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Unusual thiophilic ring-opening of fused oligothiophenes with organolithium reagents

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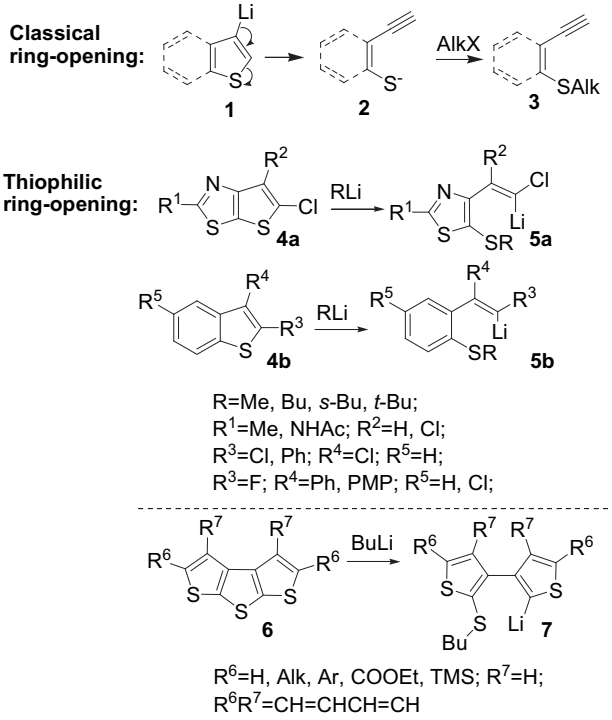
ABSTRACT

Organolithium reagents attack the sulfur atoms of fused oligothiophenes producing ring-opened organolithium intermediates that can be trapped with a suitable electrophile. The reaction was found to be general for fused thieno[2,3-*b*]-thiophenes and some [3,2-*b*]-fused oligothiophenes. Thermodynamic (organilithiums basicity) and mechanistic (RLi coordination by neighboring sulfur) aspects control the substrate scope and regioselectivity of the reaction. When competitive deprotonation of the substrate is possible, high selectivity toward ring-opening was observed with *n*-BuLi when compared with the other tested organolithiums. The recently discovered octathio[8]circulene produces multifold ring-opening products.

1. Introduction

Recently, much attention has been dedicated to fused oligothiophenes as potential organic semiconductors for various applications.[1] Stability and aromaticity of the thiophene core as well as unique properties of the sulfur atom allows even the preparation of fully thiophenic helicenes[2] and circulenes.[3] Several novel approaches toward fused oligothiophenes have been published recently demonstrating great progress achieved in this field.[4] Thus further work on the synthesis of fused oligothiophenes as well as their chemical properties is of particular interest.

Herein we report the unusual reactivity of fused oligothiophenes toward organolithium reagents, which leads to cleavage of the thiophene ring. Ring-opening of thiophene, e.g., 3-lithiothiophenes **1** (Scheme 1) and other heterocyclic cores, such as oxazoles and thiazoles is a well-known reaction type in heterocyclic chemistry.[5] However, in 1998 Belly et al. reported an addition reaction in which organolithiums attack the sulfur atoms of certain chlorothiophenes **4**. As a result, ring-opened lithium species **5** are formed that can be trapped with various electrophiles. Later, this reaction type was extended to 2-fluoro-3-arylbenzothiophenes.[6] More recently Wang et al. reported dithieno[2,3-*b*;3′,2′-*d*]thiophene systems **6** to react similarly.[7] Despite being well-known for



Scheme 1. Classical ring-opening of 3-lithiothiophenes and previously reported examples of thiophilic ring-opening.

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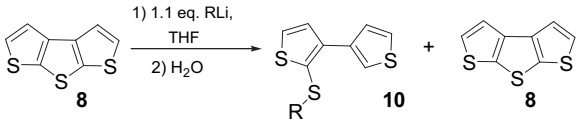
selenophenes and 1,2-thiazoles,[8] thiophilic ring-opening of thiophene was previously reported only among the mentioned substrates. Moreover no explanations were provided for such unusual thiophene reactivity and were considered to be uncommon.

2. Results and discussion

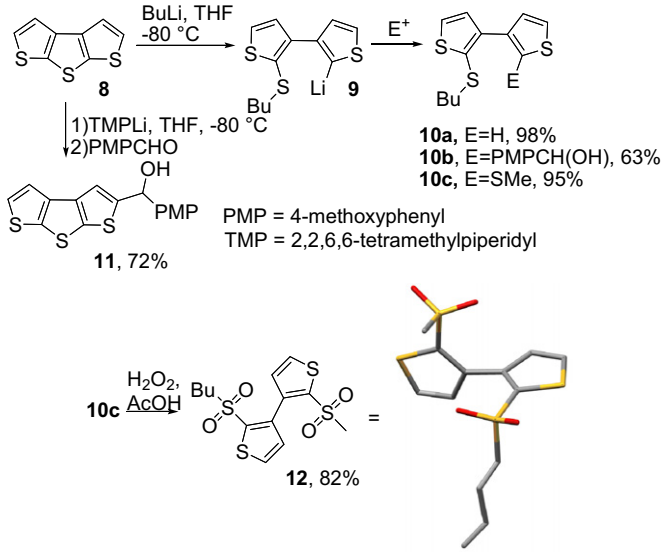
In the course of our work on dithieno[2,3-*b*;3′,2′-*d*]thiophene **8** functionalization[9] we have discovered independently thiophilic ring-opening of dithieno[2,3-*b*;3′,2′-*d*]thiophene **8**. Attempted deprotonation with *n*-butyllithium in THF at −80 °C produces almost exclusively unexpected derivatives **10**. The formed organolithium intermediate was trapped with various electrophiles: proton source (1 M HCl), 4-methoxybenzaldehyde and dimethyl disulfide to give products **10a**, **10b**, and **10c**, respectively. The methylsulfanyl derivative **10c** was oxidized to give crystalline bis-sulfone **12** and its structure was proved unambiguously by X-ray diffraction (Table 1, Scheme 2).[10] In contrast, when a lithium amide base was used, the product of deprotonation **11** was isolated in high yield.

Table 1
Distribution of ring-opening versus deprotonation products of **8** with various organolithiums[a]



R	Solvent, temperature, °C	Ring-opening product	Yield of ring-opening product, %	Yield of **8** (%)
Bu	THF, −80	**10a**	98	2
Me	THF, −80	**10d**	68	32
s-Bu	THF, −80	**10e**	23	77
t-Bu	THF, −80	**10f**	80	20
Ph	THF, rt	**10g**	40	60

[a] To solution of **8** in THF at −80 °C 1.1 equiv RLi was added and stirred at this temperature. Samples were taken after 15, 45, and 90 min and quenched with water–THF mixture. Products distribution was measured by ^{1}H NMR and was unchanged with time.



Scheme 2. Ring-opening and deprotonation of dithieno[2,3-*b*;3′,2′-*d*]thiophene **8**. X-ray structure of bis-sulfone **12**.

This surprising reactivity of dithieno[2,3-*b*;3′,2′-*d*]thiophene promoted us to study it systematically. To gain further insight into the problem the nature of the organolithium reagent was varied. Dithieno[2,3-*b*;3′,2′-*d*]thiophene **8** was chosen as a model substrate to measure the ring-opening selectivity of different organolithiums (Table 1) due to its ability to undergo both deprotonation and ring-opening reactions. The reaction mixture was treated with proton source (1 M HCl) to provide quantitative conversion of the organolithium intermediates to the respective products. For alkyllithiums the product ratio was the same after 15, 45, and 90 min, implying that the reaction was fully converted within minutes at −80 °C. The reaction with phenyllithium, which has relatively low basicity, was done at room temperature as it was unreactive at −80 °C (15% of **10g** after 45 min). Methyl- and *tert*-butyllithium led mainly to ring-opening products, though not in quantitative yield as with *n*-butyllithium. Both the relatively highly basic sec-butyllithium and the less basic phenyllithium mostly deprotonate dithieno[2,3-*b*;3′,2′-*d*]thiophene.[11] The absence of the strong correlation between basicity of the organolithium and its ring-opening selectivity argues for a more complex mechanism than just a simple nucleophilic attack of RLi on the central sulfur atom (see below).

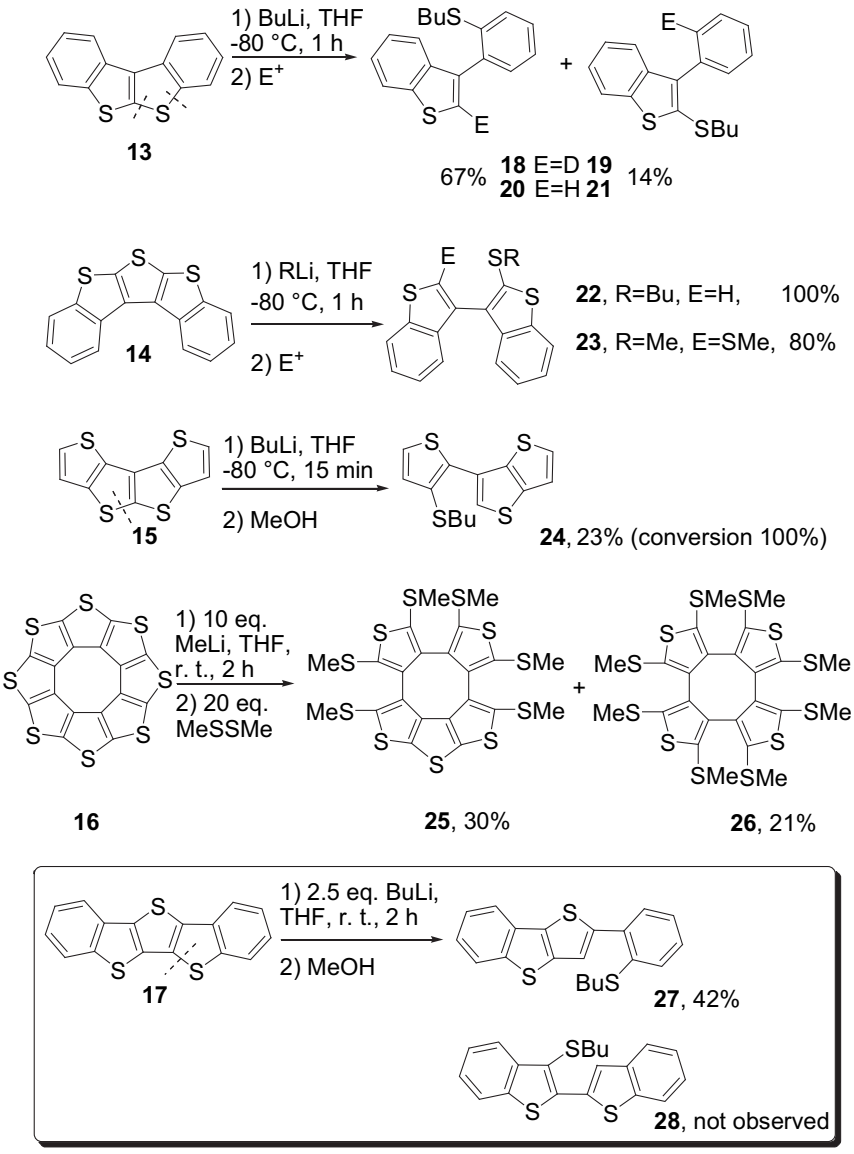
Despite the fact that previous examples of thiophilic ring-opening were fused thiophenes (2- or 3-chloro- and fluorothiophenes fused with another aromatic ring, e.g., benzene, thiazole or pyridine, and dithieno[2,3-*b*;3′,2′-*d*]thiophene core),[6,7] there were no attempts made on a wide variation of oligothiophene core. However the substrate scope of the reaction is a crucial issue shedding light on mechanism and the driving force of the thiophilic ring-opening reaction. We have screened various fused oligothiophenes using *n*-butyllithium, which was shown to be the most selective ring-opener in experiments with **8**.

We have found that the reaction of thiophilic ring-opening is general for fused oligothiophenes **13**–**15** and circulene **16** containing thieno[2,3-*b*]thiophene fragment (Scheme 3). As in the case of dithieno[2,3-*b*;3′,2′-*d*]thiophene **8** attack of organometallics is directed on the central thiophene core for substrates containing non-equivalent thiophenic nuclei. For example, when **14** was treated subsequently with MeLi and MeSSMe, symmetrical **23** was isolated as the only product.

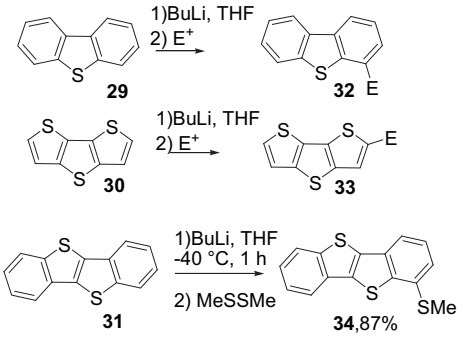
However, it is well-known from the literature that dibenzothiophene **29**[12] and isomeric dithieno[3,2-*b*:2′,3′-*d*]thiophene **30**[13] are smoothly deprotonated with butyllithium in THF to form *ortho*-substituted products **32** and **33**, respectively (Scheme 4). Moreover, we have found that [1]benzothieno[3,2-*b*][1]benzothiophene **31** gives exclusively **34**, the product of deprotonation, when treated with BuLi followed by dimethyl disulfide. Thus we concluded that [3,2-*b*]-fusion of thiophenic rings does not undergo thiophilic ring-opening, and alternative reactions, such as deprotonation occur.

In contrast, treatment of [1]benzothieno[2′,3′:4,5]thieno[3,2-*b*][1]benzothiophene **17** with BuLi leads to the ring-opened product **27** (Scheme 3). The reaction rate is very slow, even at room temperature and with 150% excess of BuLi the conversion reaches only 42% after 2 h (at longer reaction times butyllithium is fully decomposed by THF). Interestingly, in spite of [2,3-*b*]-fused **8**, **14**, and **15**, butyllithium opens regioselectively the side thiophenic core of **17**.

The vast difference in reactivity of different fused oligothiophenes can be explained by precoordination of organolithium to the sulfur atom, which facilitates attack on the conjunct thiophene ring (Fig. 2). A very high reaction rate (generally within minutes at −80 °C) in the case of [2,3-*b*]-fused oligothiophenes is likely due to optimal configuration for thiophilic attack. Longer distance between one-sided thiophene rings in **17** hampers optimal configuration and results in low reaction rate. The crucial role of complexation is also supported by the observed ring-opening regioselectivity for **17**. In **31** coordinated RLi cannot reach the sulfur atom of the conjunct thiophene ring and *ortho*-deprotonation occurs. Generally thiophenes are easily deprotonated by strong bases in α-, β- (if α-positions are occupied) and *ortho*-position



Scheme 3. Thiophilic ring-opening of fused thiophenic systems.



Scheme 4. Fused oligothiophenes producing only deprotonation products with *n*-BuLi.

(for fused thiophenes). If for kinetic reasons discussed above, ring-opening cannot occur or is slow then alternative reactions dominate. In spite of **17** being structurally similar to dithieno[3,2-*b*:2′,3′-*d*]thiophene **30** has highly kinetically acidic α-protons and is instantly deprotonated with BuLi at low temperatures.[13]

In the computed transition state for the ring-opening reaction (Fig. 3) the Li atom is found almost directly over the sulfur atom of the opened thiophene ring on its way to the α-carbon atom of the second thiophene ring. This structure of the transition state illustrates the cooperation of the adjacent thiophene rings in the ring-opening reaction.

Thermodynamically, the driving force of the reaction is a decrease in basicity from the highly basic organolithium reagent to less basic products. Intramolecular coordination of the formed organolithium intermediate by the alkyl- or arylsulfanyl substituent likely provides additional stabilization. We have found that the structure of the organolithium intermediate generated during ring-opening correlates with its basicity and mainly the less basic product is formed. For example, benzothienobenzothiophene **13** gives mainly **18** and **20** via intermediate formation of its less basic lithium derivative. Compounds **20** and **21** formed as minor products, are derived from the more basic phenyllithium salt.[14] Similarly trithienothiophene **15** yields the only type of ring-opening product **24**, due to the much lower basicity of thieno[3,2-*b*]thien-2-yllithium than the alternative thien-3-yllithium derivative.

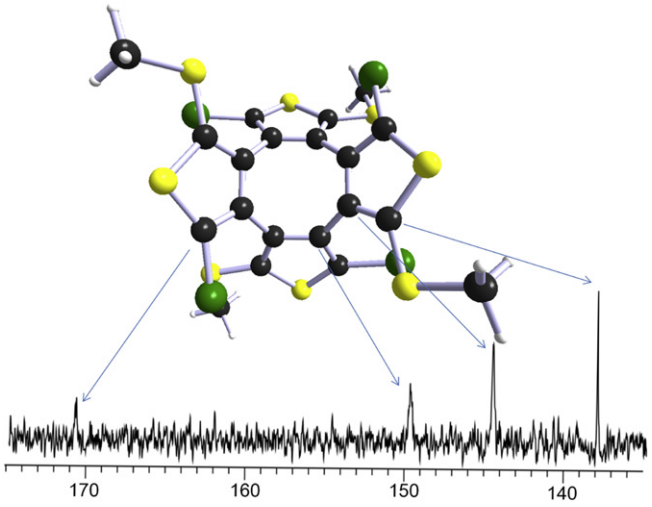


Fig. 1. Section plot of the ^{13}C NMR spectrum (100 MHz, THF-d_8, 25 °C) of the sample obtained by dissolving sulflower **16** in a 50-fold excess of MeLi/hexane and adding THF-d_8. Computed structure of the symmetric tetralithium intermediate is shown above the spectrum. The signals of the less symmetric trilithium intermediate are less intensive and probably merged into the background.

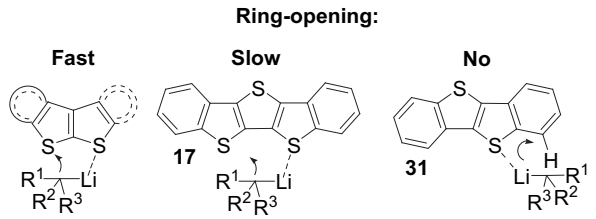


Fig. 2. Possible reaction intermediate, facilitating RLi attack on sulfur.

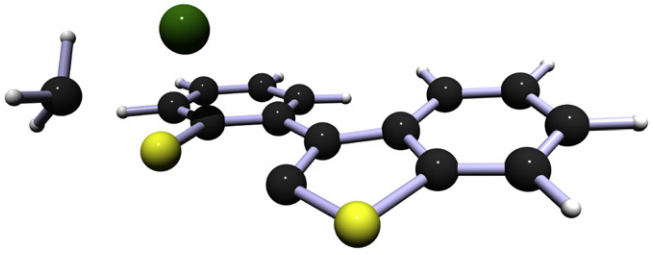


Fig. 3. Transition state for the ring-opening reaction of MeLi and dithiophene **13** computed at the B3LYP/6-311+G(d,p) level of theory.

The aggregation of organolithiums and its complexation with the solvent essentially influence its reactivity. We supposed that complexation between RLi and oligothiophenes plays a key role in thiophilic ring-opening. Therefore we varied the nature of the solvent to study its effect. We found, that when dithienothiophene **8** was treated with BuLi in the less polar diethyl ether instead of THF, (Table 2, entry 1), the conversion drops to less than 8% and ring-opening selectivity was lost (Table 1, entry 2). For the less reactive **13** a 45% conversion is achieved in THF (entry 3) and 92% in 8:1 THF–HMPT mixture in 15 min (entry 6). Thus, well coordinating and polar solvents promote ring-opening reaction.

We studied also the reaction of organolithiums with the recently synthesized sulflower **16**, the first fully thiophenic circulene.[3] Due to the unique structure of this molecule it was difficult to propose any reactions for sulflower. Therefore the unique molecule demands unique reactions. We observed here for the first time the possibility of chemical transformation of sulflower. Multiple

Table 2
Influence of solvent nature on ring-opening rate with *n*-butyllithium at −80 °C[a]

Entry	Substrate	Solvent	Time, min	Electrophilic reagent	Products distribution, yield, % (compound)
1	**8**	THF	15	H_2O	98 (**10a**); 2 (**8**)
2	**8**	Et_2O	15	PMPCHO	5.9 (**10b**); 1.4 (**11**)
3	**13**	THF	15	H_2O	35.8 (**20**); 8.6 (**21**)
4	**13**	THF	45	H_2O	60 (**20**); 10 (**21**)
5	**13**	THF	60	H_2O	67 (**20**); 14 (**21**)
6	**13**	THF–HMPT =8:1	15	H_2O	82 (**20**); 10 (**21**)

[a] Products distribution was measured by ^1H NMR and was referenced to pure samples.

thiophene ring cleavages were observed. Due to the insolubility of circulene **16**, the ring-opening was performed at room temperature to shorten the duration of the heterogeneous reaction. Interestingly, using 50-fold excess of MeLi a D_{4h}-symmetric tetralithium intermediate was detected as the major product by ^{13}C NMR measurements (Fig. 1). However treatment of the sample with proton source (methanol) provided an inseparable complex mixture of products. Quenching the reaction mixture (10 equiv of MeLi) with dimethyl disulfide gave symmetrical 3- and 4-fold products **25** and **26** in 30% and 21% yields, respectively (Scheme 4). It should be noted, that this is the first reported reaction of **16**.

3. Conclusions

In summary, fused oligothiophenes react with organolithiums to produce ring-opened products as a result of thiophilic attack by the organolithium species. The reaction proceeds very fast at low temperature in readily coordinating solvents, such as THF. When competitive deprotonation of the substrate is possible *n*-BuLi shows the highest selectivity to ring-opening among the tested organolithium reagents. The decrease of the organolithium species basicity is a driving force of the reaction and defines the ring-opening regioselectivity for non-symmetrical substrates. The coordination of organolithiums by the neighboring sulfur atom is suggested to play a key role in the ring-opening mechanism, thus restricting the scope of substrates to fused thieno[2,3-*b*]thiophenes and some thieno[3,2-*b*]thiophenes, for example, **17**. For highly fused oligothiophenes multiple ring-openings are possible as was shown for octathio[8]circulene **16**. Thiophilic ring-opening of **16** is the first chemical transformation of this unique molecule.

4. Experimental section

4.1. General experimental

^1H and ^{13}C NMR spectra were referenced to solvent. Column chromatography was performed on silica gel (63–200 mesh). Melting points are uncorrected. THF and Et_2O were freshly distilled from the sodium-benzophenone ketyl. HMPT, 2,2,6,6-tetramethylpiperidine, and dimethyl disulfide were distilled from CaH_2. The following organolithiums were used: *n*-BuLi as 1.6 or 2.5 M solution in hexane(s), *s*-BuLi as 1.6 M solution in cyclohexane, *t*-BuLi as 1.6 M solution in pentane, MeLi as 1.6 M solution in diethyl ether, PhLi as 2.0 M solution in dibutyl ether.

Starting oligothiophenes were prepared as described previously: dithieno[2,3-*b*:3′,2′-*d*]thiophene **8**,[9] [1]benzothieno[2,3-*b*][1]benzothiophene **13**,[15] [1]benzothieno[3,2-*b*][1]benzothiophene **31**,[16] thieno[3,2-*b*]thieno[2′,3′:4,5]thieno[3,2-*d*]thiophene **15**,[4b] [1]benzothieno[2′,3′:4,5]thieno[3,2-*b*][1]benzothiophene **17**,[17] [1]benzothieno[3′,2′:4,5]thieno[2,3-*b*][1]benzothiophene **14**,[7] sulflower **16**.[3a]

4.1.1. Ring-opening of dithieno[2,3-b:3′,2′-d]thiophene ***8****.* To a precooled solution of dithieno[2,3-*b*:3′,2′-*d*]thiophene (196 mg, 1 mmol) in THF (Et_2O was used instead of THF in several experiments) (5 mL) organolithium (1.1 mmol) solution was added at −80 °C. Mixture was stirred at the same temperature and after 15, 45, and 60 min 1 mL samples were taken and poured into 1 mL of 1 M aq HCl, extracted with 3×1 mL of dichloromethane and organic extracts were dried in vacuum. ^{1}H NMR spectroscopic analysis showed that in the case of *n*-, *tert*-, *sec*-butyllithiums and methyllithium the ratio of dithienothiophene to ring-opening product was unchanged among samples taken after different times, indicating that conversion was full within 15 min. Dithienothiophene was formed as a result of dithienothienyllithium back protonation, this was evident by formation of dithienothien-2-yl derivatives when non-proton electrophiles were used. Pure samples of **10d**–**g** were isolated by the column chromatography (silica gel, hexane).

*4.1.1.1. 2-(Methylsulfanyl)-3,3′-bithiophene (****10d****)*[18]*.* Yield 108 mg (51%) as colorless oil; δ_H (300 MHz CDC1$_3$) 2.43 (s, 1H), 7.18 (d, *J* 5.5 Hz, 1H), 7.29 (d, *J* 5.5 Hz, 1H), 7.36 (dd, *J* 5.0, 3.0 Hz, 1H), 7.51 (dd, *J* 5.0, 1.4 Hz, 1H), 7.66 (dd, *J* 3.0, 1.4 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 21.2, 122.6, 125.1, 126.3, 127.7, 129.1, 131.2, 136.0, 137.6; ν_{max} (liquid film) 658, 724, 757, 782, 845, 968, 1010, 1072, 1188, 1333, 1393, 1418, 1428, 3101 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 234.9662, requires $C_9H_8S_3Na^+$ 234.9680.

*4.1.1.2. 2-(Butylsulfanyl)-3,3′-bithiophene (****10a****).* Yield 214 mg (95%) as colorless oil; δ_H (300 MHz, $CDCl_3$) 0.86 (t, *J* 7.3 Hz, 3H) 1.26–1.44 (m, 2H) 1.48–1.62 (m, 2H) 2.74–2.83 (m, 2H) 7.21 (d, *J* 5.2 Hz, 1H) 7.32 (d, *J* 5.5 Hz, 1H) 7.36 (dd, *J* 5.0, 3.0 Hz, 1H) 7.53 (dd, *J* 5.1, 1.2 Hz, 1H) 7.70 (dd, *J* 3.0, 1.4 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 13.6, 21.6, 31.2, 38.1, 122.8, 125.0, 126.9, 127.9, 129.1, 129.4, 136.2, 139.0; ν_{max} (liquid film) 723, 783, 846, 1008, 1071, 1333, 1462, 2926, 2955, 3102 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 277.0160, requires $C_{12}H_{14}S_3Na^+$ 277.0150.

*4.1.1.3. 2-(tert-Butylsulfanyl)-3,3′-bithiophene (****10f****).* Yield 172 mg (68%) as colorless oil; δ_H (300 MHz, $CDCl_3$) 1.20 (s, 9H), 7.27 (d, *J* 5.6 Hz, 1H), 7.33 (dd, *J* 5.1, 3.0 Hz, 1H), 7.41 (d, *J* 5.6 Hz, 1H), 7.56 (d, *J* 5.1 Hz, 1H), 7.74 (d, *J* 3.0 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 30.6, 49.0, 123.3, 124.6, 126.6, 128.5, 129.0, 129.3, 136.7, 142.4; ν_{max} (liquid film) 726, 784, 847, 1162, 1363, 1455, 2958, 3103 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 277.0139, requires $C_{12}H_{14}S_3Na^+$ 277.0150.

*4.1.1.4. 2-(Butan-2-ylsulfanyl)-3,3′-bithiophene (****10e****).* Yield 51 mg (20%) as colorless oil; δ_H (300 MHz, $CDCl_3$) 0.92 (t, *J* 7.3 Hz, 3H), 1.18 (d, *J* 6.9 Hz, 3H), 1.45 (sxt, *J* 7.1 Hz, 1H), 1.59 (sxt, *J* 7.3 Hz, 1H), 2.94 (sxt, *J* 6.6 Hz, 1H), 7.22 (d, *J* 5.6 Hz, 1H), 7.34 (d, *J* 5.3 Hz, 1H), 7.34 (dd, *J* 5.1, 3.0 Hz, 1H), 7.55 (dd, *J* 4.9, 1.1 Hz, 1H), 7.72 (dd, *J* 3.0, 1.1 Hz, 1H); δ_C (75 MHz, CD_3COCD_3) 12.0, 21.0, 30.4, 49.7, 124.5, 126.6, 128.6, 129.4, 129.8, 130.8, 137.8, 142.0; ν_{max} (liquid film) 725, 783, 846, 1007, 1334, 1376, 1454, 2922, 2960, 3104 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 277.0133, requires $C_{12}H_{14}S_3Na^+$ 277.0150.

*4.1.1.5. 2-(Phenylsulfanyl)-3,3′-bithiophene (****10g****).* Yield 90 mg (33%) as colorless oil; δ_H (300 MHz, $CDCl_3$) 7.12–7.19 (m, 3H), 7.22–7.30 (m, 2H), 7.32 (dd, *J* 4.9, 3.0 Hz, 1H), 7.35 (d, *J* 5.5 Hz, 1H), 7.44 (dd, *J* 4.9, 1.4 Hz, 1H), 7.51 (d, *J* 5.5 Hz, 1H), 7.60 (dd, *J* 3.0, 1.4 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 123.3, 124.2, 125.2, 125.8, 126.4, 127.7, 129.1, 129.4, 129.9, 135.6, 138.6, 142.1; ν_{max} (liquid film) 686, 727, 785, 846, 1022, 1076, 1260, 1438, 1475, 1578 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 296.9837, requires $C_{14}H_{10}S_3Na^+$ 296.9837.

*4.1.1.6. 2-(Butylsulfanyl)-2′-(methylsulfanyl)-3,3′-bithiophene (****10c****).* To a precooled solution of dithieno[2,3-*b*:3′,2′-*d*]thiophene (196 mg, 1 mmol) in THF (5 mL) *n*-butyllithium (1.1 mmol) solution was added at −80 °C. After stirring for additional 15 min dimethyl disulfide (122 mg, 1.3 mmol) was added via syringe. Cooling bath was removed and reaction was allowed to warm to room temperature, quenched with water (10 mL), and extracted with dichloromethane (3×2 mL). Organic extracts were combined, passed through short column (silica gel, 5 mL, dichloromethane) and rotary evaporated. Volatile byproducts and starting materials (dimethyl disulfide, butyl methyl sulfide) were removed in vacuum (1 Torr, 50 °C) to give target product as residual yellowish oil (285 mg, 95%). δ_H (360 MHz, $CDCl_3$) 0.80–0.89 (m, 3H), 1.25–1.39 (m, 2H), 1.43–1.55 (m, 2H), 2.39 (s, 3H), 2.71 (t, *J* 7.1 Hz, 2H), 7.19 (t, *J* 4.9 Hz, 2H), 7.32 (d, *J* 5.3 Hz, 1H), 7.35 (d, *J* 5.3 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 13.5, 21.5, 21.5, 31.2, 38.2, 125.7, 126.5, 129.8, 130.1, 132.1, 133.9, 137.9, 139.3; ν_{max} (liquid film) 660, 673, 713, 846, 876, 908, 968, 1010, 1331, 1417, 1431, 1462, 2920, 2955, 3100 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 323,0015, requires $C_{13}H_{16}S_4Na^+$ 323,0027.

*4.1.1.7. 2-(Butylsulfonyl)-2′-(methylsulfonyl)-3,3′-bithiophene (****12****).* Compound **10c** (150 mg, 0.5 mmol) was dissolved in acetic acid (10 mL) and hydrogen peroxide (30% in water, 340 mg, 3 mmol) was added and stirred for 7 days. Hydrogen peroxide (340 mg) was additionally added and stirring was continued for another 7 days. Water (50 mL) was added, the product was filtered and recrystallized from acetic acid to give **12** as fine needles (300 mg, 82%); mp=164–166 °C; δ_H (400 MHz, $CDCl_3$) 0.91 (t, *J* 7.4 Hz, 2H), 1.35–1.48 (sxt, *J* 7.4 Hz, 2H), 1.68–1.80 (m, 2H), 3.085–3.15 (t, *J* 8.0 Hz, 2H), 3.13 (s, 3H), 7.15 (d, *J* 5.1 Hz, 1H), 7.18 (d, *J* 5.1 Hz, 1H), 7.71 (d, *J* 5.1 Hz, 1H), 7.73 (d, *J* 5.1 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 13.4, 21.3, 24.5, 45.8, 57.1, 131.0, 131.3, 131.8, 131.9, 137.6, 137.8, 137.8, 138.9; ν_{max} (liquid film) 754, 772, 861, 966, 1042, 1084, 1099, 1135, 1303, 1313, 3109 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 386.9844, requires $C_{13}H_{16}O_4S_4Na^+$ 386.9824; X-ray data are available from Cambridge Crystallographic Data Center, http://www.ccdc.cam.ac.uk/products/csd/request/, deposition number 813592.

*4.1.1.8. [2′-(Butylthio)-3,3′-bithien-2-yl](4-methoxyphenyl)methanol (****10b****).* To a precooled solution of dithieno[2,3-*b*:3′,2′-*d*]thiophene (98 mg, 0.5 mmol) in THF (2.5 mL) *n*-butyllithium (0.51 mmol, 0.32 mL 1.6 M) solution was added at −80 °C. After stirring for additional 15 min 4-methoxybenzaldehyde (80 mg, 0.58 mmol) in THF (1 mL) was added via syringe. Cooling bath was removed and reaction was allowed to warm to room temperature, treated with 1 mL of aq NH_4Cl and hexane (5 mL). Organic extracts were combined, passed through short column (silica gel, 5 mL, dichloromethane) and rotary evaporated. The residual oil was chromatographed (50 mL silica gel, hexane–ethyl acetate 4:1) to give **10b** as yellowish oil (124 mg, 63%) unstable in air on prolonged storage. δ_H (300 MHz, $CDCl_3$) 0.82 (t, *J* 7.1 Hz, 3H), 1.27 (m, 2H), 1.45 (m, 2H), 2.59 (t, *J* 7.4 Hz, 2H), 2.84 (dd, *J* 3.3, 1.1 Hz, 1H), 5.97 (d, *J* 3.0 Hz, 1H), 6.81 (d, *J* 8.5 Hz, 2H), 6.96 (d, *J* 5.5 Hz, 2H), 7.23 (d, *J* 8.2 Hz, 3H), 7.28 (d, *J* 5.2 Hz, 1H), 7.31 (dd, *J* 5.2, 1.1 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 13.5, 21.5, 31.1, 37.8, 55.2, 69.9, 113.6, 124.4, 127.0, 127.2, 129.2, 130.0, 131.4, 133.0, 135.4, 139.8, 145.3, 159.0; ν_{max} (liquid film) 716, 831, 851, 1030, 1172, 1245, 1509, 1610, 2955, 3424 (br) cm^{-1}; HRESI-TOF$^+$: MNa^+, found 413.0651, requires $C_{20}H_{22}O_2S_3Na^+$ 413.0674.

*4.1.1.9. Bisthieno[2,3-b:3′,2′-d]thiophen-2-yl(4-methoxyphenyl) methanol (****11****).* 2,2,6,6-Tetramethylpiperidine (80 mg, 0.56 mmol) in THF (2 mL) was treated with *n*-butyllithium (0.32 mL, 1.6 M, 0.51 mmol) at 0 °C, stirred for 15 min and cooled to −80 °C. Dithieno[2,3-*b*:3′,2′-*d*]thiophene (98 mg, 0.5 mmol) in THF (0.5 mL) was added via syringe and stirred for 10 min, then 4-methoxybenzaldehyde (80 mg, 0.58 mmol) in THF (1 mL) was added via syringe. The cooling bath was removed, allowed to warm

to room temperature and treated with 1 mL of aq NH_4Cl and hexane (5 mL). Organic phase was separated, volatiles evaporated, and the residue recrystallized from 95% ethanol (4 mL) to give **11** as yellowish crystals (120 mg, 72%) unstable in air on prolonged storage. Mp 143–145 °C; δ_H (300 MHz, $CDCl_3$) 2.47 (d, *J* 4.1 Hz, 1H), 3.81 (s, 3H), 6.04 (d, *J* 3.9 Hz, 1H), 6.91 (d, *J* 8.8 Hz, 2H), 7.10 (d, *J* 1.1 Hz, 1H), 7.27 (d, *J* 5.2 Hz, 1H), 7.34 (d, *J* 5.2 Hz, 1H), 7.40 (d, *J* 8.79 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 55.3, 72.7, 114.0, 116.5, 118.7, 127.6, 127.8, 134.9, 137.5, 138.5, 138.6, 138.2, 151.2, 159.6; ν_{max} (liquid film) 674, 724, 817, 843, 1021, 1172, 1244, 1511, 1608, 3460 (br) cm^{-1}; HRESI-TOF$^+$: MNa^+, found 354.9915, requires $C_{16}H_{12}O_2S_3Na^+$ 354.9892.

4.1.2. Ring-opening of [1]benzothieno[2,3-b][1]benzothiophene ***13****.* [1]Benzothieno[2,3-*b*][1]benzothiophene (**13**) was not fully spectroscopically characterized previously. δ_H (400 MHz, $CDCl_3$) 7.34–7.44 (m, 2H), 7.53 (td, *J* 7.6, 1.1 Hz, 2H), 7.89 (d, *J* 7.7 Hz, 2H), 8.32 (d, *J* 7.7 Hz, 2H); δ_C (100 MHz, $CDCl_3$) 121.1, 123.2, 123.9, 124.8, 133.4, 135.0, 139.8, 143.5.

Ring-openings of **13** were performed with *n*-butyllithium similar to **8**. Products distribution was defined with ^1H NMR. As shown in table below ring-opening rate is slower comparing to **8** and conversion is growing with time. Quenching with D_2O showed no deprotonation (*ortho*-lithiation) of **13**, the only compound in reaction mixture except ring-opening products was starting **13**. Addition of HMPT substantially increases ring-opening rate. Pure samples of **18**–**21** were isolated by column chromatography (hexane, silica gel).

Run	Solvent	Time, min	Electrophilic reagent	Yield of **18** or **20**	Yield of **19** or **21**
1	THF	15	H_2O	35.8%	8.6%
2	THF	45	H_2O	60%	10%
3	THF	60	H_2O	67%	14%
4	THF	60	D_2O	67%	14%
5	THF–HMPT=8:1	15	H_2O	82%	10%

*4.1.2.1. 3-[2-(Butylsulfanyl)phenyl]-1-benzothiophene (****20****).* From run 3, 176 mg (59%), colorless oil; δ_H (300 MHz, $CDCl_3$) 0.85 (t, *J* 7.3 Hz, 3H), 1.26–1.41 (m, 2H), 1.46–1.60 (m, 2H), 2.77 (t, *J* 7.3 Hz, 2H), 7.22–7.30 (m, 1H), 7.30–7.48 (m, 6H), 7.50–7.56 (m, 1H), 7.89–7.96 (m, 1H); δ_C (75 MHz, $CDCl_3$) 13.6, 22.0, 30.8, 32.7, 122.6, 123.2, 124.0, 124.3, 125.0, 125.0, 127.5, 128.3, 130.9, 135.4, 136.0, 137.7, 138.7, 139.8; ν_{max} (liquid film) 692, 730, 759, 828, 1424, 1461, 2926, 2955, 3054 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 321.0722, requires $C_{18}H_{18}S_2Na^+$ 321.0742.

*4.1.2.2. 2-(Butylsulfanyl)-3-phenyl-1-benzothiophene (****21****).* From run 3, 33 mg (11%), colorless oil; δ_H (300 MHz, $CDCl_3$) 0.84 (t, *J* 7.4 Hz, 3H), 1.33 (sxt, *J* 7.4 Hz, 2H), 1.55 (qt, *J* 7.4 Hz, 2H), 2.84 (t, *J* 7.3 Hz, 2H), 7.27–7.37 (m, 2H), 7.38–7.60 (m, 6H), 7.75–7.83 (m, 1H); δ_C (75 MHz, $CDCl_3$) 13.5, 21.6, 31.4, 36.9, 121.7, 122.9, 124.4, 124.4, 127.7, 128.3, 130.2, 133.7, 134.7, 139.1, 139.8, 140.1; ν_{max} (liquid film) 692, 730, 758, 830, 1424, 1463, 2926, 2955, 3053 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 321.0719, requires $C_{18}H_{18}S_2Na^+$ 321.0742.

4.1.2.3. 3-[2-(Butylsulfanyl)phenyl](2-^{2}*H)-1-benzothiophene (****18****).* From run 4, 185 mg (62%), colorless oil; δ_H (300 MHz, $CDCl_3$) 0.84 (t, *J* 7.3 Hz, 3H), 1.24–1.41 (m, 2H), 1.44–1.60 (m, 2H), 2.76 (t, *J* 7.4 Hz, 2H), 7.21–7.29 (m, 1H), 7.29–7.47 (m, 5H), 7.49–7.55 (m, 1H), 7.88–7.95 (m, 1H); δ_C (75 MHz, $CDCl_3$) 13.6, 22.0, 30.8, 32.7, 122.6, 123.2, 124.0, 124.3, 125.0, 127.5, 128.3, 130.9, 135.4, 135.9, 137.7, 138.8, 139.7; ν_{max} (liquid film) 668, 730, 751, 763, 1417, 1456, 2924, 2955, 3054 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 322.0804, requires $C_{18}H_{17}DS_2Na^+$ 322.0805.

4.1.2.4. 2-(Butylsulfanyl)-3-(2-^{2}*H)phenyl-1-benzothiophene (****19****).* From run 4, 36 mg (12%), colorless oil; δ_H (300 MHz, $CDCl_3$) 0.84 (t, *J* 7.4 Hz, 3H), 1.33 (sxt, *J* 7.4 Hz, 2H), 1.49–1.62 (qt, *J* 7.4 Hz, 2H), 2.83 (t, *J* 7.4 Hz, 2H), 7.27–7.37 (m, 2H), 7.38–7.58 (m, 5H), 7.74–7.83 (m, 1H); δ_C (75 MHz, $CDCl_3$) 13.5, 21.6, 31.5, 36.9, 121.7, 122.9, 124.4, 124.5, 127.7, 128.2, 128.3, 130.2, 133.7, 134.7, 139.1, 139.8, 140.1; ν_{max} (liquid film) 669, 733, 749, 735, 1430, 1461, 2931, 2971, 3054 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 322.0791, requires $C_{18}H_{17}DS_2Na^+$ 322.0805.

4.1.3. Ring-opening of fused oligothiophenes ***14****–****17****. 4.1.3.1. 3-[3-(Butylthio)thien-2-yl]thieno[3,2-b]thiophene (****24****).* Compound **15** was treated with *n*-BuLi in a manner similar to previously described for **8**. For all of the samples taken after 15, 45, and 90 min and quenched with 1 M aq HCl ring-opening conversion constitutes 23%. The rest is starting **15** as result of α-deprotonation-back protonation. Pure **24** was separated from **15** by column chromatography (hexane, silica gel). Colorless oil; darkening when stored long in air. δ_H (400 MHz, $CDCl_3$) 0.88 (t, *J* 7.3 Hz, 3H), 1.36–1.45 (m, 2H), 1.59 (quint, *J* 7.4 Hz, 2H), 2.89 (t, *J* 7.3 Hz, 2H), 7.15 (d, *J* 5.1 Hz, 1H), 7.32 (d, *J* 5.3 Hz, 1H), 7.34 (d, *J* 5.1 Hz, 1H), 7.42–7.50 (m, 1H), 7.95 (d, *J* 1.3 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 13.6, 21.8, 31.5, 35.3, 119.7 123.4, 125.4, 126.5, 127.6, 129.4, 131.0, 133.7, 138.7, 139.3; ν_{max} (liquid film) 669, 719, 808, 874, 920, 1082, 1184, 1309, 1336, 1463, 2925, 2954, 3101 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 332.9871, requires $C_{14}H_{14}S_4Na^+$ 332.9871.

*4.1.3.2. 2-(Butylsulfanyl)-3,3′-bi-1-benzothiophene (****22****).* Compound **14** (296 mg, 1 mmol) in THF (5 mL) was treated with *n*-BuLi (1.1 mmol) at −80 °C and stirred additionally for 1 h. Methanol (0.5 mL) was added, reaction was allowed to warm to room temperature and volatiles removed. Residue was treated with aqueous 1 M HCl and dichloromethane (5 mL), organic phase was separated, flashed through silica gel (5 mL), and evaporated to yield **22** (354 mg, 100%) as colorless oil; δ_H (400 MHz, $CDCl_3$) 0.83 (t, *J* 7.3 Hz, 3H), 1.24–1.39 (m, 2H), 1.50–1.65 (m, 2H), 2.80–2.95 (m, 2H), 7.25–7.46 (m, 5H), 7.49–7.54 (m, 1H), 7.55 (s, 1H), 7.86 (d, *J* 8.1 Hz, 1H), 8.00 (d, *J* 8.1 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 13.5, 21.6, 31.5, 36.9, 121.9, 122.8, 123.2, 123.6, 124.2, 124.5, 124.6, 126.7, 130.2, 132.8, 136.2, 138.6, 140.0; ν_{max} (liquid film) 729, 754, 1251, 1416, 1428, 1454, 2925, 2954, 3056 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 377.0453, requires $C_{20}H_{18}S_3Na^+$ 377.0463.

*4.1.3.3. 2,2′-Bis(methylsulfanyl)-3,3′-bi-1-benzothiophene (****23****).* Compound **23** was prepared analogously to **22**. Compound **14** was treated with MeLi similarly to previously described. Dimethyl disulfide (141 mg, 1.5 mmol) in THF (1 mL) was added instead of methanol. After warming to room temperature organic phase was evaporated, treated with water (5 mL) and dichloromethane (5 mL). Organic phase was separated, solvent evaporated, and residue purified by column chromatography (hexane–ethyl acetate=20:1, silica gel) to yield **23** (286 mg, 80%) as yellow crystals, mp=148–150 °C; δ_H (400 MHz, $CDCl_3$) 2.53 (s, 6H), 7.21–7.32 (m, 4H), 7.35 (t, *J* 6.7 Hz, 2H), 7.86 (d, *J* 7.8 Hz, 2H); δ_C (100 MHz, $CDCl_3$) 19.8, 121.9, 122.7, 124.2, 124.5, 129.8, 138.8, 139.4, 139.6; ν_{max} (liquid film) 730, 770, 970, 1380, 1470, 2850, 2980 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 380.9872, requires $C_{18}H_{14}S_4Na^+$ 380.9876.

*4.1.3.4. 2-[2-(Butylsulfanyl)phenyl]thieno[3,2-b][1]benzothiophene (****27****).* Compound **17** (1 mmol, 296 mg) in 5 mL THF was treated with *n*-BuLi (2.5 mmol) at 0 °C and stirred additionally for 2 h at room temperature. Methanol (0.5 mL) was added and volatiles evaporated. Residue was taken in dichloromethane–aqueous NH_4Cl, organic phase was separated, dried over sodium sulfate, evaporated, and purified by column chromatography (hexane–ethyl acetate=20:1, silica gel) to yield **32** (149 mg, 42%) as colorless oil; δ_H (400 MHz, $CDCl_3$) 0.91 (t, *J* 7.3 Hz, 3H) 1.37–1.50 (m, 2H) 1.63 (quint, *J* 7.4 Hz, 2H) 2.89 (t, *J* 7.5 Hz, 2H) 7.20–7.27 (m, 1H)

7.31–7.39 (m, 2H) 7.40–7.46 (m, 2H) 7.48–7.52 (m, 1H) 7.51 (s, 1H) 7.83–7.91 (m, 2H); δ_C (100 MHz, $CDCl_3$) 13.6, 22.1, 30.7, 33.2, 120.6, 121.0, 123.8, 124.4, 124.6, 125.4, 128.2, 128.6, 131.1, 132.8, 134.2, 136.8, 137.6, 142.2, 144.2; oil; ν_{max} (liquid film) 730, 760, 840, 1080, 1260, 1350, 1450, 1470, 1590, 2870, 2970, 3050 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 377.0459, requires $C_{20}H_{18}S_3Na^+$ 377.0463.

For ring-opening of **17** two alternative structures are possible as result of butyllithium attack either on central (**28**) or side sulfur atom (**27**), which are hardly distinguished by ordinary NMR. The correct structure **27** was signed based on COSY $^1H-^1H$ and HMBC correlations.

*4.1.4. Ring-openings of sulflower **16**.* To a suspension of sulflower **16** (224 mg, 0.5 mmol) in 20 mL of THF MeLi (5 mmol) was added at 0 °C. The reaction was additionally stirred at room temperature for 2 h and dimethyl disulfide (940 mg, 10 mmol in 1 mL THF) was added and additionally stirred overnight. Volatiles were removed in vacuum and residue taken in dichloromethane–H_2O, organic phase was separated, dried over sodium sulfate, solvent evaporated and volatiles removed in vacuum. Column chromatography of the residue (hexane–ethyl acetate=20:1, silica gel) gave **25** (95 mg, 30%) and **26** (73 mg, 21%).

*4.1.4.1. 3,4,6,7,9,10-Hexakis(methylsulfanyl)-1,12-epithiocycloocta[1,2-c:3,4-c′:5,6-c″:7,8-c‴]tetrakisthiophene (**25**).* Mp >300 °C, decomp.; δ_H (400 MHz, $CDCl_3$) (s, 3H), 2.36 (s, 3H), 2.48 (s, 3H); δ_C (100 MHz, $CDCl_3$) 20.9, 21.1, 22.9, 131.0, 135.2, 136.5, 137.1, 137.1, 137.9, 138.0, 139.0; ν_{max} (liquid film) 730, 760, 780, 1430, 1470, 2840, 2890, 3060 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 656.8228, requires $C_{24}H_{18}S_{11}Na^+$ 656.8229.

*4.1.4.2. 1,3,4,6,7,9,10,12-Octakis(methylsulfanyl)cycloocta[1,2-c:3,4-c′:5,6-c″:7,8-c‴]tetrakisthiophene (**26**).* Mp >300 °C, decomp.; δ_H (400 MHz, $CDCl_3$) 2.36 (s, 3H); δ_C (100 MHz, $CDCl_3$) 21.0, 136.0, 137.3; ν_{max} (liquid film) 730.0, 763.5, 780.0, 1378.0, 1430.0, 1480.2, 2820.0, 2910.4, 3050 cm^{-1}; HRESI-TOF$^+$: MH^+, found 696.8599, requires $C_{24}H_{24}S_{12}H^+$ 696.8599.

*4.1.5. Deprotonation of **31**. 1-(Methylsulfanyl)[1]benzothieno[3,2-b][1]benzothiophene (**34**).* Compound **18** (240 mg, 1 mmol) in THF (5 mL) was treated with 1.1 mmol of *n*-BuLi (solution in hexane) at −40 °C and stirred for 1 h at this temperature. Dimethyl disulfide (141 mg, 1.5 mmol) as solution in THF (1 mL) was added and the reaction was allowed to warm to room temperature. THF was removed in vacuo, residue was treated with aqueous NH_4Cl and dichloromethane (5 mL). Organic phase was separated, washed with water, and evaporated. Separation by column chromatography gave 250 mg (87%) of **34** as white powder; mp=141 °C; δ_H (400 MHz, $CDCl_3$) 2.67 (s, 3H), 7.38–7.50 (m, 4H), 7.77 (dd, *J* 7.8, 1.0 Hz, 1H), 7.93 (d, *J* 7.8 Hz, 2H); δ_C (100 MHz, $CDCl_3$) 16.9, 119.5, 121.6, 121.7, 124.0, 124.5, 124.9, 124.9, 125.0, 125.1, 125.6, 132.9, 133.0, 133.2, 133.8; ν_{max} (liquid film) 730, 759, 780, 1340, 1378, 1430, 1480, 2820, 2890 cm^{-1}; HRESI-TOF$^+$: MNa^+, found 308.9837, requires $C_{15}H_{10}S_3Na^+$ 308.9837.

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Supplementary data

NMR spectra and computational details are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.06.082.

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