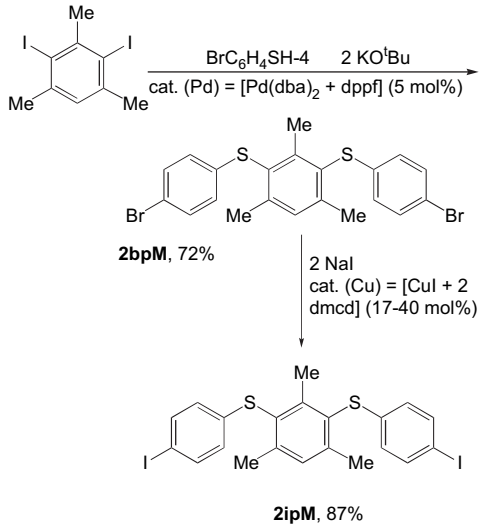



**Scheme 5.** Synthesis of phenylene thioether chains from 1,4-diiodobenzene. (i) $BrC_6H_4SH$-4+2$KO^tBu$+cat. (Pd)=[$Pd(dba)_2$+dppf] (5 mol %); (ii) 2NaI+cat. (Cu)=[CuI+2dmcd] (17–40 mol %); (iii) $BrC_6H_4SH$-2+2$KO^tBu$+cat. (Pd)=[$Pd(dba)_2$+dppf] (5 mol %).

Diiodomesitylene reacts with 2 equiv of $BrC_6H_4SH$-4 and $KO^tBu$ in the presence of 5 mol % of the catalytic mixture of $Pd(dba)_2$ and dppf (toluene, 60 °C, 24 h) to give $C_6HMe_3$-2,4,6-$(SC_6H_4Br$-4)$_2$-1,3 (**2bpM**, Scheme 6), which reacts with 2 equiv of NaI in the presence of CuI (17 mol %) and dmcd (34 mol %) to give $C_6HMe_3$-2,4,6-$(SC_6H_4I$-4)$_2$-1,3 (**2ipM**). Unfortunately, although **2ipM** is soluble in organic solvents it gives mixtures when reacted with $BrC_6H_4SH$-4 and $KO^tBu$ in the presence of 10 mol % of the catalytic mixture of $Pd(dba)_2$ and dppf (toluene, 60 °C, 24 h).

## 2.3. Synthesis of phenylene thioether chains from benzene-1,4-dithiol

The reactions between $HSC_6H_4SH$-4 and 2 equiv of $RC_6H_4$I-4 (R=MeO, MeS, R′$C_6H_4$S-4 (R′=H (**1iph**), MeO (**1ipm**), $NO_2$ (**1ipn**))) in the presence of the palladium catalyst (10 or 20 mol %, 50 or 100 °C, 1 day or 6 days, respectively) or using as catalyst CuI (10 mol %), 4 equiv of the mixture $K_2CO_3$+$(HOCH_2)_2$ in $^i$PrOH, 100 °C, 3 days,[30] gave complex mixtures or, respectively, the starting materials. However, the reaction between an $HSC_6H_4SH$-4 and 2 equiv of $RC_6H_4$I-4 (R=MeO, MeS) took place using a mixture

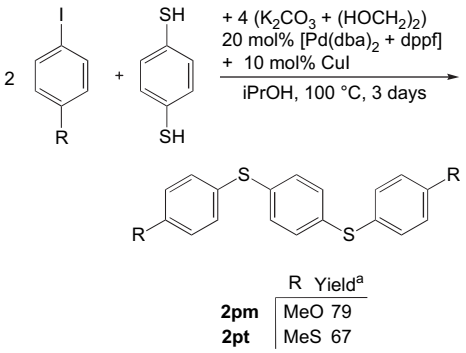



**Scheme 6.** Synthesis of phenylene thioethers from diiodomesitylene.

of both catalysts (20 mol % each of $Pd(dba)_2$ and dppf plus 10 mol % CuI and 4 equiv of the mixture $K_2CO_3$+$(HOCH_2)_2$ in $^i$PrOH, 100 °C, 3 days) to give $(RC_6H_4S\text{-}4)_2(C_6H_4\text{-}4)$ (R=OMe (**2pm**) SMe (**2pt**)) (Scheme 7). We have prepared the starting compound $MeSC_6H_4I$-4 from 4-bromothioanisole through the copper-catalyzed method for bromo by iodo exchange. Its synthesis has been reported previously by reacting 4-bromothioanisole with $^t$BuLi and $I_2$.[40]

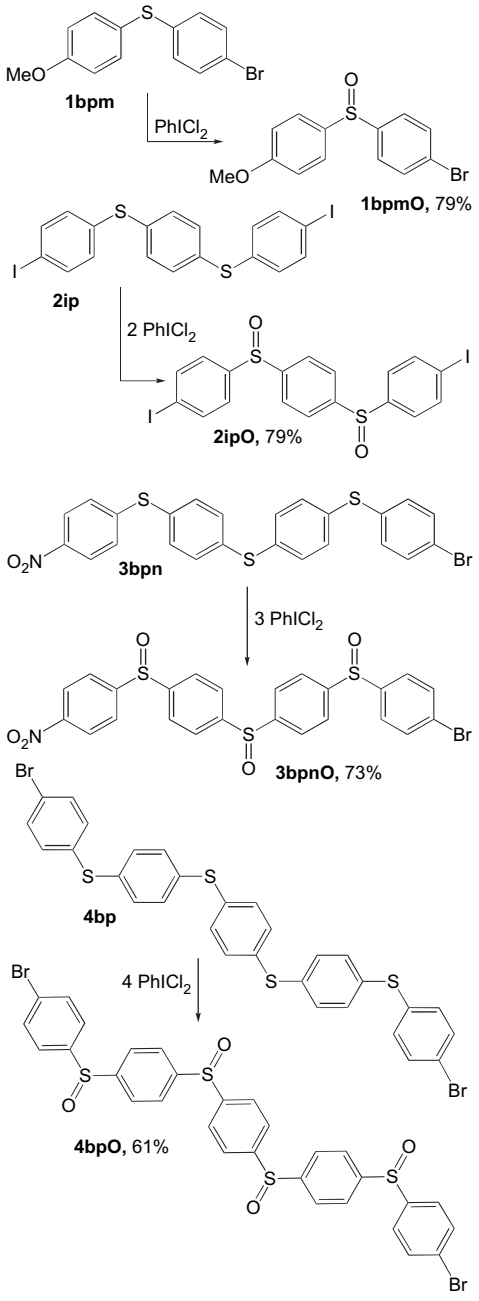
### 2.4. Synthesis of *para*-phenylene sulfoxide chains

The series of sulfoxides $X(C_6H_4S(O)\text{-}4)_nC_6H_4R$-4 (X=Br, $n$=1, R=MeO (**1bpmO**), $n$=3, R=$NO_2$ (**3bpnO**), $n$=4, R=Br (**4bpO**); X=R=I, $n$=2 (**2ipO**)) has been obtained (Scheme 8) from the corresponding thioethers and $n$ equiv of $PhICl_2$ in pyridine/water (9:1 v/v). The reactions occur almost instantaneously at room temperature. This method has been reported to give exclusively sulfoxides.[41] In fact, $^1$H and $^{13}$C of **1bpmO** shows that only *R*- and *S*-isomers are present in solution. While the $^1$H NMR spectrum of the two diastereoisomers of **2ipO** show only one set of signals, its $^{13}$C NMR spectrum shows the expected two sets of two signals for the different CH groups ortho to S(O) and for the two quaternary C–S carbon nuclei but only one signal for the CH groups ortho to I and for the CI carbon nuclei. The other sulfoxides have three (**3bpnO**) or four (**4bpO**) chiral centers. Correspondingly, more signals than expected for a single stereoisomer are observed but always less than expected. The EI mass spectra show in all cases the molecular ion and no peak for M+16*x*. Therefore, the presence of sulfones in the prepared sulfoxides should be discarded.




| | R | Yield[a] |
|---|---|---|
| **2pm** | MeO | 79 |
| **2pt** | MeS | 67 |

**Scheme 7.** Synthesis of phenylene thioether chains from benzene-1,4-dithiol. [a]Isolated yields.




**Scheme 8.** Synthesis of phenylene sulfoxide chains.

## 3. Conclusion and prospects

We have applied a step-by-step method to prepare molecular chains to the synthesis of phenylene sulfides in one or two directions. This synthetic approach is also open (1) to grow chains in three or more directions using S or other links, e.g., by reacting $C_6H_nI_{6-n}$ with HX–R–Br, or HX–R′–XH with I–R″–Br, X being C≡C, NH, O, etc., R, R′, R″ being phenylene groups; (2) to grow long chains by transforming R–$(X–R')_n$–Br into R–$(X–R')_n$–XH and then reacting it with R–$(X–R')_m$–I; (3) if R is a protecting group, to prepare the chain H–$(X–R')_n$–Br from R–$(X–R')_n$–Br that could be used to grow longer chains with few steps; (4) to prepare chains with the same or different X and phenylene links (X being C≡C, NH, O, S, etc.; R= or ≠R′), i.e., to prepare oligomeric or non-oligomeric molecular chains; (5) to build chains through C–C coupling processes (Heck, Stille or Suzuki catalytic reaction); (6) to use as skeleton or as some

of the links of the chains, other rings instead of benzene: pyridine, thiophene, etc. The only challenge is to find the experimental conditions allowing the coupling step to occur selectively with the carbon atom bonded to I but not to that bonded to Br. In conclusion, the great flexibility of this approach opens the way to prepare chains in one or more directions fulfilling some desired properties. We are successfully applying it to the synthesis of chains R–X–R′–Y–R″–Z–R‴ where X, Y, Z are different, each being S, NH or C≡C.

## 4. Experimental

### 4.1. General

4-Bromobenzenethiol, 4-iodonitrobenzene, 4-iodoanisole, 4-bromothioanisole, KO$^t$Bu, dppf, and dba were obtained from commercial sources. Pd(dba)$_2$[42] and dmcd[37] were prepared as reported previously. The synthesis of *para*-phenylene thioethers **1bpm**, **1bpn**, **1ipm**, **1ipn**, **2bpm**, **2bpn**, **2ipm**, **2ipn**, **3bpm**, **3bpn**, **3ipn**, and **4bpn** was reported in the preliminary communication.[17] Their melting points were determined in the open atmosphere. IR spectra were recorded with Nujol mulls between polyethylene sheets. $^1$H and $^{13}$C{$^1$H} chemical shifts were referenced to TMS. Chromatographic separations were carried out by preparative TLC on silica gel (70–200 mesh) with fluorescent $GF_{254}$ in the case of colorless compounds. All operations were carried out under an inert atmosphere of dry nitrogen. $CH_2Cl_2$ and $Et_2O$ were freshly distilled over sodium benzophenone and $CaH_2$, respectively. Toluene and 1,4-dioxane were from commercial sources and deoxygenated by bubbling $N_2$. *n*-Hexane was used as received.

### 4.2. General method for the C–S coupling reactions

*4.2.1. From 4- or 2-bromobenzenethiol*

Equimoleular amounts of 4- or 2-bromobenzenethiol and KO$^t$Bu (*b* (=0.13–4) mmol) were mixed in toluene (5 mL) and stirred for 15 min. The iodide (*i* (=100–138 for monoiodides or 50 for diiodides) mol %), and equimolecular amounts of dppf and Pd(dba)$_2$ (*c* (=1–10) mol %) were then added and the resulting mixture stirred at 50 °C for *t* (1–3) days. The solvent was removed under vacuum, the residue extracted with $Et_2O$ and filtered. The filtrate was concentrated (2 mL) and purified by preparative TLC ($CH_2Cl_2$/hexane 1:*h*). The appropriate band was extracted with acetone, the solution was stirred with $MgSO_4$, filtered, and the filtrate concentrated to dryness to give the thioethers as colorless (**1bpa** is orange; the nitro derivatives are yellow) solids (only **1bph** and **1boh** are liquids). The values for *b*, *i*, *c*, *t*, *h* and $R_f$ are given below for each compound.

*4.2.1.1. (2-Bromophenyl)(phenyl)thioether (**1boh**).* *b*=2.57, *i*=138, *c*=1, *t*=3, *h*=4, $R_f$=0.52. Yield: 97%; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.55 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.48–7.34 (several m, 5H), 7.14 (td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.02 (td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 6.90 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz); $^{13}$C{$^1$H} APT NMR (50.32 MHz, $CDCl_3$): $\delta$=138.8, 133.5, 133.0, 132.9, 129.8, 129.7, 128.5, 127.8, 127.3, 123.1; elemental analysis (%) calcd for $C_{12}H_9BrS$: C 54.36, H 3.40, S 12.08; found: C 54.23, H 3.44, S 11.95; MS (FAB+) *m*/*z* (%): 266 (100, M$^+$), 186 (35).

*4.2.1.2. (2-Bromophenyl)(4-methoxyphenyl)thioether (**1bom**).* *b*=2.57, *i*=138, *c*=1, *t*=3, *h*=4, $R_f$=0.20. Yield: 88%; mp: 44 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=7.52–7.44 (m, 3H, 1H), 7.11 (td, 1H, $^3J_{HH}$=7 Hz, $^4J_{HH}$=2 Hz), 6.99–6.91 (m, 3H, 1H), 6.66 (dd, 1H, $^3J_{HH}$=7 Hz, $^4J_{HH}$=2 Hz), 3.85 (s, 3H); $^{13}$C{$^1$H} APT NMR (50.32 MHz, $CDCl_3$): $\delta$=160.61, 140.87, 137.02, 132.71, 127.63, 127.36, 126.14, 122.01, 120.69, 115.41, 55.41; elemental analysis (%) calcd for $C_{13}H_{11}BrOS$: C 52.89, H 3.76, S 10.86; found: C 53.05, H 3.78, S 10.76; MS (FAB+) *m*/*z* (%): 296 (100, M$^+$), 281 (28).

*4.2.1.3. (2-Bromophenyl)(4-nitrophenyl)thioether (**1bon**).* *b*=2.57, *i*=138, *c*=1, *t*=3, *h*=2, $R_f$=0.20. Yield: 95%; mp: 90 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=8.10 (d, 2H, $^3J_{HH}$=8 Hz), 7.73 (dd, 1H, $^3J_{HH}$=7 Hz, $^4J_{HH}$=3 Hz), 7.56 (dd, 1H, $^3J_{HH}$=7 Hz, $^4J_{HH}$=3 Hz), 7.37 (td, 1H, $^3J_{HH}$=7 Hz, $^4J_{HH}$=3 Hz), 7.30 (td, 1H, $^3J_{HH}$=7 Hz, $^4J_{HH}$=3 Hz), 7.20 (d, 2H, $^3J_{HH}$=7 Hz); $^{13}$C{$^1$H} APT NMR (50.32 MHz, $CDCl_3$): $\delta$=145.98, 145.34, 136.17, 134.16, 132.26, 131.03, 129.21, 128.67, 127.52, 124.22; elemental analysis (%) calcd for $C_{12}H_8BrNO_2S$: C 46.47, H 2.60, N 4.52, S 10.32; found: C 46.21, H 2.63, N 4.52, S 10.10; MS (FAB+) *m*/*z* (%): 311 (60, M$^+$), 154 (100), 136 (91).

*4.2.1.4. (4-Bromophenyl)(4-aminophenyl)thioether (**1bpa**).* *b*=0.52, *i*=100, *c*=10, *t*=3, *h*=0.5, $R_f$=0.40. Yield: 50%; mp: 40 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.31 (d, 2H, $^3J_{HH}$=9 Hz), 7.30 (d, 2H, $^3J_{HH}$=9 Hz), 6.98 (d, 2H, $^3J_{HH}$=9 Hz), 6.66 (d, 2H, $^3J_{HH}$=9 Hz), 3.91 (br, 2H); $^{13}$C{$^1$H} APT NMR (75.48 MHz, $CDCl_3$): $\delta$=147.5, 139.2, 136.1, 131.6, 128.4, 119.0, 118.6, 115.8; elemental analysis (%) calcd for $C_{12}H_{10}BrNS$: C 51.44, H 3.56, N 5.00, S 11.43; found: C 51.78, H 3.63, N 4.93, S 11.03; MS (FAB+) *m*/*z* (%): 281 (100, M$^+$).

*4.2.1.5. (4-Bromophenyl)(phenyl)thioether (**1bph**).* *b*=2.57, *i*=138, *c*=1, *t*=3, *h*=3, $R_f$=0.55. Yield: 92%; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.39–7.1 (several m, 9H); $^{13}$C{$^1$H} APT NMR (50.32 MHz, $CDCl_3$): $\delta$=135.43, 134.76, 132.16, 132.01, 131.48, 129.32, 127.50, 120.81; elemental analysis (%) calcd for $C_{12}H_9BrS$: C 54.36, H 3.40, S 12.08; found: C 54.44, H 3.57, S 12.09; MS (FAB+) *m*/*z* (%): 266 (100, M$^+$), 186 (35).

*4.2.1.6. (4-Bromophenyl)(4-methylthiophenyl)thioether (**1bpt**).* Prepared from (4-iodophenyl)methylthioether (see below). *b*=2.4, *i*=100, *c*=5, *t*=1, *h*=5, $R_f$=0.70. Yield: 90%; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=7.35 (d, 2H, $^3J_{HH}$=9 Hz), 7.28 (d, 2H, $^3J_{HH}$=9 Hz), 7.17 (d, 2H, $^3J_{HH}$=9 Hz), 7.08 (d, 2H, $^3J_{HH}$=9 Hz), 2.45 (s, 3H); $^{13}$C{$^1$H} APT NMR (50.32 MHz, $CDCl_3$): $\delta$=139.0, 136.3, 132.8, 132.1, 131.1, 130.2, 127.1, 120.4, 15.6.[34]

*4.2.1.7. 1,2-(2-Bromophenylthio)(phenylthio)benzene (**2boh**).* *b*=0.32, *i*=109, *c*=5, *t*=1, *h*=4, $R_f$=0.30. Yield: 98%; mp: 74 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=7.50 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.33–7.18 (m, 5H), 7.15 (m, 1H), 7.08 (m, 3H), 7.01–6.93 (several m, 2H), 6.89 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz); $^{13}$C{$^1$H} APT NMR (50.32 MHz, $CDCl_3$): $\delta$=141.0, 136.9, 133.8, 133.6, 133.2, 133.0, 132.9, 130.4, 130.4, 129.5, 128.9, 128.0, 127.9, 127.8, 127.2, 124.3; elemental analysis (%) calcd for $C_{18}H_{13}BrS_2$: C 57.91, H 3.51, S 17.18; found: C 57.83, H 3.59, S 16.93; MS (FAB+) *m*/*z* (%): 374 (28, M$^+$), 293 (100), 216 (40).

*4.2.1.8. 1,2-(2-Bromophenylthio)(4-methoxyphenylthio)benzene (**2bom**).* *b*=0.44, *i*=100, *c*=5, *t*=1, *h*=2, $R_f$=0.30. Yield: 73%; mp: 98 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=7.58 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.42 (d, 2H, $^3J_{HH}$=9 Hz), 7.38 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.21–7.05 (m, 4H), 6.96–6.88 (m, 4H), 3.84 (s, 3H); $^{13}$C{$^1$H} APT NMR (50.32 MHz, $CDCl_3$): $\delta$=160.3, 144.9, 137.6, 136.5, 135.2, 133.0, 129.6, 129.5, 128.9, 127.9, 127.8, 127.1, 126.1, 122.9, 122.7, 115.2, 55.4; elemental analysis (%) calcd for $C_{19}H_{15}BrOS_2$: C 56.58, H 3.75, S 15.90; found: C 56.24, H 4.02, S 15.74; MS (FAB+) *m*/*z* (%): 404 (60, M$^+$), 323 (100), 216 (67), 154 (60), 136 (53).

*4.2.1.9. 1,2-(2-Bromophenylthio)(4-nitrophenylthio)benzene (**2bon**).* *b*=0.42, *i*=100, *c*=5, *t*=1, *h*=2, $R_f$=0.30. Yield: 69%; mp: 104 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=8.09 (d, 2H, $^3J_{HH}$=12 Hz), 7.64 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.56 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.36–7.16 (m, 7H), 7.01 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz); $^{13}$C{$^1$H} APT NMR (75.48 MHz, $CDCl_3$): $\delta$=146.5, 145.6, 141.6, 136.3, 134.5, 134.2,

133.8, 130.6, 130.1, 130.0, 129.8, 128.3, 127.7, 127.3, 128.0, 124.0; elemental analysis (%) calcd for $C_{18}H_{12}BrNO_2S_2$: C 51.68, H 2.89, S 15.33, N 3.35; found: C 52.07, H 2.99, S 15.10, N 3.30; MS (FAB+) *m*/*z* (%): 663 (32), 647 (24), 420 (25, $M^+$), 154 (80), 136 (100).

*4.2.1.10. 1,4-Bis(4-bromophenylthio)benzene (**2bp**).* *b*=1, *i*=50, *c*=5, *t*=1, *h*=1.5, $R_f$=0.50. Yield: 71%; mp: 159 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.42 (d, 4HBr, $^3J_{HH}$=8 Hz), 7.22 (s, 4H), 7.19 (d, 4H, $^3J_{HH}$=8 Hz); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=134.8, 134.5, 132.9, 132.5, 131.6, 121.7; elemental analysis (%) calcd for $C_{18}H_{12}Br_2S_2$: C 47.81, H 2.67, S 14.18; found: C 47.45, H 2.89, S 14.55; MS (FAB+) *m*/*z* (%): 452 (64, $M^+$), 184 (100).

*4.2.1.11. 1,4-(4-Bromophenylthio)(phenylthio)benzene (**2bph**).* *b*=0.32, *i*=109, *c*=5, *t*=1, *h*=4, $R_f$=0.51. Yield: 84%; mp: 60 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=7.47–7.30 (several m, 11H), 7.17 (m, 2H); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=136.2, 134.9, 134.6, 133.5, 132.4, 131.9, 131.8, 130.9, 129.4, 127.7, 121.3; elemental analysis (%) calcd for $C_{18}H_{13}BrS_2$: C 57.91, H 3.51, S 17.18; found: C 57.87, H 3.47, S 16.92; MS (FAB+) *m*/*z* (%): 374 (100, $M^+$).

*4.2.1.12. 2,4-Bis(4-bromophenylthio)-1,3,5-trimethylbenzene (**2bpM**).* *b*=4, *i*=50, *c*=5, *t*=1, *h*=3, $R_f$=0.76. Yield: 72%; mp: 133 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.27 (d, 4HBr, $^3J_{HH}$=8 Hz), 7.21 (s, 1H), 6.75 (d, 4HBr, $^3J_{HH}$=8 Hz), 2.59 (s, 3H), 2.42 (s, 6H); $^{13}C\{^1H\}$ APT NMR (100.64 MHz, $CDCl_3$): $\delta$=149.5, 145.8, 137.2, 132.1, 131.2, 129.3, 127.2, 118.5, 22.3, 20.8; elemental analysis (%) calcd for $C_{21}H_{18}Br_2S_2$: C 51.03, H 3.67, S 12.97; found: C 51.24, H 3.52, S 12.61; MS (FAB+) *m*/*z* (%): 493.8 (65, $M^+$), 257 (90), 225 (86), 108 (100).

*4.2.1.13. 1,4-Bis(4-(2-bromophenylthio)phenylthio)benzene (**4bo**).* *b*=0.54, *i*=50, *c*=6, *t*=1, *h*=1.5, $R_f$=0.30. Yield: 98%; mp: 92 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.54 (d, 2H, $^3J_{HH}$=9 Hz), 7.31–7.25 (m, 12H), 7.15 (td, 2H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=1.2 Hz), 7.04 (m, 4H); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=137.7, 135.9, 134.4, 133.3, 132.6, 132.1, 131.5, 130.9, 128.0, 128.0, 124.2; elemental analysis (%) calcd for $C_{30}H_{20}Br_2S_4$: C 53.90, H 3.02, S 19.19; found: C 54.11, H 3.12, S 19.05; MS (EI) *m*/*z* (%): 667.9 (75, $M^+$), 184 (100).

*4.2.1.14. 1,4-Bis(4-(4-bromophenylthio)phenylthio)benzene (**4bp**).* *b*=0.90, *i*=50, *c*=4, *t*=1 (60 °C). The solid resulting after removing the reaction solvent was washed with $H_2O$ (3×10 mL), $Et_2O$ (3×5 mL), and $CH_2Cl_2$ (20 mL). The low solubility of **4bp** prevented recording of its NMR spectra. Yield: 67%; mp: 202 °C;[33] MS (EI) *m*/*z* (%): 667.9 (75, $M^+$), 184 (100).

*4.2.1.15. 1,4-Bis(4-(4-(2-bromophenylthio)phenylthio)phenylthio)-benzene (**6bo**).* *b*=0.4, *i*=50, *c*=5, *t*=1, *h*=1, $R_f$=0.45. Yield: 57%; mp: 135 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.57 (d, 2H, $^3J_{HH}$=8 Hz), 7.36–7.25 (m, 20H), 7.18 (t, 2H, $^3J_{HH}$=7 Hz), 7.05 (m, 4H); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=137.7, 136.1, 135.1, 134.6, 134.1, 133.3, 132.5, 132.2, 131.9, 131.7, 131.4, 130.9, 128.0, 128.0, 124.2; elemental analysis (%) calcd for $C_{42}H_{28}Br_2S_6$: C 57.01, H 3.19, S 21.74; found: C 57.36, H 3.38, S 21.65; MS (EI) *m*/*z* (%): 884 (10, $M^+$), 184 (100).

*4.2.2. From benzene-1,4-dithiol*

To a suspension of benzene-1,4-dithiol (36 mg, 0.25 mmol) and $K_2CO_3$ (138 mg, 1 mmol) in $^i$PrOH (5 mL) were added the corresponding iodoanisole (0.5 mmol), dppf (28 mg, 0.05 mmol), $Pd(dba)_2$ (29 mg, 0.05 mmol), CuI (5 mg, 0.025 mmol), and ethylene glycol (0.06 mL, 1 mmol). The suspension was stirred at 100 °C during 3 days, the solvent was evaporated, and the residue was extracted with $Et_2O$ (3×5 mL). This solution was concentrated (2 mL) and purified by preparative TLC ($CH_2Cl_2$/hexane 1:2). The appropriate band was extracted with acetone, the solution was stirred with $MgSO_4$, filtered, and the filtrate concentrated to dryness to give the thioethers as colorless solids. The $R_f$ value is given below for each compound.

*4.2.2.1. 1,4-Bis(4-methoxyphenylthio)benzene (**2pm**).* $R_f$=0.20. Yield: 79%; mp: 87 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.36 (d, 4H, $^3J_{HH}$=9 Hz), 7.04 (s, 4H), 6.86 (d, 4H, $^3J_{HH}$=9 Hz), 3.79 (s, 6H); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=160.1, 136.4, 135.4, 129.3, 124.7, 115.3, 55.6; elemental analysis (%) calcd for $C_{20}H_{18}O_2S_2$: C 67.76, H 5.12, S 18.09; found: C 67.77, H 5.30, S 17.94; MS (FAB+) *m*/*z* (%): 354 (100, $M^+$).

*4.2.2.2. 1,4-Bis(4-(methylthio)phenylthio)benzene (**2pt**).* $R_f$=0.15. Yield: 67%; mp: 122 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.29 (d, 4H, $^3J_{HH}$=8 Hz), 7.18 (d, 4H, $^3J_{HH}$=9 Hz), 7.15 (s, 4H), 2.47 (s, 6H); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=138.7, 135.3, 132.6, 130.8, 130.5, 127.2, 15.7; elemental analysis (%) calcd for $C_{20}H_{18}S_4$: C 62.13, H 4.69, S 33.18; found: C 61.82, H 4.82, S 33.00; MS (FAB+) *m*/*z* (%): 386 (100, $M^+$), 231 (60).

### 4.3. General method for the bromo by iodo exchange

A Schlenk tube was charged successively with CuI (*x* (=7–80) mol %), NaI (200 mol % for monobromides or 264 mol % for dibromides), the thioether (th (=0.19–2) mmol), dmcd (2*x* mol %), and 1,4-dioxane (5 mL) and the reaction mixture was stirred at 140 °C for 2 days. The solvent was removed under vacuum, the residue extracted with $Et_2O$ (3×5 mL), and filtered. The filtrate was concentrated to dryness and the residue purified by preparative TLC ($CH_2Cl_2$/hexane 1:*h*). The appropriate band was extracted with acetone, the solution was stirred with $MgSO_4$, filtered, and the filtrate concentrated to dryness to give the thioether as a colorless (the nitro derivatives are yellow) solid (only **1iph** is liquid). The *x*, *h* and $R_f$ values are given below for each compound.

*4.3.1. (4-Iodophenyl)methylthioether*

*x*=8, th=2, *h*=3, $R_f$=0.52. Yield: 82%; mp: 30 °C (37–38 °C);[40] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=7.57 (d, 2H, $^3J_{HH}$=8 Hz), 6.96 (d, 2H, $^3J_{HH}$=8 Hz), 2.46 (s, 3H); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=138.3, 137.2, 127.7, 89.7, 15.5; elemental analysis (%) calcd for $C_7H_7IS$: C 33.60, H 2.80, S 12.80; found: C 33.84, H 2.81, S 13.10; MS (FAB+) *m*/*z* (%): 249.9 (100, $M^+$).

*4.3.2. (2-Iodophenyl)(phenyl)thioether (**1ioh**)*

*x*=20, th=1.89, *h*=2, $R_f$=0.75. Yield: 85%; mp: 49 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.75 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.39–7.24 (m, 5H), 7.09 (td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 6.90 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 6.77 (td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=142.0, 139.4, 133.6, 132.9, 129.4, 129.1, 128.5, 128.1, 127.2, 99.3; elemental analysis (%) calcd for $C_{12}H_9IS$: C 46.17, H 2.91, S 10.27; found: C 46.51, H 2.75, S 10.28; MS (FAB+) *m*/*z* (%): 312 (100, $M^+$).

*4.3.3. (2-Iodophenyl)(4-methoxyphenyl)thioether (**1iom**)*

*x*=20, th=1.69, *h*=3, $R_f$=0.40. Yield: 69%; mp: 65 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.72 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.42 (d, 2H, $^3J_{HH}$=9 Hz), 7.08 (td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 6.90 (d, 2H, $^3J_{HH}$=9 Hz), 6.73 (td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 6.64 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 3.78 (s, 3H); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=160.4, 144.2, 139.1, 136.5, 128.8, 126.8, 126.2, 123.0, 115.2, 96.1, 55.4; elemental analysis (%) calcd for $C_{13}H_{11}IOS$: C 45.63, H 3.24, S 9.37; found: C 45.80, H 3.19, S 9.40; MS (FAB+) *m*/*z* (%): 342 (100, $M^+$).

*4.3.4. (2-Iodophenyl)(4-nitrophenyl)thioether (**1ion**)*

*x*=20, th=1.61, *h*=2, $R_f$=0.25. Yield: 75%; mp: 105 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=8.08 (d, 2H, $^3J_{HH}$=12 Hz), 7.99 (dd, 1H,

$^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.59 (dd, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.41(td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz), 7.17 (d, 2H, $^3J_{HH}$=12 Hz), 7.11 (td, 1H, $^3J_{HH}$=8 Hz, $^4J_{HH}$=2 Hz); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=146.3, 145.5, 140.7, 136.0, 135.4, 130.8, 129.6, 127.2, 124.2, 106.7; elemental analysis (%) calcd for $C_{12}H_8INO_2S$: C 40.35, H 2.26, N 3.92, S 8.98; found: C 40.74, H 2.19, N 3.89, S 8.76; MS (FAB+) *m*/*z* (%): 663 (100), 647 (48), 358 (25, $M^+$), 154 (46), 136 (38).

*4.3.5. (4-Iodophenyl)(phenyl)thioether (**1iph**)*

*x*=15, th=0.75, *h*=2, $R_f$=0.75. Yield: 75%; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=7.56 (d, 2HI, $^3J_{HH}$=9 Hz), 7.38–7.20 (m, 5H), 6.99 (d, 2H, $^3J_{HH}$=9 Hz); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=138.2, 136.6, 134.6, 132.1, 131.8, 129.4, 127.7, 92.0; elemental analysis (%) calcd for $C_{12}H_9IS$: C 46.17, H 2.91, S 10.27; found: C 46.09, H 2.96, S 10.19; MS (FAB+) *m*/*z* (%): 312 (100, $M^+$), 235 (54), 184 (54).

*4.3.6. 1,4-Bis(4-iodophenylthio)benzene (**2ip**)*

*x*=31, th=1.3. Due to the low solubility of **2ip** the solid resulting after removing the reaction solvent was washed with $H_2O$ (3×10 mL), $Et_2O$ (3×5 mL), and $CH_2Cl_2$ (20 mL). Yield: 75%; mp: 184 °C; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=7.63 (d, 4H, $^3J_{HH}$=8 Hz), 7.24 (s, 4H), 7.06 (d, 4H, $^3J_{HH}$=8 Hz); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=138.5, 135.5, 134.7, 132.9, 131.8, 92.8; elemental analysis (%) calcd for $C_{18}H_{12}I_2S_2$: C 39.58, H 2.21, S 11.74; found: C 39.71, H 2.21, S 11.71; MS (EI) *m*/*z* (%): 546 (100, $M^+$), 184 (70).

*4.3.7. 2,4-Bis(4-iodophenylthio)-1,3,5-trimethylbenzene (**2ipM**)*

*x*=17, th=0.36, *h*=3, $R_f$=0.70. Yield: 87%; mp: 137 °C; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=7.47 (d, 4H, $^3J_{HH}$=8 Hz), 7.22 (s, 1H), 6.64 (d, 4H, $^3J_{HH}$=8 Hz), 2.58 (s, 3H), 2.42 (s, 6H); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=149.4, 145.7, 138.1, 137.9, 131.1, 129.1, 127.4, 89.1, 22.3, 20.8; elemental analysis (%) calcd for $C_{21}H_{18}I_2S_2$: C 42.87, H 3.08, S 10.90; found: C 43.26, H 3.13, S 10.84; MS (EI) *m*/*z* (%): 587.8 (100, $M^+$), 257 (64), 225 (87).

*4.3.8. 1,4-Bis(4-(4-iodophenylthio)phenylthio)benzene (**4ip**)*

*x*=42, th=0.19. The solid resulting after removing the reaction solvent was washed with $H_2O$ (3×10 mL), $Et_2O$ (3×5 mL), and $CH_2Cl_2$ (20 mL). The low solubility of **4ip** prevented recording of its NMR spectra. Yield: 75%; mp: 203 °C;[33] MS (EI) *m*/*z* (%): 762 (100, $M^+$), 184 (100).

*4.3.9. (4-(4-Nitrophenylthio)phenylthio)(4-(4-iodophenylthio)phenylthio)benzene (**4ipn**)*

*x*=40, th=0.24, *h*=0.75, $R_f$=0.30. Yield: 49%; mp: 148 °C; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=8.09 (d, 2H, $^3J_{HH}$=9 Hz), 7.62 (d, 2H, $^3J_{HH}$=8 Hz), 7.41 (d, 2H, $^3J_{HH}$=8 Hz), 7.35 (d, 2H, $^3J_{HH}$=8 Hz), 7.31–7.26 (m, 8H), 7.19 (d, 2H, $^3J_{HH}$=9 Hz), 7.07 (d, 2H, $^3J_{HH}$=8 Hz); $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): $\delta$=148.0, 139.3, 138.5, 136.5, 135.3, 135.2, 133.9, 133.4, 133.1, 132.4, 131.6, 131.4, 130.6, 128.8, 127.1, 124.3, 93.0. Due to the low solubility of **4ipn**, an analytically pure sample could not be obtained; MS (EI) *m*/*z* (%): 681 (38, $M^+$), 184 (100).

### 4.4. General method for the synthesis of sulfoxides

A suspension of the thioether (th (=0.09–0.22 mmol)) and dichloroiodobenzene (*d* (=100–400 mol %)) in pyridine/$H_2O$ (9:1 v/v, 5 mL) is stirred at room temperature during 15 min. $CHCl_3$ (10 mL) and $H_2SO_4$ (aq), to extract pyridine, were added. The organic phase was washed with $H_2O$, dried with anhydrous $MgSO_4$, filtered, and the solvent evaporated. $Et_2O$ (5 mL) was added, the suspension filtrated, and the solid washed with $Et_2O$ (3×5 mL) to give the sulfoxide as a colorless solid. The th and *d* values are given below for each compound.

*4.4.1. 4,4′-(Bromo)(methoxy)diphenylsulfoxide (**1bpmO**)*

th=0.15, *d*=100. Yield: 79%; mp: 91 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.58 (d, 2H, $^3J_{HH}$=8 Hz), 7.55 (d, 2H, $^3J_{HH}$=8 Hz), 7.47 (d, 2H, $^3J_{HH}$=8 Hz), 6.96 (d, 2H, $^3J_{HH}$=8 Hz), 3.82 (s); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=162.3, 145.1, 136.4, 132.4, 127.3, 126.2, 125.2, 115.0, 55.6; elemental analysis (%) calcd for $C_{13}H_{11}BrO_2S$: C 50.18, H 3.54, S 10.29; found: C 50.32, H 3.67, S 10.17; MS (EI) *m*/*z* (%): 310.9 (95, $M^+$), 296 (51).

*4.4.2. 1,4-Bis(4-iodophenylsulfinyl)benzene (**2ipO**)*

th=0.45, *d*=204. Yield: 79%; mp: 254 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.81 (d, 4H, $^3J_{HH}$=8 Hz), 7.72 (s, 4H), 7.35 (d, 4H, $^3J_{HH}$=8 Hz); $^{13}C\{^1H\}$ APT NMR (100.64 MHz, $CDCl_3$): $\delta$=148.84, 148.81, 144.81, 144.78, 138.78, 126.25, 126.23, 125.60, 125.57, 98.35; elemental analysis (%) calcd for $C_{18}H_{12}I_2O_2S_2$: C 37.39, H 2.09, S 11.09; found: C 36.99, H 2.10, S 10.74; MS (EI) *m*/*z* (%): 578 (15, $M^+$), 235 (73), 108 (70), 76 (100).

*4.4.3. 4,4′-(4-Bromophenylsulfinyl)(4-nitrophenylsulfinyl)-diphenylsulfoxide (**3bpnO**)*

th=0.33, *d*=300. Yield: 73%; mp: 174 °C; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=8.34 (d, 2H, $^3J_{HH}$=8 Hz), 7.83 (d, 2H, $^3J_{HH}$=8 Hz), 7.77 (m, 8H), 7.61 (d, 2H, $^3J_{HH}$=8 Hz), 7.49 (d, 2H, $^3J_{HH}$=8 Hz); $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): $\delta$=151.83, 149.62, 149.25, 149.17, 149.14, 148.23, 148.16, 143.70, 132.91, 126.37, 126.35, 126.24, 126.22, 126.20, 125.83, 125.78, 125.76, 125.74, 125.60, 125.34, 125.32, 124.80; elemental analysis (%) calcd for $C_{24}H_{16}BrNO_5S_3$: C 50.18, H 2.79, N 2.44, S 16.73; found: C 50.49, H 2.71, N 2.44, S 16.96; MS (EI) *m*/*z* (%): 573.9 (40, $M^+$).

*4.4.4. 1,4-Bis(4-(4-bromophenylsulfinyl)phenylsulfinyl)-benzene (**4bpO**)*

th=0.09, *d*=400. Yield: 61%; mp: 275 °C; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=7.72 (br s, 12H), 7.65 (d, 4H, $^3J_{HH}$=9 Hz), 7.49 (d, 4H, $^3J_{HH}$=9 Hz); $^{13}C\{^1H\}$ APT NMR (100.64 MHz, $CDCl_3$): $\delta$=149.32, 149.26, 148.80, 148.72, 148.26, 148.24, 143.86, 133.10, 126.32, 126.29, 125.87, 125.84, 125.79, 125.74, 125.69, 125.66; elemental analysis (%) calcd for $C_{30}H_{20}Br_2O_4S_4$: C 49.19, H 2.74, S 17.49; found: C 48.83, H 2.96, S 17.48; MS (EI) *m*/*z* (%): 731.8 (20, $M^+$), 699.8 (40), 667.7 (30), 183.8 (100).

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## Supplementary data

IR, $^1H$, and $^{13}C$ NMR spectra of new compounds. Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.tet.2008.04.108.

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