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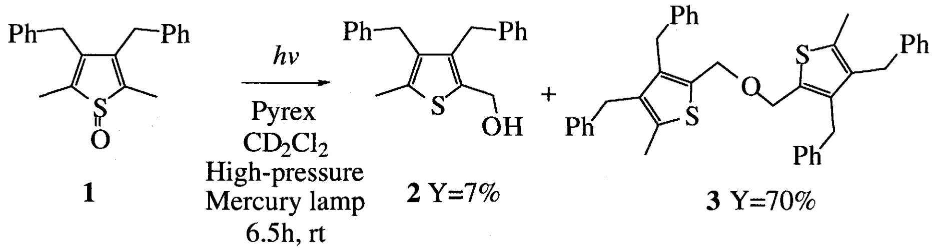
STUDIES TOWARDS DIBENZOTHIOPHENE-*S*-OXIDE ARRAYS AND THEIR PHOTOCHEMICAL REACTIVITY

Thies THIEMANN, Kazuya KUMAZOE,[a] Kazuya ARIMA,[a] Shuntaro MATAKA

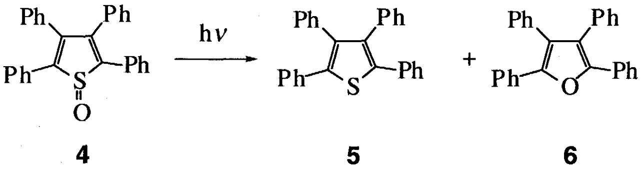
A novel access to oligo(dibenzothiophenes) is described. Here, the trimethylsilyl-group is used both as positional protective group and as a directive group which can be exchanged. The reagents benzyltrimethylammonium tribromide (BTMABr$_3$) and benzyltrimethylammonium iododichloride (BTMAICl$_2$) are used for the first time in silyl-halo exchange reactions. The dimeric, trimeric and tetrameric dibenzothiophene building blocks are prepared by Suzuki-Kumada C-C coupling reactions. Exemplary oxygenations of these building blocks to the corresponding dibenzothiophene-*S*-oxides is shown.

Introduction

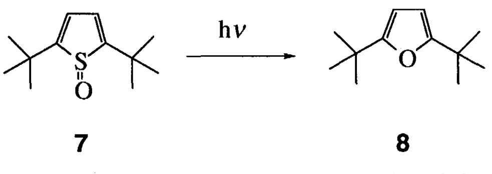
Thiophene-*S*-oxides have been known to have cytotoxic activity.[1] It is believed that gradual loss of oxygen in these molecules may contribute to their biochemical activity.[2] On the other hand it has been found that the deoxygenation of thiophene-*S*-oxides can be accelerated by photoirradiation of the molecules.[2] Depending on the substitution pattern of the thiophene-*S*-oxides, photoirradiation can also lead to hydroxylation of alkyl (*i.e.*, methyl) groups in positions C-2 or C-5 of the thiophene-unit (Scheme 1).[2,3] In the case of substituents at C-2 and/or C-5 that possess a proton at the carbon *α* to the linkage with the thiophene-unit, *e.g.* as in the case of a *tert*-butyl group, the oxygen is included into the heterocyclic ring system and thiophene-*S*-oxides are transformed into furans (Schemes 2 and 3).[4] A good knowledge of the photochemical stability of thiophene-*S*-oxides may be of value as these molecules themselves have been forwarded as subunits in organic oligomers and polymers with low optical energy gaps.[5] Foremost, the mechanisms operating in the different photochemical transformations of the thiophene-*S*-oxides need clarification. Two possible mechanisms for the deoxygenation of the thiophene-*S*-oxides would involve a.) an oxenoid species in a monomolecular reaction or b.) the evolution of oxygen, either in the singlet or triplet



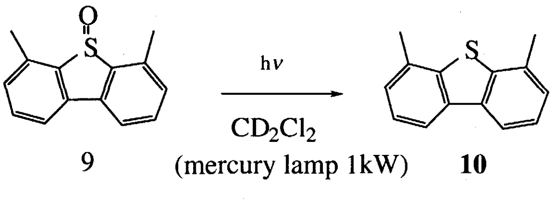
Scheme 1



Scheme 2



Scheme 3



Scheme 4

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Dedicated to Professor Yukio Nishimura on the occasion of his retirement

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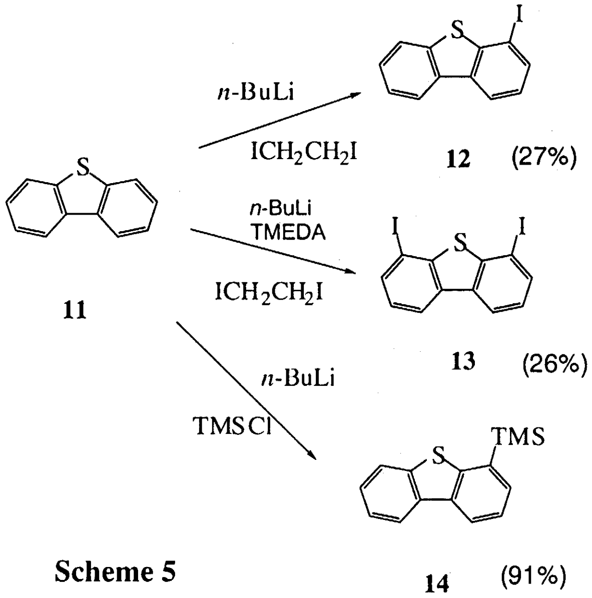
state, from an excited thiophene-*S*-oxide dimer.[6,7] While the hydroxyl-ation of the methyl group of methyl substituted thiophene-*S*-oxides indicated that either an oxenoid species or singlet oxygen might be involved, the inability of the liberated oxygen species to hydroxylate one of the methyl groups in the 4,6-dimethyl-dibenzothiophene-*S*-oxide (**9**)[8] seemed to exclude the involvement of atomic oxygen at least in the case of the irradiation of **9** (Scheme 4).

Thus, it is of interest to suppress the dimer formation of the thiophene-*S*-oxides by steric hinderance either by placing a sterically demanding substituent at the C2 and/or C5-position(s) or by enlargening the molecule as such. This way it would be possible to assess whether dimer-formation is necessary for the progression of the simple deoxygenation process. That thiophene-*S*-oxides which cannot readily form dimers may follow other pathways in the photochemical transformation can be seen in the photoirradiation of 2,5-diphenylthiophene-*S*-oxide (**4**), where a mixture of 2,5-diphenylthiophene (**5**) and 2,5-diphenylfuran (**6**) is produced (Scheme 2).[2,8] The sterically more congested 2,5-*tert*-butylthiophene-*S*-oxide (**7**) gives the corresponding furan **8** even exclusively (Scheme 3).[2,8]

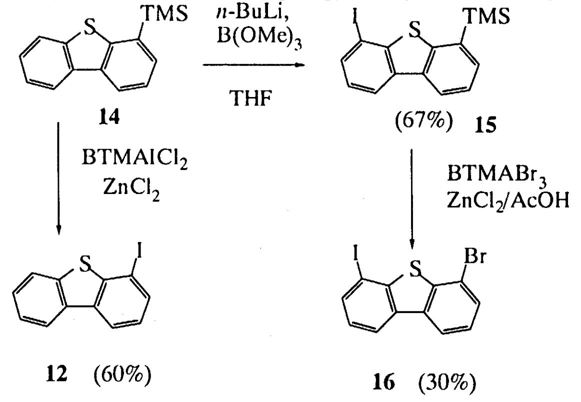
In the following, the preparation of dibenzothiophene-dimers, trimers and tetramers as a starting point for arrays of dibenzothiophene-*S*-oxides and an examplary study of the photochemical behaviour of a bis(dibenzothiophene-*S*-oxide) are presented. The arrays have been prepared to more closely study the photochemistry, *i.e.*, the photodeoxygenation of dibenzothiophene-*S*-oxides. The results may be helpful to acquire additional insights in the mechanisms governing the photochemical behaviour of thiophene-*S*-oxides themselves. Furthermore, oligodibenzothiophene-*S*-oxides may provide materials with interesting electro-optical properties.

Results and Discussion

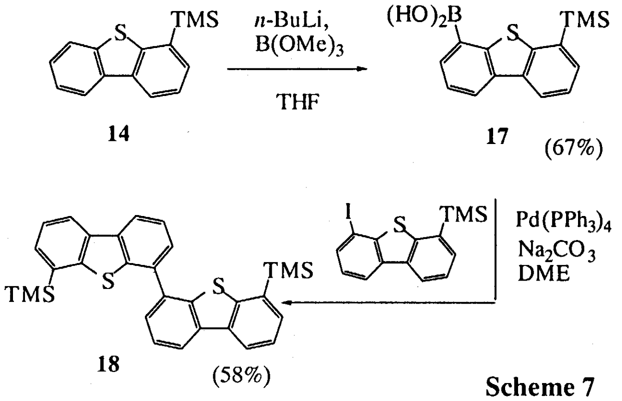


Scheme 5

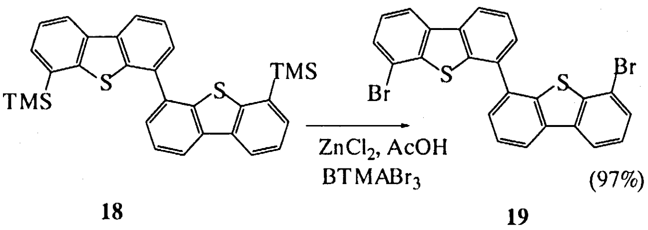
The preparation of arrays of dibenzothiophenes necessitates C-C coupling between dibenzothiophenes. As there are a number of C-C bond forming (cross-coupling) reactions known involving aryl halides and aryl boronic acids (Suzuki-Kumada Coupling) or aryl stannanes (Stille coupling), a versatile access to halogenated dibenzothiophenes was needed. Lithiation of dibenzothiophene with *n*-BuLi in THF proceeds at C-4. Reaction of the lithiated species with 1,2-diiodoethane leads to 4-iododibenzothiophene (**12**) (Scheme 5). A lithiation of dibenzothiophene can be achieved selectively at C-4 and C-6 with an excess of *n*-BuLi/TMEDA in THF. Reaction of this dilithiated species with 1,2-diiodoethane yields 4,6-diiododibenzo-thiophene (**13**), albeit in very moderate yield (Scheme 5). The mono-lithiated product can also be reacted with chlorotrimethylsilane to yield 4-trimethylsilyldibenzothiophene (**14**) (Scheme 5).[9] This is of interest as the trimethylsilyl group at C-4 can serve either as a positional protective group or as a directive, exchangeable functionality. Thus, as an example of the first case, 4-trimethylsilyldibenzothiophene (**14**) itself



Scheme 6

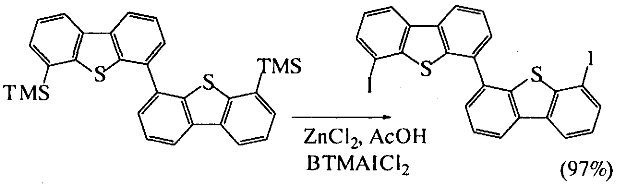


Scheme 7



Scheme 8

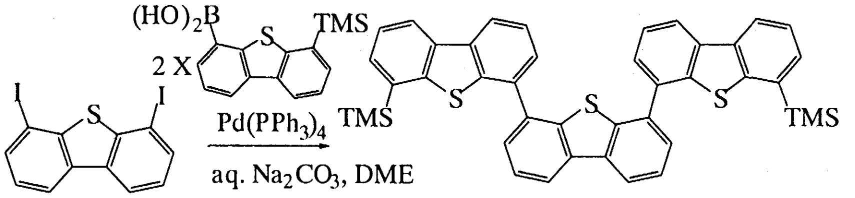
can be lithiated at C-6 and easily reacted with 1,2-diiodoethane to yield 4-iodo-6-trimethyl-silyldibenzothiophene (**15**) (Scheme 6). As an example of the second case, 4-trimethylsilyldibenzothiophene (**14**) can be reacted with benzyl trimethylammonium iododichloride (BTMAICl$_2$)[10] in an iodo-silyl exchange to give the 4-iododibenzothiophene (**12**) (Scheme 6). Alternatively, the same reaction with benzyltrimethylammonium tribromide gives the analogous 4-bromo-derivative. Interestingly, the direct bromination of a (substituted) dibenzothiophene with benzyltrimethylammonium tribromide leads to a different regioisomer, namely to the corresponding 3-bromo derivative. Thus, it is also possible to selectively produce different regioisomers of 'mixed' dihalogenated dibenzothiophenes. Reaction of 4-iodo-6-trimethylsilyldibenzothiophene (**15**) with benzyltrimethylammonium tribromide (BTMABr$_3$) leads via iodo-trimethylsilyl exchange to the 6-bromo-4-iododibenzothiophene, while the reaction of 4-iododibenzothiophene (**12**) with BTMABr$_3$ leads to 7-bromo-4-iododibenzothiophene.[11]



18 **20**

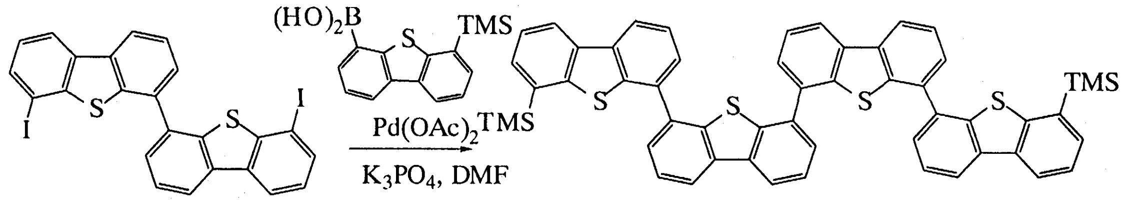
Scheme 9

When 4-trimethylsilyldibenzothiophene (**14**) is lithiated (*n*-BuLi, THF) it can be reacted with trimethylborate to give upon acidic work-up 4-trimethylsilyldibenzothiophene 6-boronic acid (**17**) (Scheme 7). **17** can be reacted with 4-iodo-6-trimethylsilyldibenzothiophene (**15**) under normal Suzuki-Kumada conditions [2M aq. Na$_2$CO$_3$, DME, Pd(PPh$_3$)$_4$][12,13] to furnish 6,6'-bis-(trimethylsilyl)-4,4'-bis(dibenzothiophene) (**18**) (Scheme 7). This, in turn, can undergo silyl-halo exchange with either BTMABr$_3$ to yield the brominated dimer **19** or with BTMAICl$_2$ to give the iodinated dimer **20**. Further coupling reactions of these dihalogenated bis(dibenzothiophenes) to higher homologues is hindered by the low solubility of the starting material in the reaction solvent. Here, the use of DMF as the solvent is beneficial and other reaction conditions [K$_3$PO$_4$, Pd(OAc)$_2$][14] provide better results and the tetramer **22** could be prepared (Scheme 11). In an analogous way the trimer **21** was prepared from 4,6-diiododibenzothiophene (**13**) (Scheme 10). Here, however, the 4,6-diiododibenzothiophene (**13**) (as opposed to the diiodinated dimer **20**) showed sufficient solubility in DME for the reaction to proceed under the normal Suzuki-Kumada conditions [2M aq. Na$_2$CO$_3$, DME, Pd(PPh$_3$)$_4$] (Scheme 10).



13 **21**

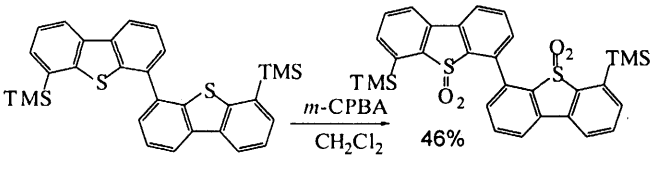
Scheme 10



13 **22**

Scheme 11

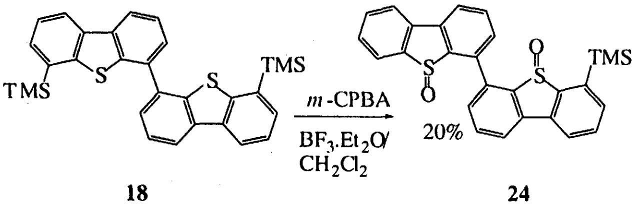
A number of methods are known for the oxidation of dibenzothiophenes to the corresponding sulfoxides. When bis(trimethylsilyldibenzothiophene) **18** was treated with *m*-CPBA, only the bis(trimethylsilyldibenzothiophene-*S*,*S*-dioxide) (**23**) could be isolated (Scheme 12). On the other hand the use of *m*-CPBA in the presence of the Lewis acid BF$_3$·Et$_2$O yields the mono-silylated bis(dibenzothiophene *S*-oxide) **24** (Scheme 13). This partial desilylation of the starting material is very likely due to the presence of BF$_{4-}$ and F$^-$ in the reaction mixture.[15]



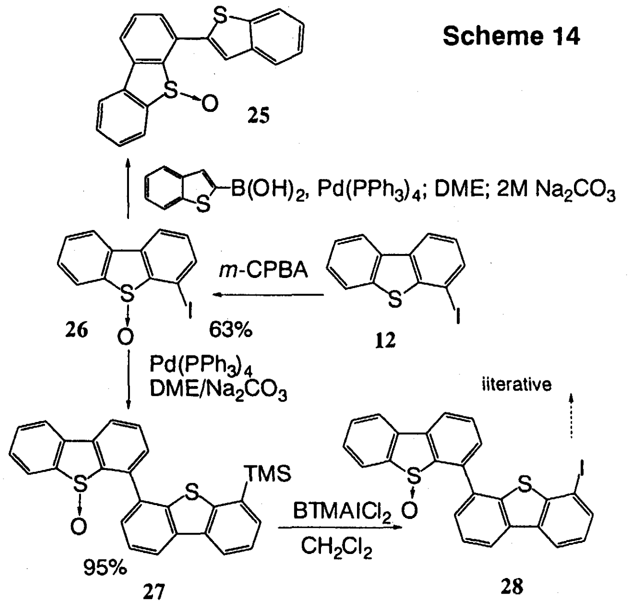
18 **23**

Scheme 12

The authors feel that the problems in the coupling of larger dibenzothiophene-arrays due to the low solubility of the starting material and the problems encountered in the selective oxidation of individual dibenzothiophene-units in the arrays can be circumvented by following an alternative approach. Here, the dibenzothiophene-*S*-oxide (i.e., **26**) itself as a mono-subunit is subjected to a coupling reaction with the trimethylsilyl substituted dibenzothiopheneboronic acid **17**. Facultatively, after halo-silyl exchange this process can be repeated (Scheme 14). Potentially, other types of silyl substituted aryl/hetarylboronic acids can be used in these reactions. This leads to the possibility of preparing both arrays with neighboring dibenzothiophene-*S*-oxide units and arrays with alternating units of dibenzothiophene and dibenzothiophene-*S*-oxide. The Suzuki-Kumada coupling of dibenzothiophene-*S*-oxides is a general reaction as evidenced by a second coupling with a benzothiopheneboronic acid (i.e., to **25**) (Scheme 14). The dibenzothiophene-*S*-oxide is not deoxygenated by the process. This is similar to the C-C-coupling via Stille-reaction that has been carried out on a bromobenzothiophene-*S*-oxide – in that case, however, the halo-aryl exchange was accompanied by a 1,2-transposition.[16]

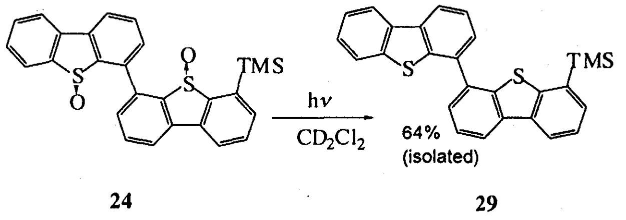


Scheme 13



Scheme 14

If it is true that one main pathway of the deoxygenation process of dibenzothiophene-*S*-oxides proceeds via the formation of an excited dimer species (of dibenzothiophene-*S*-oxides), it may be possible to control the release of oxygen by the number of adjacent dibenzothiophene-*S*-oxide units in an array. To better understand the possible contribution of adjacent dibenzothiophene-*S*-oxide units to the photodeoxygenation, an exact analysis of the distribution of different conformers in such arrays still needs to be carried out. It is supposed that the intermolecular dimer formation in larger arrays becomes increasingly difficult with the size and the complexity of these molecules, especially when these molecules themselves are included within polymeric material. The possibility of using monomeric dibenzothiophene-*S*-oxide in the photochemical hydroxylation of side chains in 'finished' polymers has already been demonstrated recently.[17] The inclusion of dibenzothiophene-*S*-oxide arrays in such polymeric material may lead to a better control of the oxygen release and to a better control of the hydroxylation of such materials.



Scheme 15

The photoirradiation itself of the dimers, such as **24**, leads to the deoxygenated product after 19 h (completion of the reaction). No dibenzofuran could be observed. After 1h the turnover of the reaction was minimal (Scheme 15). Thus, viewed in a qualitative manner, the photodeoxygenation of this dibenzothiophene-*S*-oxide is slower than the photodeoxygenation of the monomeric diebenzothiophene-*S*-oxide. The study of the kinetics of this reaction is underway. Moreover, the use of dibenzothiophene-*S*-oxides and thiophene-*S*-oxides - either as single molecules or in arrays – as photochemical oxidants in the preparation of conducting polymers is under development.[18]

Experimental

General. IR spectra were recorded on a JASCO IR-700 spectrometer (KBr pellets or NaCl plates [designated as *neat*). ^{1}H NMR spectra were measured on a JEOL EX-270 (270 MHz), a JEOL JNM-LA 395 (400 MHz), and a JEOL JNM-LA 600 (600 MHz) spectrometer. ^{13}C NMR spectra were measured on a JEOL EX-270 (67.9 MHz), a JEOL 395 (100.4 MHz) and a JEOL JNM-LA 600 (150.8 MHz) spectrometer. Assignments of ^{13}C signals were aided by DEPT (= Distortionless Enhancement by Polarisation Transfer) measurements; (+) denotes primary and tertiary, (-) secondary, and (C_{quat}) quaternary carbon atoms; Mass spectra were taken on a JEOL-01-SG-2 machine at 70 eV using a direct inlet system. Wakogel C-300 was used as silica gel in all column chromatographic separations. Analytical thin layer chromatography (TLC) was carried out on TLC aluminum sheets (silica gel 60 F_{254}, Merck).

Dibenzothiophene (Acros), 1,2-diiodomethane (TCI), trimethylborate (Kishida), chlorotrimethylsilane (Aldrich), *n*-BuLi (Kanto Chemicals) and *tert*-BuLi (Kanto Chemicals) were commercially available. Benzyltrimethylammonium tribromide (BTMABr$_3$) and benzyl trimethylammonium iododichloride (BTMAICl$_2$) were prepared according to literature procedures.

4-Iododibenzothiophene (12).- *Route A.* To dibenzothiophene (**11**) (4.5 g, 24.4 mmol) in THF, cooled to –78°C, was added gradually *n*-BuLi (2.6M, 10.3 mL, 26.8 mmol). Thereafter, the solution was warmed to rt and stirred for 3h. Later the reaction mixture was cooled again to –78°C and 1,2-diiodoethane (8.25 g, 29.3 mmol) was added slowly. The reaction was warmed to rt and stirred for 14h at rt. The reaction mixture was poured into sat. aq. $Na_2S_2O_3$ (10 mL) and the product was extracted with CH_2Cl_2 (10 mL). The organic phase was dried over anhydrous $MgSO_4$ and subsequently the solvent was evaporated *in vacuo* to give 4-iododibenzothiophene (**12**) (2.05 g, 27%) as a colorless powder; mp 102°C; IR (KBr) ν 1540, 1432, 1381, 1099, 1021, 784, 746 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (dd, 1H, ^3J 8.0, ^3J 8.2 Hz), 7.45 (d, 2H, J 1.3 Hz), 7.81 (m, 2H), 8.04 (m, 2H). *Route B.* In an inert atmosphere $ZnCl_2$ (69 mg, 0.48 mmol) was added to a mixture of 4-trimethylsilyldibenzothiophene (**14**) (for preparation, see below) (100 mg, 0.4 mmol) and benzyltrimethylammonium iododichloride (135 mg, 0.4 mmol) in acetic acid (2 mL). The resulting mixture was stirred at 80℃ for 22h. Thereafter, the mixture was poured into water (10 mL) and the product was extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and dried over $MgSO_4$. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give **12** (72 mg, 0.38 mmol, 60%).

4,6-Diiododibenzothiopene (13). – To a mixture of dibenzothiophene (**11**) (4.0 g, 22.0 mmol) and *N,N,N'N'*-tetramethylethylenediamine (TMEDA) (5 mL) in THF (10 mL), cooled to –78℃, was added gradually tert-BuLi (2.6 M, 20 mL, 24 mmol). The resulting solution was warmed to rt and stirred for 2h. Thereafter, it was cooled to –78℃ and 1,2-diiodoethane (14.0 g, 32.0 mmol) was slowly added. The solution was warmed to rt and stirred at rt for 17h. Then the reaction mixture was poured into sat. aq. $Na_2S_2O_3$ (10 mL) and the organic material was extracted with CH_2Cl_2 (2X10 mL). The organic phase was dried over $MgSO_4$ and evaporated to give 4,6-diiododibenzo-thiophene (**13**) (2.46 g, 11.7 mmol, 26%) as a pale yellow solid; mp 140.5 – 143.9°C; IR (KBr) ν 1536, 1407, 1367, 1315, 1014, 809, 762 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.51 (dd, 2H, ^3J 7.6, ^3J 7.3Hz), 7.84 (d, 2H, ^3J 7.6 Hz), 8.08 (d, 2H, ^3J 7.3 Hz); MS (70 eV) *m/z* 435 (M$^+$-1, 100). HRMS Found: 435.8273. Calcd.: 435.8280.

4-Trimethylsilyldibenzothiophene (14). – To a solution of dibenzothiophene (**11**) (21.9 g, 116 mmol) in THF (5 mL), cooled to 78℃, was added *n*-BuLi (2.6M, 16.7 mL, 127 mmol). Thereafter, the mixture was warmed to rt and stirred for 3h. Then, the solution was cooled to –78°C and chlorotrimethylsilane (16.7 mL, 139 mmol) was added dropwise and the solution was warmed to rt and stirred for additional 5h at rt. The reaction was poured into a sat. aq. $NaHCO_3$ solution (5 mL) and the product was extracted with CH_2Cl_2 (10 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to give **14** (27.1 g, 91%) as a yellow oil, which upon standing crystallizes very slowly; IR (neat) ν 3058, 2954, 2894, 1439, 1427, 1366, 1250, 856, 838, 747 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.46 (s, 9H, $SiMe_3$), 7.37 – 8.11 (m, 7H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 0.02, 122.85, 124.56, 125.08, 125.26, 128.89, 135.72, 136.56, 136.60, 136.67, 136.75, 140.82, 146.38.

4-Bromodibenzothiophene. - In an inert atmosphere $ZnCl_2$ (690 mg, 0.48 mmol) was added to a mixture of 4-trimethylsilyldibenzothiophene (**14**) (1.0 g, 3.9 mmol) and benzyltrimethylammonium tribromide (1.53 g, 3.9 mmol) in acetic acid (15 mL). The resulting mixture was stirred at 80℃ for 5h. Thereafter, the mixture was poured into water (20 mL) and the product was extracted with CH_2Cl_2 (20 mL). The organic phase was washed with water (20 mL) and dried over $MgSO_4$. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give 4-bromodibenzothiophene (667 mg, 2.38 mmol, 61%) as a yellowish powder; mp 54.5 – 58.9℃; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.33 – 8.12 (m, 7H); MS (70 eV) 280 (^{81}BrM$^+$, 36), 278 (^{79}BrM$^+$, 35).

4-Iodo-6-trimethylsilyldibenzothiophene (15). – To 4-trimethylsilyldibenzothiophene (**14**) (1.0 g, 3.9 mmol) in dry THF (5 mL) was added gradually at –78℃ *tert*-BuLi (2.6 M, 2.3 mL, 4.7 mmol). Thereafter, the solution was warmed to rt and stirred for 2h. Then the solution was cooled to –78°C and diiodoethane (1.32 mL, 5.6 mmol) was added slowly. The resulting solution was warmed to rt and stirred at rt for 17h. Then the reaction mixture was poured into sat. aq. $Na_2S_2O_3$ (20 mL) and the product was extracted with CH_2Cl_2 (50 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to give **15** (1.0 g, 67%) as colorless crystals; IR (KBr) ν 3048, 2952, 1401, 1242, 1109, 861, 750 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.46 (s, 9H, $SiMe_3$), 6.85 (dd, 1H, ^3J 5.7, ^3J 5.4 Hz), 7.05 (dd, 1H, ^3J 5.6, ^3J 5.4 Hz), 7.22 (d, 1H, ^3J 5.5 Hz), 7.45 (d, 1H, ^3J 5.5 Hz), 8.77 (m, 2H); MS (70 eV) *m/z* (%) 382 (M$^+$, 100). HRMS Found: 381.9704. Calcd. for $C_{15}H_{15}ISiS$: 381.9708.

4-Bromo-6-iododibenzothiophene (16). - In an inert atmosphere $ZnCl_2$ (43 mg, 0.3 mmol) was added to a mixture of 4-iodo-6-trimethylsilyldibenzothiophene (**15**) (100 mg, 0.26 mmol) and benzyltrimethylammonium tribromide (102 mg, 0.26 mmol) in acetic acid (4 mL). The resulting mixture was stirred at 80°C for 5h. Thereafter, the mixture was poured into water (10 mL) and the product was extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and dried over $MgSO_4$. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give **16** (98 mg, 2.52 mmol, 97%) as a colorless powder; mp 60.4 – 62.4°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.30 – 8.20 (m, 6H); MS (70 eV) *m/z* (%) 389 (^{81}BrM$^+$, 16), 387 (^{79}BrM$^+$, 16). HRMS Found: 387.8419. Calcd. for $C_{12}H_6{}^{79}BrIS$: 387.8418.

7-Bromo-4-iododibenzothiophene. - In an inert atmosphere $ZnCl_2$ (408 mg, 2.6 mmol) was added to a mixture of 4-iododibenzothiophene (**12**) (700 mg, 2.34 mmol) and benzyltrimethylammonium tribromide (897 mg, 2.3 mmol) in acetic acid (10 mL). The resulting mixture was stirred at rt for 5h. Thereafter, the mixture was poured into water (20 mL) and the product was extracted with CH_2Cl_2 (20 mL). The organic phase was washed with water (20 mL) and dried over $MgSO_4$. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give 7-bromo-4-iododibenzothiophene (667 mg, 1.7 mmol, 74%) as yellow crystals; mp 147 – 149°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.80 (m, 2H), 8.01 (m, 2H); MS (70 eV) *m/z* (%) 389 (^{81}BrM$^+$, 21), 387 (^{79}BrM$^+$, 21). HRMS Found: 387.8418. Calcd. for $C_{12}H_6{}^{79}BrIS$: 387.8418.

4-Trimethylsilyldibenzothiophene-6-boronic acid (17). – To a cooled solution of 4-trimethylsilyldibenzothiophene (**14**) (1.0 g, 3.9 mmol) in THF (5 mL) was added at –78°C *n*-BuLi (2.6 M, 1 mL, 3.9 mmol). Thereafter, the solution was warmed to rt and stirred for 3h. Then, the solution was cooled to –78°C and trimethylborate (269 mg, 3.9 mmol) was added slowly. The resulting mixture was warmed to rt and stirred for 16 h at rt. Then, the reaction mixture was poured into 10w% aq. HCl (10 mL) and the product was extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was washed with hexane. The product was dried *in vacuo* to give **17** (96.7 mg, 2.6 mmol, 67%) as a colorless solid; mp 399°C; IR (KBr) ν 3052, 2952, 1565, 1339, 1273, 1246, 1133, 1096, 1037, 838, 730, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.46 (s, 9H, $SiMe_3$), 3.51 (br.s, 2H), 7.64 (m, 3H), 8.12 (m, 1H), 8.46 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 1.38, 121.90, 122.64, 122.91, 123.65, 124.20, 124.60, 124.94, 126.93, 132.64, 133.24, 134.66, 138.07.

6,6'-Bis(trimethylsilyl)-4,4'-bis(dibenzothiophene) (18). – Under an inert atmosphere, a mixture of 4-trimethylsilyldibenzothiophene (**14**) (26 mg, 0.067 mmol) and 4-trimethylsilyldibenzothiophene 6-boronic acid (**17**) (20 mg, 0.067 mmol), $Pd(PPh_3)_4$ (2.0 mg, 1.10^{-3} mmol) and aq. 2.3 M Na_2CO_3 (0.2 mL) in DME (1 mL) was heated under reflux for 24 h. Thereafter, the solution was poured into water (5 mL) and extracted with CH_2Cl_2 (10 mL). The resulting organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: hexane) to give **18** (20 mg, 0.04 mmol, 58%) as colorless crystals; mp 100.2 – 102.0°C; IR (KBr) ν 3052, 2950, 1566, 1248, 1037, 838, 750, 618 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.38 (s, 18H, 2 $SiMe_3$), 7.60 – 7.86 (m, 8H), 8.31 – 8.45 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 122.19, 122.92, 123.09, 124.38, 125.25, 125.44, 127.32, 127.43, 133.30, 134.57, 135.31, 136.70; MS (70 eV) *m/z* 510 (M$^+$, 100). HRMS Found: 510.1328. Calcd. for $C_{30}H_{30}Si_2S_2$: 510.1327.

6,6'-Dibromo-4,4'-bis(dibenzothiophene) (19). – To a mixture of 6,6'-bis(trimethylsilyl)-4,4'-bis(dibenzothiophene) (**18**) (73.0 mg, 0.14 mmol) and $BTMABr_3$ (134 mg, 0.28 mmol) in acetic acid (6 mL) was added in an inert atmosphere $ZnCl_2$ (23 mg, 0.34 mmol) and the resulting reaction mixture was stirred at 80°C for 13 h. Thereafter, the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic phase was washed with water (20 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was washed with ether (10 mL). The product was dried *in vacuo* to give **19** (72 mg, 0.14 mmol, 97%) as a brownish powder; mp 119 –120°C; IR (KBr) ν 3054, 1545, 1436, 1025, 774, 701 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.33 – 8.12 (m, 6H), 8.52 – 8.82 (m, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 117.54, 121.47, 124.01, 125.93, 127.34, 128.46, 129.65, 131.14, 133.26, 137.16, 138.02, 140.61; MS (70 eV) *m/z* (%) 523 (35). HRMS Found: 523.8726. Calcd. for $C_{24}H_{12}{}^{79}Br^{81}BrS_2$: 523.8727.

6,6'-Diiodo-4,4'-bis(dibenzothiophene) (20). – To a mixture of 6,6'-bis(trimethylsilyl)-4,4'-(dibenzothiophene) (**18**) (50 mg, 0.1 mmol) and $BTMAICl_2$ (68 mg, 0.2 mmol) in acetic acid (2 mL) was added $ZnCl_2$ (27 mg, 0.24 mmol) and the resulting mixture was stirred at 80°C for 22h. Thereafter, the mixture was poured into water (10 mL) and extracted with CH_2Cl_2 (20 mL). The organic phase was washed with water (10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was washed with diethylether (10 mL). The product was dried *in vacuo* to afford **20** (85 mg, 0.38 mmol, 98%) as a brownish powder; mp 64.2 – 68.2°C; IR (KBr) ν 2960, 1541, 1438, 1260, 1098, 1022, 743 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.16 (dd, 1H, ^3J 5.2, ^3J 5.0 Hz), 7.42 – 7.56 (m, 2H), 7.70 – 7.86 (m, 2H), 8.04 – 8.11 (m, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 121.94, 122.03, 122.86, 125.67, 127.65, 128.74, 129.87, 131.93, 133.40; MS (70 eV) *m/z* (%) 618 (100). HRMS Found: 617.8749;

Calcd. for $C_{24}H_{12}S_2I_2$: 617.8470.

6,6'-Bis(trimethylsilyl)-4,4'-bis(dibenzothiophene-*S*,*S*-dioxide) (23). – To a solution of bis(4-trimethylsilyldibenzothiophene) (**18**) (50 mg, 0.098 mmol) in CH_2Cl_2 (2 mL) was given at rt *m*-CPBA (80 mg, 0.47 mmol). The reaction mixture was stirred at rt for 2h. Then it was poured into sat. aq. $NaHCO_3$ (20 mL) and the organic material was extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (2 X 20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was subjected to column chromatography on silica gel (ether/hexane 1:1) to give **23** (26 mg, 0.045 mmol, 46%) as a colorless powder; ^1H NMR (600 MHz, $CDCl_3$) δ 0.05 (s, 18H, 2 $SiMe_3$), 6.99 – 7.35 (m, 12H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 0.62, 122.14, 122.44, 131.59, 132.51, 132.81, 132.88, 133.24, 133.66, 135.99, 137.98, 143.68; MS (FAB, 3-nitrobenzyl alcohol) *m/z* 575 (MH^+). HRMS Found: 575.1204. Calcd. for $C_{30}H_{31}O_4Si_2S_2$ (MH^+, FAB).

Oxidation of 6,6'-Bis(trimethylsilyl)-4,4'-bis(dibenzothiophene) with *m*-CPBA/$BF_3{\cdot}Et_2O$ - (24). – To a solution of **18** (50 mg, 0.098 mmol) in CH_2Cl_2 (2 mL), cooled to 0°C, was added $BF_3{\cdot}Et_2O$ (0.04 mL, 0.39 mmol) and subsequently in *m*-CPBA (40 mg, 0.22 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred for 2h. Then the mixture was given into conc. aq. $NaHCO_3$ (20 mL). The organic material was extracted with CH_2Cl_2 (2 X 10 mL). The organic phase was washed with water (10 mL) and dried over anhydrous $MgSO_4$. Thereafter, the solvent was evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (ethyl acetate / hexane = 1 : 1) give **24** (9.0 mg, 0.019 mmol, 20%) as colorless crystals; ^1H NMR (270 MHz, $CDCl_3$) δ 0.32 (s, 9H, $SiMe_3$), 7.44 – 7.91 (m, 13H); MS (70 eV) *m/z* (%) 470 (M^+, 18), 454 (M^+-[O], 41), 438 (M^+-[2O], 100), 423 (438-CH_3, 89). HRMS Found: 470.0829. Calcd. for $C_{27}H_{22}O_2SiS_2$: 470.0831.

Trimer 21. – Under an inert atmosphere, a mixture of 4,6-diiodobenzothiophene (**13**) (100 mg, 0.23 mmol), 4-trimethylsilyldibenzothiopheneboronic acid (**17**) (83 mg, 0.023 mmol), $Pd(PPh_3)_4$ (5.0 mg, 1.10^{-6} mol) and aq. Na_2CO_3 (63 mg) in DME (6 mL) was heated under reflux at 60°C for 6d. Thereafter, the solution was poured into water (5 mL) and extracted with CH_2Cl_2 (10 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (eluant: hexane) to give **21** (20 mg, 0.03 mmol, 13%) as colorless plates, mp 98.2° - 99.2°C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.05 (s, 18H, 2 $SiMe_3$), 7.38 – 7.44 (m, 12H), 7.87 – 7.89 (m, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 1.30, 121.09, 121.37, 122.44, 124.73, 124.99, 126.82, 127.09, 134.04, 134.91, 135.32, 136.22, 136.78, 148.30, 148.51, 149.86; MS (70 eV) *m/z* (%) 692 (21). HRMS Found: 692.1512. Calcd. for $C_{42}H_{36}Si_2S_3$; 692.1518.

Tetramer 22. – Under an inert atmosphere, a mixture of bis(iodobdibenzothiophene) (**20**) 55 mg, 0.089 mmol), 4-trimethylsilyldibenzothiopheneboronic acid (**17**), $Pd(PPh_3)_4$ (2 mg, $2{\cdot}10^{-3}$ mmol) and aq. Na_2CO_3 (48 mg) in DME (4 mL) was heated under reflux at 60°C for 4d. Thereafter, the reaction mixture was poured into water (5 mL) and the organic material was extracted with CH_2Cl_2 (10 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: hexane:ether 4:1) to give **22** (6 mg, $6.9{\cdot}10^{-3}$ mmol, 8%) as a colorless powder; mp 80.2 – 81.0°C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.66 (s, 18H, 2 $SiMe_3$), 7.12 – 7.39 (m, 16H), 7.82 – 7.88 (m, 8H); MS (70 eV) *m/z* (%) 874 (6). HRMS Found: 874.1700. Calcd. for $C_{54}H_{42}Si_2S_4$: 874.1708.

4-Iododibenzothiophene-*S*-oxide (26). – To 4-iododibenzothiophene (**12**) (1.0 g, 3.2 mmol) in CH_2Cl_2 (10 mL) was added solid *m*-CPBA (580 mg, 3.4 mmol) at rt and in 15 portions over a time period of 1.5h. The reaction mixture was stirred at rt for 2h. Thereafter, the mixture was poured into water (20 mL) and extracted with chloroform. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: chloroform) to give **26** (618 mg, 63%) as a colorless solid; mp 183.7 – 185.0°C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.25 (dd, 1H, ^3J 9.0, ^3J 8.0 Hz), 7.52 (m, 2H), 7.68 – 7.81 (m, 3H), 7.99 (d, 1H, J 6.0 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 94.63, 121.49, 122.26, 127.51, 130.08, 132.63, 133.69, 136.76, 138.94, 139.21, 144.40, 148.27; MS (70 eV) *m/z* (%) 325 (45, M^+-1).

Suzuki-Kumada Coupling Reactions with 26. – Example 1: A mixture of **26** (72 mg, 0.22 mmol), benzo[*b*]thiopheneboronic acid (99 mg, 0.55 mmol), $Pd(PPh_3)_4$ (20 mg, $17.3{\cdot}10^{-3}$ mmol) in a solvent mixture of DME (3.5 mL) and 2M aq. Na_2CO_3 solution (1.5 mL) was heated at reflux for 9h. Thereafter, the mixture was poured into water (20 mL) and extracted with chloroform (2 X 15 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: ether/hexane 5:1) to give **25** (72 mg, 0.21 mmol, 98%) as an off-white solid; mp 177.9 – 181.6°C (ether); IR (KBr) ν 1447, 1022, 764 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.32 – 8.01 (m, 11H), 8.26 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT) δ 121.29 (+, CH), 121.98 (+, CH), 122.07 (+, CH), 124.74 (+, CH), 124.83 (+, CH), 125.21 (+, CH), 127.06 (+, CH), 127.33 (+, CH), 130.01 (+, CH), 130.78 (+, CH), 132.54 (+, CH), 133.19 (+, CH), 136.57 (C_{quat}), 136.93 (C_{quat})*; MS (FAB, 3-nitrobenzyl alcohol) (%) 333 (MH^+, 18), 316 (M^+-[O]), 307 (27), 289 (12), 154 (100). HRMS Found: 333.0410. Calcd. for $C_{20}H_{13}OS_2$: 333.0408 (MH^+, FAB); *not all of the quaternary carbons are listed.

Example 2: A mixture of **26** (500 mg, 1.5 mmol), 4-trimethylsilyldibenzothiophene boronic acid (**17**) (1.2 g, 3.3 mmol), and $Pd(PPh_3)_4$ (20 mg, 17.3 10^{-3} mmol) in a solvent mixture of DME (7.5 mL) and 2M aq. Na_2CO_3 solution (3 mL) was heated at reflux for 19h. Thereafter, the solution was poured into water (20 mL) and extracted with chloroform. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: chloroform) to give **27** (650 mg, 95%) as a colorless oil; IR (neat) ν 3052, 2954, 1572, 1445, 1354, 1249, 1063, 1028 840, 756, 730 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.12 (s, 9H, $SiMe_3$), 6.9 – 8.0 (m, 13H); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT) δ –1.2 (+, CH_3, $SiMe_3$), 121.60 (+, CH), 121.80 (+, CH), 121.92 (+, CH), 122.64 (+, CH), 124.06 (+, CH), 124.75 (+, CH), 127.42 (+, CH), 129.22 (C_{quat}), 129.79 (+, CH), 130.62 (+, CH), 131.95 (C_{quat}), 132.44 (+, CH), 132.78 (+, CH), 133.03 (+, CH), 134.03 (C_{quat}), 134.97 (C_{quat}), 136.12 (C_{quat}), 137.14 (C_{quat}), 138.82 (C_{quat}), 139.01 (C_{quat}), 142.05 (C_{quat}), 143.76 (C_{quat}), 145.14 (C_{quat}); MS (50 eV) *m/z* (%) 454 (M^+, 26), 438 (M^+-[O], 26); 423 (438-CH_3, 27), 73(100). HRMS Found: 454.0879. Calcd. for $C_{27}H_{22}OSiS_2$: 454.0881.

Photoirradiation of 24. – 24 (5 mg) in deaerated CD_2Cl_2 (1 mL) was photoirradiated for 19h at rt. A pyrex tube was used. Thereafter, the solvent was evaporated and the residue was subjected to column chromatography on silica gel (ethyl acetate/hexane 1:3) to give **29** (3 mg, 64%); ^1H NMR (600 MHz, $CDCl_3$) δ 0.62 (s, 9H, $SiMe_3$), 7.36 – 7.81 (m, 10H), 8.07 – 8.21 (m, 3H); MS (70 eV) *m/z* (%) 438 (100). HRMS Found: 438.0933. Calcd. for $C_{27}H_{22}SiS_2$: 438.0932.

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