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Synthesis of thiophenes from allenyl sulfones involving α,β-unsaturated sulfines as intermediates

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Abstract. The synthesis of thiophenes starting from allenyl sulfones, via intermediate formation of α,β-unsaturated sulfines, is described. The allenyl sulfones were synthesized by a [2,3]-sigmatropic rearrangement of appropriately substituted prop-2-ynyl sulfinates. Treatment of the allenyl sulfones with *n*-butyllithium and chlorotrimethylsilane gave α-silylated allenyl sulfones in almost quantitative yield, which, on heteroconjugate addition of organolithium reagents, gave the desired α-silyl carbanions. These reacted with sulfur dioxide to give the α,β-unsaturated sulfines, which underwent *in-situ* rearrangement to 2-sulfonylthiophenes. The yield of the thiophenes depends on the organolithium reagents used. The use of exocyclic allenyl sulfones was more troublesome, and a thiophene was obtained for only one example.

Introduction

During the past three decades, the synthesis of a large variety of substituted sulfines has been reported[1], but vinylsulfines [b] have, so far, received little attention. They have been prepared by oxidation of the corresponding α,β-unsaturated thiones[2], by rearrangement of vinylsulfinyl carbenes[3], by oxidation of 2,5-dimethylthiophene with singlet oxygen[4] and as intermediates in a thermal fragmentation of their formal dimers[5]. All these methods have a limited scope.

Oxidation of thiocarbonyl compounds is the most general route to sulfines[1], although there are some limitations regarding the availability of suitable starting materials. An alternative, and also general approach, to the synthesis of sulfines involves the Peterson alkylidenation of sulfur dioxide[1]. The α-silyl carbanions required for this method of preparation can be obtained either by deprotonation of appropriate silyl compounds[6] or by heteroconjugate addition[7] of alkyllithium to vinylsilanes[8].

This paper deals with a newly developed synthesis of vinylsulfines **D** involving heteroconjugate addition of a suitable nucleophile to α-silylallenyl sulfones **B**, as outlined in Scheme 1.

Attractive features of this reaction are that allenyl sulfones **A** are readily available starting materials[9] and that heteroconjugate addition of various nucleophiles to these unsaturated sulfones has already been demonstrated[10,11]. α-Silylation of these allenyl sulfones is quite feasible, thus providing the required substrates **B**. *Takayama* et al.[11] synthesized a silylated allenyl sulfone, substituted at γ-C with a steroïd skeleton, using a similar route.

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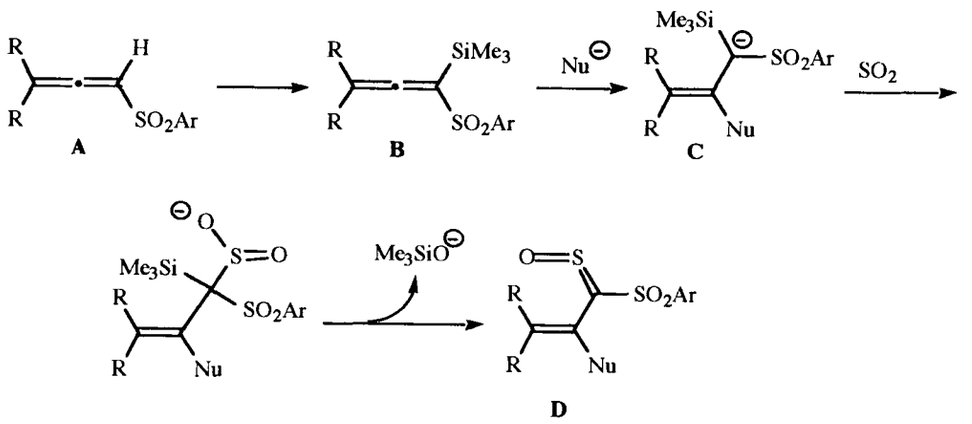
[b] Sulfines are thione oxides.

Results and discussion

Synthesis of allenyl sulfones

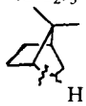
For the synthesis of allenyl sulfones, a [2,3]-sigmatropic rearrangement of appropriately substituted propargyl sulfinates was chosen[12]. The acetylenic alcohols derived from cyclic ketones were prepared starting from addition of (trimethylsilyl)acetylene, instead of acetylene itself. Three cyclic ketones were incorporated in this study, *viz.* cyclopentanone (**1a**), cyclohexanone (**1b**) and D(+)-camphor (**1c**). The sequence of events is depicted in the Scheme 2, path A. Treatment of the lithium (trimethylsilyl)acetylide with cyclic ketone gave **2a,b,c**. Subsequently, a reaction with *p*-toluenesulfinyl chloride in the presence of triethylamine produced the sulfinates **3a,b,c** almost quantitatively. Then thermal rearrangement in refluxing acetonitrile in the presence of 2,6-lutidine gave the allenyl sulfones **4a,b,c** in good overall yields (see Table I). It should be noted that complete desilylation took place in this step partly during rearrangement (according to ^{1}H-NMR of the crude product) and for the remaining part during column chromatography on silica gel.

Non-exocyclic allenyl sulfones **4d-h** were synthesized from prop-2-ynyl sulfinates in a manner which differs slightly from the method used above (Scheme 2, path B). This sequence of reactions allows the preparation of a variety of allenyl sulfones suitable for this study. The required prop-2-ynyl sulfinates **3d-h** are obtained from alcohols **2d-h** and *p*-toluenesulfinyl chloride in the presence of triethylamine. Heating of these sulfinates **3d-h** in acetonitrile in the presence of 2,6-lutidine as the base, results in [2,3]-sigmatropic rearrangement to allenyl sulfones **4** in good yield. The overall yields are collected in Table 1. It should be noted that the rearrangement of **3d** ($R^1 = R^2 =$ H) requires modified conditions, *viz.* heating in chlorobenzene in the presence of calcium carbonate as



Scheme 1.

Table I. Synthesis of allenyl sulfones 4.

Substrate	R^1	R^2	Product	Yield (%)
3a	-$(CH_2)_4$-		4a	65
2b	-$(CH_2)_5$-		4b	58
2c			4c	61
3d	H	H	4d	75 [a]
3e	Me	Me	4e	67
2f	Et	Et	4f	58
2g	Me	Et	4g	72
2h	Me	Ph	4h	78

[a] Perfored in chlorobenzene containing $CaCO_3$.

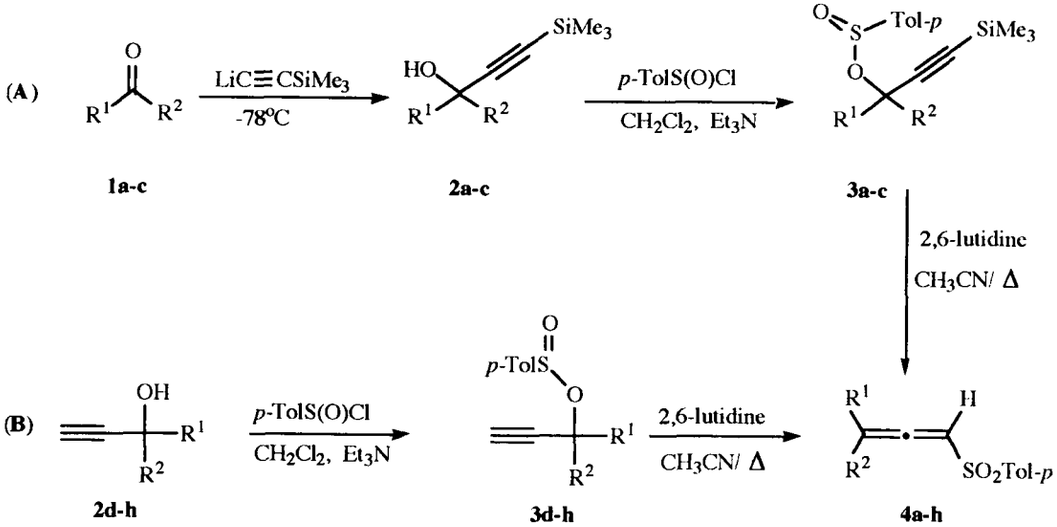
the base. When the usual conditions (*i.e.* heating in acetonitrile containing 2,6-lutidine) are employed a further rearrangement to prop-2-ynyl 4-tolyl sulfone takes place, whereby 2,6-lutidine serves as proton-transfer agent. The use of a heterogeneous base, such as $CaCO_3$, prevents this prototopic shift. Allene **4h** was formed spontaneously from sulfinate **3h**; in fact, this sulfinate could not be isolated.

Silylation of allenyl sulfones

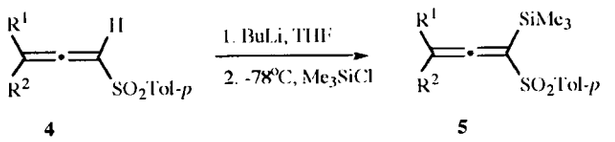
Treatment of sulfones **4d-h** with 1.1 equivalent of *n*-butyllithium at −78°C for 3 hours, followed by addition of 1.2 equivalent of chlorotrimethylsilane at the same temperature, resulted in the formation of the silylated allenyl sulfones **5d-h**, in almost quantitative yield (Scheme 3). For the silylation of exocyclic allenyl sulfones **4a,b,c**, the yields of **5a,b,c** were somewhat lower (see Experimental).

It should be emphasized that the silylation conditions are very critical. In initial experiments the reaction mixture obtained after treatment of allenyl sulfone **4e** with 1.1 equivalent of *n*-butyllithium at −78°C, was allowed to reach 0°C before chlorotrimethylsilane was added. With this minor change in conditions, dimer **6** was obtained as the sole product in high yield.

Formation of this dimer only needed a catalytic amount of base. Almost quantitative dimerization was achieved by treatment of **4e** with 10 molar% of *n*-butyllithium. The dimerization is essentially a Michael addition of lithiated sulfone **4e** to the substrate itself[10d]. A second remark concerns the purification of silylated allenyl sulfones **5**.

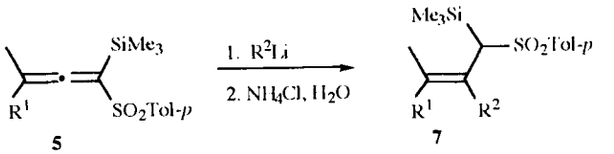


Scheme 2.



4 5

Scheme 3.



5 7

Scheme 5.

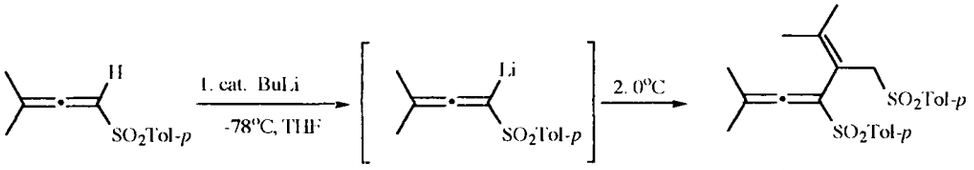
The usual chromatographic work-up cannot be applied, due to the instability of the products. Desilylation readily takes place during chromatography on alumina and silica gel. Attempted recrystallization gave almost complete desilylation. From a spectral analysis, it was concluded that the desilylation reaction described above takes place virtually quantitatively. Therefore, these products were used without further purification in the next reaction step. Silylation of all allenyl sulfones took place in a satisfactory manner, provided the proper conditions were applied. α-Silylallenyl sulfones are practically unknown[11], probably because of their instability.

Heteroconjugate addition to α-silylallenyl sulfones

The addition of an alkyllithium to α-silylallenyl sulfones was tested with substrate **5e** and methyllithium as the reagent. Treatment of allenyl sulfone **5e** with methyllithium (1.1 equivalents) at -78°C gave, after quenching with aqueous ammonium chloride, product **7a**, in quantitative yield. Similary, *n*-butyllithium gave product **7b**.
No loss of the silyl substituent was observed. Conjugate addition of the methyl group to allenyl sulfone **5g** using either methyllithium, methylmagnesium iodide or dimethylcopperlithium gave a mixture of geometrically isomeric **7d$_1$** and **7d$_2$** in a ratio of 63/37 (see Scheme 6). In both isomers the methyl signal of the ethyl group is shifted to a higher field by 0.5–0.6 ppm in comparison with the starting material, probably as the result of a deshielding by the aromatic ring. Mass spectral analysis and ^{13}C-NMR spectra confirmed that **7d** consists of a mixture of geometrical isomers in ratio of *ca.* 3:2.
Addition of phenyllithium to **5e** was without success, only unindentified products were obtained. However, diphenylcopperlithium gave the desired conjugated product **7c** in good yield. The results are collected in Table II.

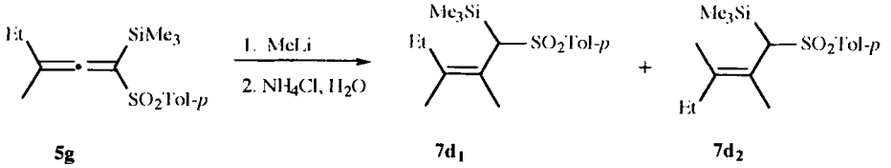
Thiophene formation

The aim of this project was to react the α-silyl carbanions obtained by the heteroconjugate addition of nucleophiles to α-silylallenyl sulfones **5**, with sulfur dioxide in order to synthesize α,β-unsaturated sulfines, as outlined in Scheme 1. Accordingly, the heteroconjugate adduct obtained from **5e** and 3 equivalents of methyllithium was treated with a solution of an excess of sulfur dioxide in THF at -78°C. The expected *p*-tolylsulfonyl-substituted sulfines **D** (see Scheme 1) are usually reactive species and therefore, 2,3-dimethylbuta-1,3-diene was added to the reaction mixture as a typical sulfine-trapping agent[13,6b]. Surprisingly, no sulfine adduct was obtained, but 3,4-dimethyl-2-(*p*-tolylsulfonyl)thiophene **9a** was isolated instead (Scheme 7). The same result was obtained in the absence of 2,3-dimethylbuta-1,3-diene. When 1.1 equivalent of methyllithium was employed instead of 3 equivalents during the inital heteroconjugate addition, the same yield of the thiophene was obtained. Apparently, the intramolecular



4e 6

Scheme 4.

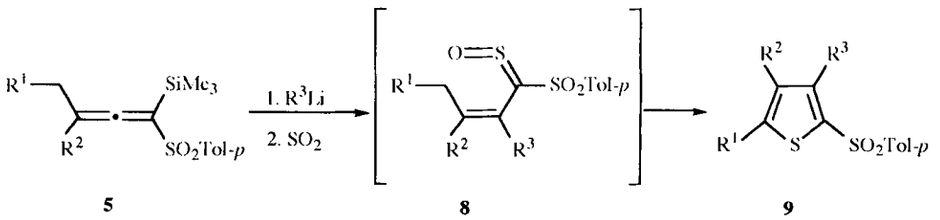


5g 7d$_1$ 7d$_2$

Scheme 6.

Table II. Heteroconjugate addition of organometallics to α-silylallenyl sulfones 5.

Substrate	R^2	R^2	Reagent	Product	Yield (%)
5e	Me	Me	MeLi	**7a**	100
5e	Me	Bu	BuLi	**7b**	95
5e	Me	Ph	Ph_2CuLi	**7c**	75
5g	Et	Me	MeLi	**7d**	92
5g	Et	Me	MeMgI	**7d**	97
5g	Et	Me	Me_2CuLi	**7d**	99
5h	Ph	Me	MeLi	**7e**	75



5 8 9

Scheme 7.

cyclization to thiophenes, shown in Scheme 7, is very efficient, because trapping of the intermediate sulfonyl-substituted sulfine with excess of 2,3-dimethylbuta-1,3-diene could not be accomplished.

Thiophene formation was also accomplished in 75% yield starting from heteroconjugate adduct **7a** (Scheme 6) by successive treatment with 1.1 equivalent of *n*-butyllithium and excess sulfur dioxide in THF. It should be noted that in the reaction mentioned above, the anion obtained by heteroconjugate addition or deprotonation, is added to a THF solution containing an excess of sulfur dioxide. This procedure was generally followed in the synthesis of sulfines by the modified Peterson reaction.

Thiophene formation was also studied for α-silylallenyl sulfones **5** (according to the general Scheme 7). The results are collected in Table III. The data reveal that this thiophene formation is sensitive to the steric bulk of the organometallic reagent used in the heteroconjugate addition. With *tert*-butyllithium as the nucleophile, no intramolecular cyclization could be accomplished, instead the *tert*-butyl adduct **7** (R^1=Me and R^2=^{t}Bu) was obtained (80%). It is conceivable that a sterically demanding group has a negative influence on the cyclization (see intermediates in Scheme 9). When diphenylcopperlithium is used, the yield of thiophene is low.

When γ-C bears an ethyl group a tetrasubstituted thiophene is obtained. The reaction of substrate **5f** with methyllithium as reagent in the heteroconjugate addition leads to thiophene **9h** in an acceptable yield. If γ-C has an ethyl and a methyl substituent, as in substrate **5g**, heteroconjugate addition of methyllithium followed by reaction with sulfur dioxide leads to two products, *viz.* **9i** and **9j** (Scheme 8). The ratio of the two thiophenes formed was determined by ^{1}H-NMR, and has the statistically determined ratio **9i**/**9j** = 3/2. The two thiophenes could not be separated by column chromatography and were isolated in a combined yield of 36%.

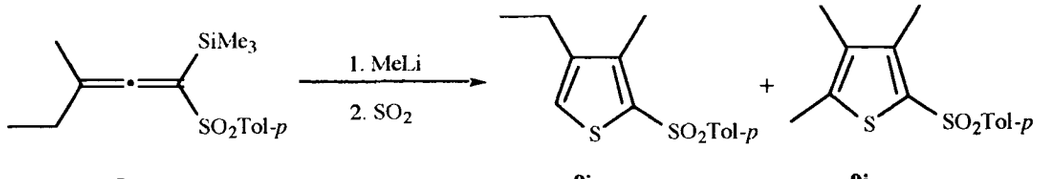
α-Silylallenyl sulfone **5d** having two hydrogen atoms at γ-C, does not undergo the desired heteroconjugate addition upon reaction with methyllithium, only unidentified products were obtained. Consequently, the subsequent reaction with sulfur dioxide was not carried out.

The novel cycloaromatization, shown in Scheme 7, can be rationalized mechanistically by assuming that initially an α,β-unsaturated sulfine **8** is formed as expected according to Scheme 1. Subsequent proton abstraction, with trimethylsilanolate acting as the base, from the γ-carbon atom of **8** leads to allylic anion **10a**, alternatively described in its mesomeric form **10b** (see Scheme 9). Intramolecular addition, which is conceivable from either mesomeric form of anion **10**, leads to product **10c**. Deoxygenation and concomitant aromatization can be envisaged by invoking a reaction with the excess sulfur dioxide as pictured in structure **10d**. The elimination of SO_3^{2-} is reminiscent of a novel Pummerer-type rearrangement, induced by sulfur dioxide under basic conditions.

Recently *Baudin* et al.[14] also found a similar rearrangement of α,β-unsaturated sulfines to thiophenes. It was found that these thioaldehyde *S*-oxides underwent a rearrangement in which a thiophene derivative was formed.

Table III Thiophene formation from α-silylallenyl sulfones **5**.

Substrate	R^1	R^2	R^3Li	Product	Yield (%)
5e	H	Me	Me	**9a**	75
5e	H	Me	Et	**9b**	53
5e	H	Me	*n*-Bu	**9c**	35
5e	H	Me	*t*-Bu	**9d**	–
5e	H	Me	Ph_2Cu	**9e**	10
5h	H	Ph	Me	**9f**	57
5h	H	Ph	Et	**9g**	38
5f	Me	Et	Me	**9h**	63

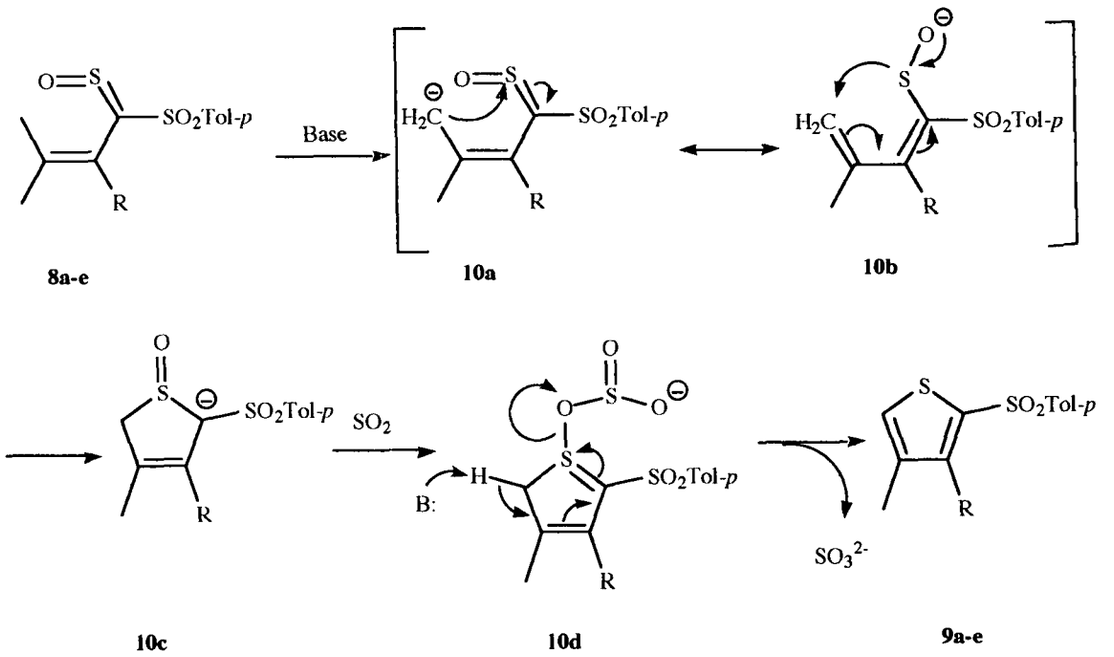


5g **9i** **9j**

3:2

combined yield 36%

Scheme 8.

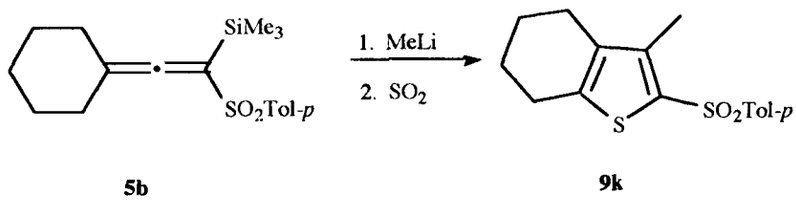


Scheme 9.

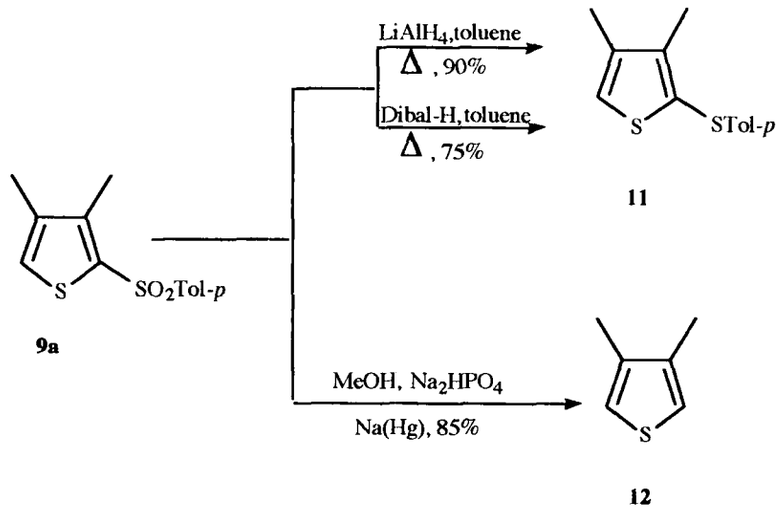
However, for the corresponding thioketone *S*-oxides (sulfines) no thiophene formation was observed. A mechanism analogous to that shown in Scheme 9 was proposed for the rearrangement.

The exocyclic α-silylallenyl sulfones **5a,b,c** were similarly treated with methyllithium at low temperature and subsequently subjected to a reaction with excess sulfur dioxide in order to accomplish thiophene formation. The silylallenyl sulfone **5b** derived from cyclohexanone gave the expected thiophene derivative **9k** in 27% yield (Scheme 10).

As mentioned above, the α-silylallenyl sulfones **5a** and **5c** derived from cyclopentanone and D(+)-camphor, respectively, could not be obtained in quantitative yield. Therefore, crude (impure) starting material had to be used in these instances. The attempted thiophene formation failed with these substrates, probably due to the impurity of the starting material, although the ring strain in the resulting



Scheme 10.



Scheme 11.

thiophenes that would have been formed in these reactions, may hamper their formation.

Some reactions of thiophene **9a**

Thiophene **9a** was subjected to desulfonylating conditions, *i.e.* sodium amalgam in buffered methanol. The *p*-tolylsulfonyl group was smoothly removed to give 3,4-dimethylthiophene[22] **12** in high yield (Scheme 11). This reaction provides unequivocal evidence for the structure of this thiophene produced in the intramolecular cyclization reaction shown in Scheme 9. Reduction of the sulfone function was readily accomplished with lithium aluminium hydride as well as with diisobutylaluminium hydride, giving thioether **11** in good yield (Scheme 11).

Concluding remarks

A variety of allenyl sulfones has been synthesized by the sigmatropic rearrangement of *p*-toluenesulfinates derived from alkynols using a literature procedure. These allenyl sulfones can readily be α-silylated in practically quantitative yield. However, the resulting α-silylallenyl sulfones undergo desilylation during purification.
Heteroconjugate addition of various organometallic reagents to α-silylallenyl sulfones can be accomplished in high yields. An interesting new reaction was discovered when the initial adducts obtained during the heteroconjugate addition were subjected to treatment with sulfur dioxide. Instead of the expected α,β-unsaturated sulfine, intramolecular cyclization to thiophenes has taken place. The thiophene formation was rationalized by invoking an intramolecular carbanion addition to initially formed α,β-unsaturated sulfine, followed by a novel Pummerer-type aromatization reaction.

Acknowledgements

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Experimental section

General remarks

IR spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. The 90-MHz ^{1}H-NMR spectra were recorded on a Varian EM-390 spectrometer (Me_4Si as internal standard) and for the 100-MHz ^{1}H-NMR spectra, a Bruker AC 100 spectrometer (Me_4Si as internal standard) was used. For the ^{13}C-NMR spectra, a Bruker AC 100 spectrometer ($CDCl_3$ as internal standard) was used. For mass spectra a double focussing VG7070E mass spectrometer was used. Melting points were measured with a Reichert Thermopan microscope and are uncorrected. Elemental analyses were performed on a Carlo Erba Instruments CHNS-O EA 1108 element analyzer. Dichloromethane was distilled from P_2O_5. Tetrahydrofuran was distilled from $LiAlH_4$. Diethyl ether was distilled from NaH. Petroleum ether 60–80 was distilled from CaH_2. Hexane was distilled from CaH_2. Acetonitrile was distilled from P_2O_5. Ethyl acetate was distilled from K_2CO_3. All reactions were performed in an argon atmosphere. n-Butyllithium was used as a standard solution of 1.6 M in hexane. Methyllithium was used as a standard solution of 1.6 M in diethyl ether, salt-free. Phenyllithium was used as a standard solution of 2.0 M in benzene/diethyl ether. *p*-Toluenesulfinyl chloride was prepared as described in the literature[15]. Thin-layer chromatography (TLC) was carried out on Merck precoated silica gel 60 F254 plates (0.25 mm) using the eluents indicated. Spots were visualized with UV and spraying with 5% H_2SO_4 solution in ethanol followed by charring at 140°C for 15 min. Flash chromatography was carried out at a pressure of *ca.* 1.5 bar, a column length of 15–25 cm and a column diameter of 1–4 cm, using Merck Kieselgel 60H, unless stated otherwise.

General procedure for the synthesis of alkynols **2a-c**

n-Butyllithium (1.6 M in hexane, 1.1 equiv., 0.03 mol, 20.7 ml) was added to a stirred and cooled (−78°C) solution of (trimethylsilyl) acetylene (2.94 g, 0.03 mol) in diethyl ether. After a period of 1 h, the mixture was treated with a solution of the appropriate cyclic ketone (0.8 equiv.) in diethyl ether (50 ml) and stirring was continued for 1 h at −78°C and then 1 h at 0°C. The resulting mixture was washed (3×) with a saturated aqueous ammonium chloride solution and the organic layers were dried over magnesium sulfate and concentrated *in vacuo* to give the corresponding alkynols.
The following compounds were prepared:

1-[2-(Trimethylsilyl)ethynyl]cyclopentan-1-ol (**2a**). (4.20 g, 97%) from cyclopentanone **1a** (2.0 g, 23 mmol). ^{1}H-NMR ($CDCl_3$): δ 0.00 (s, 9H, $SiMe_3$), 1.3–1.9 (m, 11H, cyclopentane), 2.1–2.3 (br s, 1H, –OH) ppm.

1-[2-(Trimethylsilyl)ethynyl]cyclohexan-1-ol (**2b**). (4.64 g, 99%) from cyclohexanone **1b** (2.35 g, 23.9 mmol), m.p. 72–74°C. ^{1}H-NMR ($CDCl_3$): δ 0.00 (s, 9H, $SiMe_3$), 1.9–2.8 (m, 10H, cyclohexane), 2.9 (br s, 1H, –OH) ppm.

2-[2-(trimethylsilyl)ethynyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**2c**). (5.61 g, 99%) from D-(+)-camphor **1c** (3.33 g, 23.8 mmol). ^{1}H-NMR ($CDCl_3$): δ 0.00 (s, 9H, $SiMe_3$), 1.60 (s, 3H, CCH_3), 1.9 (s, 3H, CCH_3), 2.0–3.4 (m, 8H, camphor) ppm.

General procedure for the synthesis of sulfinate esters **3a-h**

p-Toluenesulfinyl chloride (2.62 g, 15 mmol) dissolved in dichloromethane (50 ml) was added dropwise in 10 min intervals to a solution of derivative **2a-h** (15 mmol) and triethylamine (1.52 g, 15 mmol) in dichloromethane (150 ml), kept at −78°C. After 2 h of stirring at −78°C and 1 h at 0°C, the reaction mixture was extracted with a saturated aqueous ammonium chloride solution (3×30 ml). The organic layer was dried over magnesium sulfate and concentrated *in vacuo*.

1-[2-(Trimethylsilyl)ethynyl]cyclopentyl p-*toluenesulfinate* (**3a**). Starting from **2a** (2.73 g, 15 mmol), product **3a** was synthesized according to the general procedure in a yield of 4.75 g (99%). ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 1.3–2.0 (m, 8H, cyclopentane), 2.2 (s, 3H, $ArCH_3$), 7.0 and 7.4 (AB, 4H, *J* 9.0 Hz, Ar) ppm.

Prop-2-ynyl p-*toluenesulfinate* (**3d**). Starting from prop-2-yn-1-ol **2d** (0.84 g, 15 mmol), product **3d** was synthesized according to the general procedure in a yield of 2.85 g (98%). ^{1}H-NMR ($CDCl_3$): δ 2.1 (s, 3H, Ar-CH_3), 2.3 (t, 1H, *J* 3Hz, C–H), 4.1 (dd, 2H, J_1 18 Hz, J_2 3 Hz, O–CH_2–), 7.0 and 7.3 (AB, *J* 9 Hz, 4H, Ar) ppm.

2-Methyl-but-3-yn-2-yl p-*toluenesulfinate* (**3e**). Starting from 2-methyl-but-3-yn-2-ol **2e** (1.26 g, 15 mmol), product *3e* was synthesized according to the general procedure in a yield of 3.03 g (91%). m.p. 66–67°C (lit.[16] m.p. 67–69°C).

Propa-1,2-diene-1-yl p-*tolyl sulfone* (**4d**)

A stirred mixture of **3d** (2.91 g, 15 mmol) and calcium carbonate (1.50 g, 15 mmol) in chlorobenzene (200 ml) was heated under reflux for 12 h. Then the mixture was cooled to room temperature, treated with 10 g of activated carbon and stirred at room temperature for 30 min. The insoluble material was removed by filtration through a layer of hyflo (1 cm), washed with dichloromethane (3×25 ml) and the combined filtrate and washings were concentated *in vacuo*. The resulting crude material was recrystallized from toluene/hexane, to give 2.18 g (75%) of **4d**, as pale yellow needles, m.p. 82–84°C. (lit.[17] m.p. 88°C.). IR(KBr): ν 1150 (S=O), 1320 (S=O), 1940 (C=C=C) cm^{-1}. MS (EI) *m/z* 194 (M^+).

General procedure for the synthesis of substituted allenyl sulfones **4a-h**

A solution of sulfinate ester **3a-h** (10 mmol) and 2,6-lutidine (2,6-dimethylpyridine, 1 equiv, 10 mmol, 1.07 g) in 200 ml of acetonitrile

was heated under reflux for 6 h Then the reaction mixture was cooled to room temperature, activated carbon was added and the mixture was stirred for 30 min, and subsequently filtered over a glass-filter with a layer of hyflo (1.0 cm). The solids were washed with acetonitrile (3×10 ml), the combined organic layers were concentrated *in vacuo*.

2-Cyclopentylideneehenyl p-*tolyl sulfone* (**4a**). Starting from **3a** (2.48 g, 7.75 mmol), product **4a** was synthesized according to the general procedure. The reaction product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 1.44 g (58%) of **4a**, m.p. 99–102°C. ^{1}H-NMR ($CDCl_3$): δ 1.6–1.8 (m, 4H, $-CH_2-CH_2-CH_2-CH_2-$), 2.3–2.6 (m, 7H, $ArCH_3$; $-CH_2-CH_2-CH_2-CH_2-$), 6.1 (d, 1H, *J* 8 Hz, =C–H), 7.2 and 7.6 (AB, 4H, *J* 8 Hz, Ar) ppm. IR (KBr): ν 1950 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}. MS(EI) *m/z*: 248 (M^+).

2-Cyclohexylideneethenly p-*tolyl sulfone* (**4b**). Starting from **2b** (1.56 g, 7.94 mmol) and *p*-toluenesulfinyl chloride (1.39 g, 7.94 mmol), product **3b** was synthesized according to the general procedure for the synthesis of sulfinate esters in a yield of 2.65 g, (100%). The crude product was immediately treated according to the general procedure for the synthesis of allenyl sulfones. The thus obtained reaction product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 12/1, v/v) to give 1.72 g (65%) of **4b**, m.p. 70°C (lit.[16] m.p. 77–78°C).

2-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-yidene)ethenyl p-*tolyl sulfone* (**4c**). Starting from **2c** (2.05 g, 8.20 mmol) and *p*-toluenesulfinyl chloride (1.43 g, 8.20 mmol), product **3c** was synthesized according to the general procedure for the synthesis of sulfinate esters in a yield of 3.20 g (100%). The crude product was immediately treated according to the general procedure for the synthesis of allenyl sulfones. The thus obtained reaction product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v), to give 1.95 g (61%) of **4c**, m.p. 62°C. ^{1}H-NMR ($CDCl_3$): δ 0.65 (s, 3H, CCH_3), δ 0.7 (s, 3H, CCH_3), δ 0.75 (s, 3H, CCH_3), δ 0.9–2.2 (m, 7H, camphor-H's), 5.85–6.0 (m, 1H, =C–H), 7.1 and 7.6 (AB, 4H, *J* 7.5 Hz, Ar) ppm.

3-Methylbuta-1,2-dien-1-yl p-*tolyl sulfone* (**4e**). Starting from 2-methylbut-3-yn-2-yl *p*-toluenesulfinate **3e** (2.66 g, 11.98 mmol), product **4e** was synthesized according to the general procedure. The reaction product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 3/1, v/v) to give 1.78 g (67%) of **4e**; m.p. 73°C (lit[16] m.p. 77–78°C). ^{1}H-NMR ($CDCl_3$): δ 1.8 [d, *J* 3 Hz, 6H, $=C-(CH_3)_2$], 2.4 (s, 3H, $Ar-CH_3$), 6.0 (septet, 1H, =C–H), 7.3 and 7.7 (AB, 4H, *J* 7.5 Hz, Ar) ppm. IR (KBr): ν 1940 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}. MS (EI) *m/z*: 222 (M^+).

3-Ethylpenta-1,2-dienyl p-*tolyl sulfone* (**4f**). Starting from **2f** (1.456 g, 13.0 mmol), and *p*-toluenesulfinyl chloride (2.27 g, 13.0 mmol) sulfinate ester **3f** was synthesized according to the general procedure for the synthesis of sulfinate esters to give 3.25 g (100%) of **3f**. This was immediately treated according to the general procedure for the synthesis of allenyl sulfones. The thus obtained reaction product was purified by crystallization from toluene/hexane to give 1.89 g (58%) of **4f**; m.p. 50°C (lit.[16] m.p. 49–51°C). IR (KBr): ν 1940 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}.

3-Methylpenta-1,2-dienyl p-*tolyl sulfone* (**4g**). Starting from **2g** (1.07 g, 11.02 mmol) and *p*-toluenesulfinyl chloride (1.92 g, 11.02 mmol), sulfinate ester **3g** was synthesized according to the general procedure for the synthesis of sulfinate esters to give 2.60 g (100%) of **3g**. The crude product was immediately treated according to the general procedure for the synthesis of allenyl sulfones. The thus obtained reaction product was purified by crystallization from toluene/hexane to give 1.872 g (72%) of **4g**; m.p. 70°C (lit.[18] m.p. 70–71°C). ^{1}H-NMR ($CDCl_3$): δ 1.0 (t, 3H, *J* 7.5 Hz, $-CH_2CH_3$), 1.8 (d, 3H, *J* 3Hz, $=C-CH_3$), 2.1 (m, 2H, $=C-CH_2-$), 2.4 (s, 3H, $Ar-CH_3$), 6.1–6.2 (m, 1H, =C–H), 7.3 and 7.8 (AB, 4H, *J* 7.5 Hz, Ar) ppm. IR (KBr): ν 1940 (C=C=C), 1310 (SO_2), 1140 (SO_2) cm^{-1}.

3-Phenyl-buta-1,2-diene-1-yl p-tolyl sulfone (**4h**). Starting from **2h** (1.68 g, 11.5 mmol) and *p*-toluenesulfinyl chloride (2.01 g, 11.5 mmol), sulfinate ester **3h** was synthesized according to the general procedure for the synthesis of sulfinate esters to give the allenyl sulfone **4h** as a yellow solid. The crude product was purified by crystallization from toluene/hexane, to give 2.54 g (78%) of **4h**; m.p. 99°C (lit.[17] m.p. 99–100°C). IR (KBr): ν 1940 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}.

General procedure for the synthesis of silylallenyl sulfones (**5a-h**)

A solution of allenyl sulfones **4a-h** (5 mmol) in THF (25 ml) was added to a solution of *n*-butyllithium (1.1 equiv, 1.6 M in hexane) in THF (50 ml) while kept at −78°C. After stirring for 3 h at −78°C, chlorotrimethylsilane (1.2 equiv.) was added in one portion. After 3 h at −78°C, the reaction mixture was allowed to warm to room temperature. Saturated aqueous ammonium chloride solution was added and the aqueous layer was extracted with dichloromethane (3×25 ml), the combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*.

2-Cyclopentylidene-1-(trimethylsilyl)ethen-1-yl p-*tolyl sulfone* (**5a**). Starting from **4a** (1.44 g, 4.5 mmol), *n*-butyllithium (3.1 ml, 1.6 M, 4.95 mmol) and chlorotrimethylsilane (0.586 g, 5.4 mmol), product **5a** was synthesized according to the general procedure, to give a mixture of starting material and product which could not be separated. This mixture was used as such in further experiments.

2-Cyclohexylidene-1-(trimethylsilyl)ethen-1-yl p-*tolyl sulfone* (**5b**). Starting from **4b** (1.72 g, 5.16 mmol), *n*-butyllithium (3.55 ml, 1.6 M, 5.68 mmol) and chlorotrimethylsilane (0.672 g, 6.19 mmol) product **5b** was synthesized according to the general procedure, to give 2.1 g (100%) of **5b** as an oil. ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 0.9–1.3 (m, 6H, $-CH_2-CH_2-CH_2-CH_2-CH_2-$), 1.5–1.9 (m, 4H, $-CH_2-CH_2-CH_2-CH_2-CH_2-$), 2.2 (s, 3H, $Ar-CH_3$), 7.1 and 7.5 (AB, 4H, *J* 8.0 Hz, Ar) ppm.

p-*Tolyl 2-(1.7.7-trimethylbicyclo[2.2.1]hept-2-ylidene)-1-(trimethylsilyl)ethenyl sulfone* (**5c**). Starting from **4c** (1.95 g, 5.03 mmol), *n*-butyllithium (3.5 ml,1.6 M, 5.53 mmol) and chlorotrimethylsilane (0.655 g, 6.04 mmol), product **5c** was synthesized according to the general procedure, to give a mixture of starting material and product which could not be separated. This mixture was used as such in further experiments.

p-*Tolyl 1-(trimethylsilyl)propa-1,2-dien-1-yl sulfone* (**5d**). Starting from **4d** (1.45 g, 7.5 mmol), *n*-butyllithium (5.2 ml, 1.6 M, 8.25 mmol) and chlorotrimethylsilane (0.977 g, 9.0 mmol) product **5d** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 9/1, v/v), to give **5d** as a light yellow solid, in a yield of 0.66 g (33%), m.p. 66–68°C. ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 2.3 (s, 3H, $Ar-CH_3$), 3.8 (s, 2H, $=CH_2$), 7.2 and 7.7 (AB, 4H, *J* 7.5 Hz, Ar) ppm. IR (CCl_4): ν 1940 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}. MS (EI) *m/z*:: 266 (M^+).

3-Methyl-1-(trimethylsilyl)buta-1,2-dien-1-yl p-*tolyl sulfone* (**5e**). Starting from **4e** (1.33 g, 6.0 mmol), *n*-butyllithium (4.2 ml, 1.6 M, 6.6 mmol) and chlorotrimethylsilane (0.781 g, 7.2 mmol) product **5e** was synthesized according to the general procedure, to give 1.76 g (100%) of **5e** as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 1.3 [s, 6H, $=C-(CH_3)_2$], 2.2 (s, 3H, $Ar-CH_3$), 7.0 and 7.5 (AB, 4H, *J* 8.0 Hz, Ar) ppm. IR(CCl_4): ν 1940 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}. MS (EI) *m/z*: 294 (M^+).

3-Ethyl-1(-trimethylsilyl)penta-1,2-dien-1-yl p-*tolyl sulfone* (**5f**). Starting from **4f** (2.0 g, 8.0 mmol), *n*-butyllithium (5.5 ml, 1.6 M, 8.8 mmol) and chlorotrimethylsilane (1.04 g, 9.6 mmol) product **5f** was synthesized according to the general procedure, to give 2.58 g (100%) of **5f**, m.p. 40°C. ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 0.5 (t, 6H, *J* 7.5 Hz, $-CH_2CH_3$), 1.7 (q, 4H, *J* 7.5 Hz, $=C-(CH_2-CH_3)_2$), 2.2 (s, 3H, $Ar-CH_3$), 7.1 and 7.5 (AB, 4H, *J* 7.5 Hz, Ar) ppm. IR (CCl_4): ν 1940 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}. MS (EI) *m/z*: 322 (M^+).

3-Methyl-1-(trimethylsilyl)penta-1,2-dien-1-yl p-*tolyl sulfone* (**5g**). Starting from **4g** (1.77 g, 7.6 mmol), *n*-butyllithium (5.23 ml, 1.6 M, 8.4 mmol) and chlorotrimethylsilane (0.99 g, 9.12 mmol), product **5g** was synthesized according to the general procedure to give 2.33 g (100%) of **5g** as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 0.6 (t, 2H, *J* 7.5 Hz, $-CH_2CH_3$), 1.4 (s, 3H, $=C-CH_3$), 1.7 (q, *J* 7.5 Hz, 2H, $=C-CH_2-CH_3$), 2.2 (s, 3H, $Ar-CH_3$), 7.1 and 7.5 (AB, 4H, *J* 7.5 Hz, Ar) ppm. IR (CCl_4): ν 1940 (C=C=C), 1310 (SO_2), 1140 (SO_2) cm^{-1}. MS (EI) *m/z*: 308 (M^+).

3-Phenyl-1-(trimethylsilyl)buta-1,2-dien-1-yl p-*tolyl sulfone* (**5h**). Starting from **4h** (1.70 g, 6.0 mmol), *n*-butyllithium (4.2 ml, 1.6 M, 6.6 mmol) and chlorotrimethylsilane (0.781 g, 7.2 mmol), product **5h** was synthesized according to the general procedure to give 2.13 g (100%) of **5h** as a yellow solid, m.p. 93°C. ^{1}H-NMR ($CDCl_3$): δ 0.2 (s, 9H, $SiMe_3$), 1.8 (s, 3H, =C–CH_3), 2.2 (s, 3H, Ar–CH_3), 7.0–7.3 (m, 7H, Ar), 7.6 (d, 2H, *J* 7.5 Hz, Ar) ppm. IR (KBr): ν 1950 (C=C=C), 1320 (SO_2), 1150 (SO_2) cm^{-1}. MS (EI) *m/z*: 356 (M^+).

*2,6-Dimethyl-5-[(*p-*tolylsulfonyl)methyl]-hepta-2,3,5-trien-4-yl* p-*tolyl sulfone* (**6**)

A solution of **4e** (1.33 g, 6.0 mmol) in THF (25 ml) was added to a solution of *n*-butyllithium (4.2 ml, 1.1 equiv, 1.6 M in hexane) in THF (50 ml) while kept at −78°C. After stirring for 2 h at −78°C and 30 min at 0°C, the reaction mixture was cooled to −78°C and chlorotrimethylsilane (0.781 g, 7.2 mmol, 1.2 equiv.) was added in one portion. After 3 h at −78°C, the reaction mixture was allowed to warm to room temperature. Saturated aqueous ammonium chloride solution was added and the aqueous layer was extracted with dichloromethane (3×25 ml), the combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The product was purified by crystallization from toluene/hexane to give 1.20 g (90%) of **6**. m.p. 138–142°C. (lit.[16] m.p. 142–144°C) IR (KBr): ν 1960 (C=C=C), 1315 (SO_2), 1140 (SO_2) cm^{-1}. MS (EI) *m/z*: 444 (M^+).

2,3-Dimethyl-1-(trimethylsilyl)but-2-en-1-yl p-*tolyl sulfone* (**7a**)

A solution of **5e** (0.29 g, 1.0 mmol) in dry THF (50 ml) was gradually added to a solution of methyllithium (1.1 mmol, 1.8 ml) in dry THF (75 ml), while kept at −78°C. After stirring for 3 h at −78°C the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (20 ml). The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 3/1, v/v) to give product **7a** as a light yellow oil, 0.306 g (100%). ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 0.7 (s, 3H, =C–CH_3), 1.2 (s, 3H, =C–CH_3), 1.5 (s, 3H, =C–CH_3), 2.0 (s, 3H, Ar–CH_3), 3.5 (s, 1H, –SO_2–CH–$SiMe_3$), 6.8 and 7.3 (AB, 4H, *J* 9.0 Hz, Ar) ppm. MS (EI) *m/z*: 310 (M^+).

2-Butyl-3-methyl-1-(trimethylsilyl)but-2-en-1-yl p-*tolyl sulfone* (**7b**)

A solution of **5e** (0.29 g, 1.0 mmol) in dry THF (50 ml) was gradually added to a solution of *n*-butyllithium (3.0 mmol, 1.8 ml) in dry THF (75 ml), while kept at −78°C under argon. After stirring for 3 h at −78°C the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (20 ml). The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 3/1, v/v) to give **7b** as a light yellow oil in a yield of 0.330 g (95%). ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 0.4–1.2 [m, 15H, –Bu; =C–$(CH_3)_2$], 2.0 (s, 3H, Ar–CH_3), 3.5 (s, 1H, –SO_2–CH–$SiMe_3$), 6.8 and 7.3 (AB, 4H, *J* 9.0 Hz, Ar) ppm. MS (EI) *m/z*: 352 (M^+).

3-Methyl-2-phenyl-1-(trimethylsilyl)but-2-en-1-yl p-*tolyl sulfone* (**7c**)

A solution of **5e** (0.29 g, 1.0 mmol) in dry THF (50 ml) was added dropwise to a solution of diphenylcopperlithium [synthesized from phenyllithium (6.0 mmol, 3.0 ml) and copper(I)iodide (0.571 g, 3.0 mmol)] in dry THF (75 ml), while kept at −78°C. After stirring for 3 h at −78°C, the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (20 ml). The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 12/1, v/v) to give **7c** as a light brown oil containing two inseparable stereoisomers (1:1) in a yield of 0.275 g (75%).
Isomer A. ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 1.2 (s, 3H, =C–CH_3), 2.1 (s, 3H, =C–CH_3), 2.3 (s, 3H, Ar–CH_3), 3.7 (s, 1H, –SO_2–CH–$SiMe_3$), 6.1–7.9 (m, 9H, Ar) ppm.
Isomer B. ^{1}H-NMR ($CDCl_3$): δ 0.4 (s, 9H, $SiMe_3$), 1.3 (s, 3H, C=C–CH_3), 1.4 (s, 3H, =C–CH_3), 2.3 (s, 3H, Ar–CH_3), 4.2 (s, 1H, –SO_2–CH–$SiMe_3$), 6.1–7.9 (m, 9H, Ar) ppm. MS (EI) *m/z*: 372 (M^+).

2,3-Dimethyl-1-(trimethylsilyl)-pent-2-en-1-yl p-*tolyl sulfone* (**7d**)

Procedure A. A solution of **5g** (0.25 g, 0.82 mmol) in dry THF (50 ml) was added dropwise to a solution of methyllithium (2.5 mmol, 1.54 ml) in dry THF (75 ml), while kept at −78°C. After stirring for 3 h at −78°C the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (20 ml). The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate/ 6/1, v/v) to give **7d** as a light yellow oil in a yield of 0.242 g (92%) as two isomers (A:B) in a ratio of 63:37, which could not be separated.
Isomer A. ^{1}H-NMR ($CDCl_3$): δ 0.33 (s, 9H, $SiMe_3$), 0.51 (t, 3H, *J* 7.5 Hz, –CH_2–CH_3), 1.22 (sextet, 1H, *J* 7.3 Hz, =C–CH_2–CH_3), 1.40 (sextet, 1H, *J* 7.3 Hz, =C–CH_2–CH_3), 1.49 [d, 3H, *J* 0.9 Hz, C=C(Et)–CH_3], 1.88 (s, 3H, Et–(Me)C=C–CH_3), 2.40 (s, 3H, Ar–CH_3), 3.89 (s, 1H, $SiCHSO_2$), 7.2 and 7.6 (AB, 4H, *J* 8.1 Hz, Ar) ppm. ^{13}C-NMR ($CDCl_3$): δ −0.02 [$Si(CH_3)_3$], 12.1 (–CH_2–CH_3), 17.6 (CH_3), 18.2 (CH_3), 21.5 (Ar–CH_3), 26.4 (–CH_2–CH_3), 62.4 ($SiCHSO_2$), 119.3 (Et–C=C–Me), 127.7 (o-C Tol), 128.9 (m-C Tol), 137.6 (p-C Tol), 138.1 (*ipso*-C Tol), 143.2 (Et–C=C–Me) ppm.
Isomer B. ^{1}H-NMR ($CDCl_3$): δ 0.32 (s, 9H, $SiMe_3$), 0.71 (t, 3H, *J* 7.5 Hz, –CH_2–CH_3), 1.02 (d, 3H, *J* 1.4 Hz, C=C(Et)–CH_3), 1.85 (dt, 1H, *J* 7.3 Hz, –CH_2–CH_3), 1.88 [s, 3H, Et–(Me)C=C–CH_3], 1.93 (dt, 1H, *J* 7.3 Hz, C–CH_2–CH_3), 2.40 (s, 3H, Ar–CH_3), 3.87 (s, 1H, $SiCHSO_2$), 7.2 and 7.6 (AB, 4H, *J* 8.1 Hz, Ar) ppm. ^{13}C-NMR ($CDCl_3$): δ −0.02 [$Si(CH_3)_3$], 11.5 (–CH_2–CH_3), 16.4 (CH_3), 17.6 (CH_3), 21.5 (Ar–CH_3), 27.8 (–CH_2–CH_3), 63.0 ($SiCHSO_2$), 119.3 (Et–C=C–Me), 127.7 (o-C Tol), 128.9 (m-C Tol), 137.6 (p-C Tol), 138.1 (*ipso*-C Tol), 143.2 (Et–C=C–Me) ppm.
Both isomers. IR (KBr): ν 1315 (SO_2), 1145 (SO_2)cm^{-1}. MS (EI) *m/z*: 324 (M^+), 73 (100%; $SiMe_3^+$).
Procedure B. A solution of **5g** (0.25 g, 0.82 mmol) in dry THF (50 ml) was added dropwise to a solution of dimethylcopperlithium [prepared from copper(I) iodide (0.463 g, 1.23 mmol) and methyllithium (3.0 ml, 2.5 mmol) at 0°C] in dry THF (75 ml), while kept at −78°C. After stirring for 3 h at −78°C the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (20 ml). The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give **7d** as a light yellow oil in a yield of 0.26 g (99%) as two isomers (A/B) in a ratio of 63/37. Spectral data, see above.
Procedure C. A solution of **5g** (0.25 g, 0.82 mmol) in dry THF (50 ml) was added dropwise to a solution of methylmagnesium iodide [prepared from methyl iodide (0.15 ml, 2.43 mmol) and magnesium (0.12 g, 4.86 mmol)] in dry THF (75 ml), while kept at −78°C. After stirring for 3 h at −78°C the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (20 ml). The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give **7d** as a light yellow oil in a yield of 0.258 g (97%) as two isomers (A/B) in a ratio of 63/37. Spectral data, see above.

2-Methyl-3-phenyl-1-(trimethylsilyl)but-2-ene-1-yl p-*tolyl sulfone* (**7e**)

A solution of **5h** (0.23 g, 0.65 mmol) in dry THF (50 ml) was added dropwise to a solution of methyllithium (1.94 mmol, 1.21 ml) in dry THF (75 ml), while kept at −78°C. After stirring for 3 h at −78°C the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (20 ml). The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate/6/1, v/v) to give product **7e** as a light yellow oil in a yield of 0.18 g (75%). ^{1}H-NMR ($CDCl_3$): δ 0.3 (s, 9H, $SiMe_3$), 1.71 (s, 3H, =CPh–CH_3), 2.03 (s, 3H, Ph–C=C–CH_3), 2.4 (s, 3H, Ar–CH_3), 3.7 (s, 1H, –SO_2–CH–Si), 6.1–6.2 (m, 2H, Ar), 6.9–7.1 (m, 3H, Ar), 7.2 and 7.4 (AB, *J* 8.4 Hz, 4H, Ar) ppm.

*General procedure for the synthesis of 2-(*p-*tolylsulfonyl)thiophenes* **9a-k**

A solution of silylallenyl sulfones **5a-h** (1.0 mmol) in dry THF (50 ml) was added dropwise to a solution of organolithium reagent (3 equiv.) in dry THF (75 ml), while kept at −78°C. After stirring for 3 h at

– 78°C, the reaction mixture was added (using a metal siphon) to a solution of an excess of sulfur dioxide in THF (100 ml) kept at – 78°C. After 12 h at – 78°C, the volatiles were evaporated *in vacuo* and the crude product was dissolved in diethyl ether and washed with a saturated aqueous ammonium chloride solution (3×20 ml). The organic layer was dried over magnesium sulfate and concentrated *in vacuo*.

*3,4-Dimethyl-2-(*p*-tolylsulfonyl)thiophene* (**9a**). Starting from **5e** (0.29 g, 1.0 mmol) and methyllithium (3.0 mmol, 1.9 ml) product **9a** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 3/1, v/v) to give 0.197 g (75%) of **9a** as a white solid, which was crystallized from toluene/hexane, m.p. 125°C. ^{1}H-NMR ($CDCl_3$): δ 2.1 (s, 3H, Ar–CH_3), 2.3 (s, 3H, Ar–CH_3), 2.4 (s, 3H, Ar–CH_3), 7.2 (s, 1H, thiophene-H), 7.3 and 7.8 (AB, 4H, *J* 7.5 Hz, Ar) ppm. IR(KBr): ν 1315 (SO_2), 1150 (SO_2) cm^{-1}. MS (EI) *m/z*: 266 (M^+). Anal. calcd. for $C_{13}H_{14}S_2O_2$: C 58.62, H 5.30, S 24.07; found: C 58.47, H 5.39, S 23.07%.

*3-Ethyl-4-methyl-2-(*p*-tolylsulfonyl)thiophene* (**9b**). Starting from **5e** (0.32 g, 1.1 mmol) and ethyllithium [4.4 mmol, prepared from ethyl bromide (0.78 ml, 4.9 mmol) and Li (0.08 g, 11,5 mmol) as described in the literature[16]] product **9b** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 2/1, v/v) to give 0.162 g (53%) of **9b** as a white solid, which was crystallized from toluene/hexane, m.p. 96°C. ^{1}H-NMR ($CDCl_3$): δ 1.0 (t, 3H, Ar–CH_2–CH_3), 2.2 (s, 3H, Ar–CH_3), 2.4 (s, 3H, Ar–CH_3), 2.8 (q, 2H, Ar–CH_2–CH_3), 7.2 (s, 1H, thiophene-H), 7.3 and 7.9 (AB, 4H, *J* 8.0 Hz, Ar) ppm. MS (EI) *m/z*: 280 (M^+). EI/HRMS *m/z*: 280.0594 ± 0.0005; calcd. for $C_{14}H_{16}S_2O_2$ (M^+): 280.0592.

*3-Butyl-4-methyl-2-(*p*-tolylsulfonyl)thiophene* (**9c**). Starting from **5e** (0.29 g, 1.0 mmol) and *n*-butyllithium (3.0 mmol, 1.9 ml), product **9c** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.106 g (35%) of **9c** as a white solid, which was crystallized from toluene/hexane, m.p. 98°C. ^{1}H-NMR ($CDCl_3$): δ 0.9 [t, 3H, Ar–CH_2–$(CH_2)_2$–CH_3], 1.0–1.5 [m, 4H, Ar–CH_2–$(CH_2)_2$–CH_3], 2.1 (s, 3H, Ar-CH_3), 2.4 (s, 3H, Ar–CH_3), 2.7 [q, 2H, Ar–CH_2–$(CH_2)_2$–CH_3], 7.2 (s, 1H, thiophene-H), 7.3 and 7.8 (AB, 4H, *J* 7.5 Hz, Ar) ppm. IR (KBr): ν 1315 (SO_2), 1150 (SO_2) cm^{-1}. MS (EI) *m/z*: 308 (M^+). Anal. calcd. for $C_{16}H_{20}S_2O_2$: C 62.30, H 6.53, S 20.79; found: C 62.13, H 6.21, S 20.24%.

*Attempted synthesis of 3-tert-butyl-4-methyl-2-(*p*-tolylsulfonyl) thiophene* (**9d**). Starting from **5e** (0.29 g, 1.0 mmol) and *tert*-butyllithium (3.0 mmol, 1.8 ml), the general procedure was followed. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.278 g (80%), 2-*tert*-butyl-3-methyl-1-(trimethylsilyl)but-2-en-1-yl *p*-tolyl sulfone as the only product. ^{1}H-NMR ($CDCl_3$): δ 0.0 (s, 9H, $SiMe_3$), 0.6 (s, 9H, ^{t}Bu), 1.55 (s, 3H, =C–CH_3), 1.60 (s, 3H, C=C–CH_3), 2.1 (s, 3H, Ar–CH_3), 3.8 (s, 1H, –SO_2–CH–Si), 6.9 and 7.3 (AB, 4H, *J* 7.5 Hz, Ar) ppm. MS (EI) *m/z*: 352 (M^+).

*4-Methyl-3-phenyl-2-(*p*-tolylsulfonyl)thiophene* (**9e**). Starting from **5e** (0.29 g, 1.0 mmol) and diphenylcopperlithium [synthesized from phenyllithium (6.0 mmol, 3.0 ml) and copper(I) iodide (0.571 g, 3.0 mmol)] product **9e** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 12/1, v/v) to give 0.032 g (10%) of **9e** as a white solid, which was crystallized from toluene/hexane, m.p. 138°C. ^{1}H-NMR ($CDCl_3$): δ 1.9 (s, 3H, Ar–CH_3), 2.3 (s, 3H, Ar–CH_3), 6.9–7.5 (m, 10H, Ar) ppm. MS (EI) *m/z*: 328 (M^+). EI/HRMS *m/z*: 328.0593 ± 0.0006; calcd. for $C_{18}H_{16}S_2O_2$ (M^+): 328.0592.

*3-Methyl-4-phenyl-2-(*p*-tolylsulfonyl)thiophene* (**9f**). Starting from **5h** (0.35 g, 1.0 mmol) and methyllithium (3.0 mmol, 1.9 ml) product **9f** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.184 g (57%) of **9f**, as a light yellow solid, which was crystallized from toluene/hexane, m.p. 141–143°C. ^{1}H-NMR ($CDCl_3$): δ 2.4 (s, 3H, Ar–CH_3), 2.5 (s, 3H, Ar–CH_3), 7.2–7.5 (m, 8H, Ar), 7.9 (d, 2H, *J* 7.5 Hz, Ar) ppm. MS (EI) *m/z*: 328 (M^+). EI/HRMS *m/z*: 328.0593 ± 0.0009; calcd. for $C_{18}H_{16}S_2O_2$ (M^+): 328.0592.

*3-Ethyl-4-phenyl-2-*p*-tolylsulfonylthiophene* (**9g**). Starting from **5h** (0.35 g, 1.0 mmol) and ethyllithium [4.4 mmol, prepared from ethyl bromide (0.78 ml, 4.9 mmol) and Li(0.08 g, 11,5 mmol) as described in the literature[19]] product **9g** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.128 g (38%) of **9g**, as a light yellow solid, which was crystallized from toluene/hexane, m.p. 136–137°C. ^{1}H-NMR ($CDCl_3$): δ 0.8 (t, 2H, *J* 7.5 Hz, –CH_2–CH_3), 2.4 (s, 3H, Ar–CH_3), 2.9 (q, 2H, *J* 7.5 Hz, Ar–CH_2-CH_3), 7.2–7.5 (m, 8H, Ar), 7.9 (d, 2H, *J* 7.5 Hz, Ar) ppm. MS (EI) *m/z*: 342 (M^+). Anal. calcd. for $C_{19}H_{18}S_2O_2$: C 66.63, H 5.30, S 18.72; found: C 66.69, H 5.17, S 18.95%.

*3,5-Dimethyl-4-ethyl-2-(*p*-tolylsulfonyl)thiophene* (**9h**). Starting from **5f** (0.32 g, 1.0 mmol) and methyllithium (3.0 mmol, 1.9 ml) product **9h** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.184 g (63%) of **9h**, as a white solid, which was crystallized from toluene/hexane, m.p. 141–143°C. ^{1}H-NMR ($CDCl_3$): δ 1.0 (t, 3H, *J* 9.0 Hz, –CH_2–CH_3), 2.29 (s, 3H, Ar–CH_3), 2.37 (s, 3H, Ar–CH_3), 2.4 (s, 3H, Ar–CH_3), 2.42 (q, 2H, *J* 9.0 Hz, Ar–CH_2–CH_3), 7.3 and 7.9 (AB, 4H, *J* 9.0 Hz, Ar) ppm. MS (EI) *m/z*: 294 (M^+). EI/HRMS *m/z*: 294.0741 ± 0.0009; calcd. for $C_{14}H_{18}S_2O_2$ (M^+): 294.0749.

*4-Ethyl-3-methyl-2-(*p*-tolylsulfonyl)thiophene* **9i** *and 3,4,5-trimethyl-2-(*p*-tolylsulfonyl)thiophene* **9j**. Starting from **5g** (0.31 g, 1.0 mmol) and methyllithium (3.0 mmol, 1.9 ml), **9i** and **9j** were synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 9/1, v/v) to give 0.101 g (36%), of the oily product consisting of the thiophenes **9i**/**9j** in the ratio 65/35.
Spectral data of **9i**. ^{1}H-NMR ($CDCl_3$): δ 1.2 (t, 3H, *J* 6.7 Hz, thiophene–CH_2–CH_3), 2.29 (s, 3H, thiophene–CH_3), 2.4 (s, 3H, Tol–CH_3), 2.46 (q, 3H, *J* 6.7 Hz, thiophene–CH_2–CH_3), 7.2 (s, 1H, thiophene–H), 7.3 and 7.9 (AB, 4H, *J* 8.3 Hz, Ar) ppm.
Spectral data of **9j**. ^{1}H-NMR ($CDCl_3$): δ 1.95 (s, 3H, thiophene–CH_3), 2.26 (s, 3H, thiophene–CH_3), 2.34 (s, 3H, thiophene–CH_3), 2.40 (s, 3H, Tol–CH_3), 7.3 and 7.9 (AB, 4H, *J* 8.3 Hz, Ar) ppm.

*3-Methyl-2-(*p*-tolylsulfonyl)-4,5,6,7-tetrahydrobenzo*[b]*thiophene* (**9k**). Starting from **5b** (0.34 g, 0.84 mmol) and methyllithium (3.0 mmol, 1.9 ml), product **9k** was synthesized according to the general procedure. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.069 g (27%) of **9k**, as a white solid, which was crystallized from toluene/hexane, m.p. 158–161°C. ^{1}H-NMR ($CDCl_3$): δ 1.6–1.9 (m, 4H, Ar–CH_2–CH_2–CH_2–CH_2–Ar), 2.2 (s, 3H, thiophene–CH_3), 2.4 (m, 5H, Ar–CH_3, Ar–CH_2–), 2.6–2.8 (m, 2H, Ar–CH_2–), 7.3 and 7.8 (AB, 4H, *J* 7.0 Hz, Ar) ppm. MS (EI) *m/z*: 306 (M^+). EI/HRMS *m/z*: 306.0749 ± 0.0006 calcd. for $C_{16}H_{18}S_2O_2$ (M^+): 306.0748.

*3,4-Dimethyl-2-(*p*-tolylthio)thiophene* (**11**)

Procedure A. A solution of 3,4-dimethyl-2-(*p*-tolylsulfonyl)thiophene **9a** (0.25 g, 0.94 mmol) and lithium aluminium hydride (0.342 g, 9.4 mmol) in toluene (75 ml) was heated under argon relux for two days. After cooling to room temperature a saturated aqueous ammonium chloride solution (50 ml) was added and the aqueous layer was extracted with dichloromethane (3×25 ml), the combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.198 g (90%) of **11**, as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 2.16 (s, 3H, Ar–CH_3), 2.18 (s, 3H, Ar–CH_3), 2.27 (s, 3H, Ar–CH_3), 7.25 (s, 1H, thiophene–H), 7.1 and 7.35 (AB, 4H, *J* 10.0 Hz, Ar) ppm. MS (EI) *m/z*: 234 (M^+).
Procedure B. A solution of **9a** (0.25 g, 0.94 mmol) and diisobutylaluminium hydride (9.4 ml, 1 M in toluene, 9.4 mmol) in toluene (75 ml) was heated under argon relux for two days. After cooling to room temperature a saturated aqueous ammonium chloride solution (50 ml) was added and the aqueous layer was extracted with dichloromethane (3×25 ml), the combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 6/1, v/v) to give 0.165 g (75%) of **11**, as a yellow oil. Spectral data, see above.

3,4-Dimethylthiophene (**12**)

A solution of **9a** (0.25 g, 0.94 mmol) in THF (10 ml) was added to mixture of sodium amalgam[20,21] (6.0 g, 2%) and dry disodium hydrogen phosphate (0.62 g, 4.4 mmol) in dry methanol (50 ml). The reaction mixture was stirred overnight. The contents of the flask were decanted into a separatory funnel. The flask was rinsed with pentane (2×40 ml), and the combined organic layers were washed with water (4×25 ml) and a saturated aqueous sodium chloride solution (40 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel 60H, petroleum ether 60–80°C/ethyl acetate, 19/1, v/v) to give 0.09 g (85%) of **12**[22], as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 2.1 (s, 6H, Ar–CH_3), 6.8 (s, 2H, thiophene–H) ppm. MS (EI) *m/z*: 112 (M^+).

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