Cycloaddition of thiophene *S*-oxides to allenes, alkynes and to benzyne

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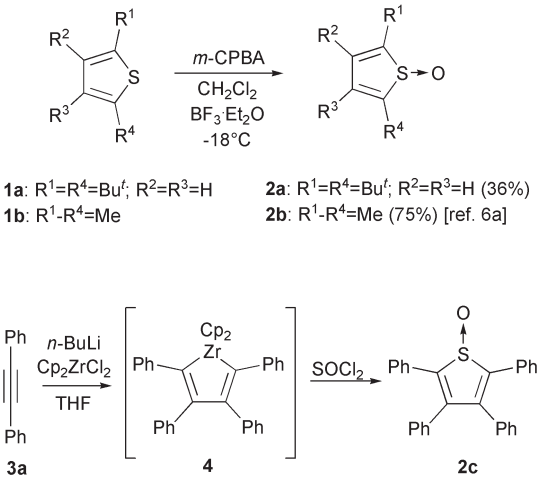
Thiophenes have been treated with alkynes in the presence of *m*-chloroperoxybenzoic acid to give substituted arenes as cycloadducts. Alternatively, thiophene *S*-oxides have been prepared by oxidation from thiophenes and have been subjected to cycloaddition with alkynes in a subsequent step. The outcome of the reaction is dependent on the steric demand of the thiophene *S*-oxide. Some thiophene *S*-oxides can be reacted at temperatures as high as 140 °C without decomposition. Thiophenes as deoxygenated products are the main by-products. Reactions of thiophene *S*-oxides with allenes give in part thiabicyclo[2.2.1]heptene *S*-oxides of type **12a** and **13** along with aromatized products. Thiophene *S*-oxides also cycloadd to benzyne.

Introduction

Until about 10 years ago, thiophene *S*-oxides[1] **2** were quite elusive molecules. They had been postulated as reactive intermediates in the peracid-mediated oxidation of thiophenes **1** to thiophene *S*,*S*-dioxides, where dimerisation products, so-called sesquioxides,[2] could be isolated that clearly stemmed from the reaction of intermediately formed thiophene *S*-oxides **2**, reacting in these cases as both dienes and dienophiles. Later these reactive species were prepared and reacted *in situ* with a number of alkenes, where again the intermediate thiophene *S*-oxides **2** reacted as dienes in a formal [4 + 2]-cycloaddition,[3] but where the thiophene *S*-oxides were not isolated as such. Nevertheless in the last 8 years, two main routes towards the synthesis of these compounds have been established: a) by oxidation of the corresponding thiophenes;[4] and b) by the reaction of alkynes with zirconocene dichloride *via* the corresponding substituted zirconacyclopentadienes, which with sulfur dioxide or thionyl chloride are transformed to the thiophene *S*-oxides.[5] (Scheme 1) Also these isolated thiophene *S*-oxides are effective dienes in [4 + 2]-cycloaddition reactions with alkenes,[6] where alkenes, that are normally susceptible to reaction with peracids, such as methylenecyclopropanes,[6c] also can be used. Often, the sulfur originating from the thiophene can be extruded in a subsequent step from the primary cycloadducts. This method not only presents a two-step route to functionalised arenes from thiophenes under mild conditions, but may also may point to a way of desulfurizing thiophene containing fuels, although in the latter case the nature of the oxidant needs to be changed; dibenzothiophenes, however, will not be converted. It is not yet clear what versatility thiophene *S*-oxides **2** possess as dienes in [4 + 2]-cycloaddition reactions. In the following the reactivity of thiophene *S*-oxides **2**, both as reactive intermediates and as isolated species, towards alkynes, allenes and benzyne will be discussed.



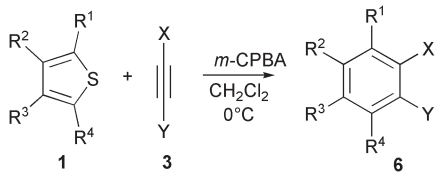
Scheme 1 Synthesis of thiophene *S*-oxides **2a–c**.

Results and discussion

Cycloaddition of thiophene *S*-oxides with alkynes

Substituted thiophene *S*-oxides **2** may be viewed as reactive dienes and can be utilized as the 4π-component in Diels–Alder type reactions.[3,6] When thiophenes **1** are reacted with *m*-chloroperoxybenzoic acid in the presence of alkynes **3** substituted arenes **6** can be isolated, albeit in varying and usually in quite low yields (Table 1). These reactions are run in dichloromethane at 0 °C. In order for the reactions to proceed, the alkynes have to be substituted with electron-withdrawing substituents and the thiophenes have to be substituted at least at positions C2/C5 with electron donating groups. In the reactions, thiophene *S*-oxides are produced *in situ*, which cycloadd to the alkynes (Scheme 2). Thiabicyclo[2.2.1]heptadienes **5** as

Table 1 Cycloaddition of thiophene *S*-oxides prepared *in situ* with alkynes

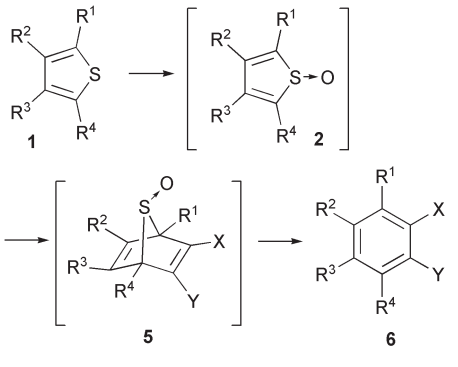


Reactants	Product (yield)
1d: $R^1 = R^4 = Me$, $R^2 = R^3 = H$, **3b**: $X = Y = CO_2Me$	**6a** (41%)
1d: $R^1 = R^4 = Me$, $R^2 = R^3 = H$, **3c**: $X = Y = COPh\text{-}p\text{-}Bu^t$	**6b** (29%)
1d: $R^1 = R^4 = Me$, $R^2 = R^3 = H$, **3d**: $X = CO_2Me$, $Y = COPh$	**6c** (32%)
1b: $R^1 - R^4 = Me$, **3b**: $X = Y = CO_2Me$	**6d** (23%)

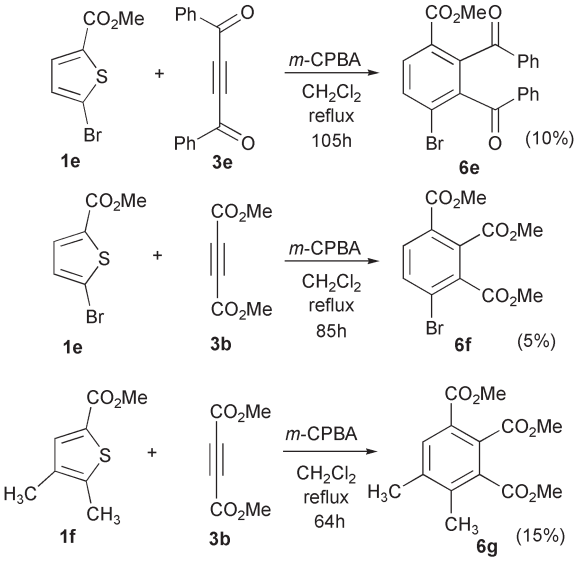
the primary cycloadducts cannot be isolated, but spontaneously extrude the SO-bridge under the conditions used to form the substituted aromatic compounds **6**. In these reactions it could be seen that both electronic factors as well as steric factors play an important role in the outcome of the reaction, especially to determine whether the cycloaddition proceeds at all. Generally, the limiting factors peculiar to thiophene *S*-oxides are the ease of self dimerisation, shared with some other cyclic dienes, and the oxidation of the thiophene *S*-oxides to thiophene *S*,*S*-dioxides, when the reactions are performed under these oxidizing conditions. The thiophene *S*,*S*-dioxides are not reactive as dienes under the conditions described, but necessitate higher reaction temperatures.

It is much more difficult to oxidize thiophenes with electron-withdrawing substituents (Scheme 3). Nevertheless, it is possible to subject methyl thienylcarboxylates such as **1e** and **1f** to an oxidative cycloaddition when heating a mixture of **1e** or **1f** with an excess of acetylene in presence of *m*-CPBA. The product, however, can only be isolated in a low yield. Additionally, the reaction times are long.

Alternatively, thiophene *S*-oxides with electron-donating or slightly electron-withdrawing substituents can be prepared and isolated. Then, they can be reacted with alkynes in a second step. For these studies, three differently substituted thiophene *S*-oxides, tetraphenylthiophene *S*-oxide (**2c**), tetramethylthiophene *S*-oxide (**2b**), and di-*tert*-butylthiophene *S*-oxide (**2a**) have been used. **2c** is a sterically congested compound with substituents of slightly withdrawing nature. **2b** is sterically a less exacting molecule with electron donating substituents, while **2a** is sterically hindered, where the *tert*-butyl groups are electron-donating. **2c** was prepared by the reaction of diphenylethyne (tolane) (**1**) with zirconocene dichloride,[5] while **2a** and **2b** were obtained from the oxidation of tetramethylthiophene (**1b**) and 2,5-di-*tert*-butylthiophene (**1a**), respectively, with *m*-CPBA in the presence of $BF_3{\cdot}Et_2O$ as a Lewis acid catalyst (Scheme 1).[4b,6a,7] When the thiophene *S*-oxides were reacted with alkynes with one or both substituents of electron-withdrawing character, the reactions proceeded smoothly to give the aromatic products in good yields (Table 2). Side products were the thiophenes, which are produced at higher temperature by simple deoxygenation. Mixing of thiophene *S*-oxide **2b** and dimethyl acetylenedicarboxylate (**3b**) without addition of solvent resulted in an exothermic reaction. Tolane (**3h**) on the other hand did not react with either **2b** or **2c**. When **2b** was reacted with phenylacetylene as a solvent at 100 °C, **6u** could be isolated.



Scheme 2



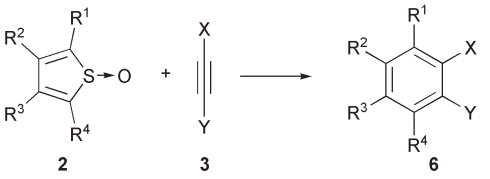
Scheme 3 Oxidative cycloaddition of electron-poor thiophenes with alkynes.

For alkynes with two electron withdrawing groups the thiophene *S*-oxide is the preferable reaction partner when compared to an analogously substituted thiophene *S*,*S*-dioxide. When higher reaction temperatures are necessary, such as with sterically more demanding alkynes, the thiophene *S*,*S*-dioxides[8] are more advantageous to use. While their reactivity may be lower, their stability is inherently greater, as side reactions due to deoxygenation of the starting material can be avoided. Also, the dimerisation of similarly substituted thiophene *S*,*S*-dioxides can be suppressed more readily than with the thiophene *S*-oxides. In general, the tetraphenylcyclopentadienone (tetracyclone) (**7**), which has been frequently used as the diene component in [4 + 2]-cycloaddition reactions,[9] most recently also in the preparation of novel materials,[10] gives slightly higher yields than tetraphenylthiophene *S*-oxide (**2c**), when reacted with the same alkynes (Scheme 4).

It must be remarked, however, that tetraphenylthiophene *S*-oxide (**2c**) is compatible with reaction temperatures as high as 140 °C (Scheme 5). This can be seen in the reaction of **2c** with ethyl *o*-tolylpropiolate (**3i**). Reaction of 2,5-di-*tert*-butylthiophene *S*-oxide (**2a**) with dimethyl acetylenedicarboxylate (**3b**) at 135 °C also gave the cycloadduct as product, albeit with a larger amount of thiophene **1a** as the deoxygenation product.[11] On the other hand, the tetramethyl-substituted analog can decompose even at temperatures as low as 100 °C, if it cannot react with its partner at that temperature.

Thiophene *S*-oxides are non-planar compounds.[12] Thus, the X-ray of 2,5-diphenylthiophene *S*-oxide has shown that the pyramidalised sulfur is positioned outside of the plane defined by the four carbon atoms of the heterocyclic structure. The oxygen of the sulfoxy-moiety is located on the opposing side of the ring. In contrast, the cyclopentadienone system in tetraphenylcyclopentadienone is planar.[13] Consequently, the thiophene *S*-oxide is sterically more exacting than the corresponding cyclopentadienones.

Table 2 Cycloaddition of thiophene *S*-oxides with alkynes



2 3 6

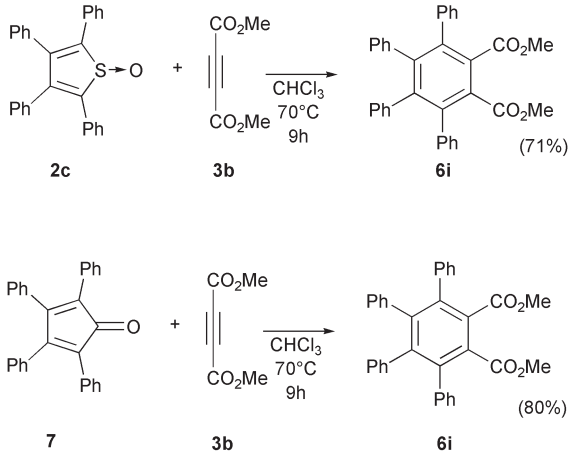
Reactants	Conditions	Product (yield)
2c: R^1 - R^4 = Ph, **3e**: X = Y = COPh	benzene, 60°C, 20h	**6h** (60%)
2c: R^1 - R^4 = Ph, **3b**: X = Y = CO_2Me	$CHCl_3$, 70°C, 9h	**6i** (71%)
2c: R^1 - R^4 = Ph, **3f**: X = H, Y = CO_2Et	$CHCl_3$, 70°C, 9h	**6j** (80%)
2c: R^1 - R^4 = Ph, **3d**: X = COPh, Y = CO_2Me	benzene, 80°C, 10h	**6k** (81%)
2b: R^1 - R^4 = Me, **3f**: X = H, Y = CO_2Et	$CHCl_3$, 70°C, 3h	**6l** (83%)
2b: R^1 - R^4 = Me, **3b**: X = Y = CO_2Me	$CHCl_3$, 70°C, 10h	**6m** (73%)
2b: R^1 - R^4 = Me, **3e**: X = Y = COPh	benzene, 60°C	**6n** (quant)
2b: R^1 - R^4 = Me, **3d**: X = COPh, Y = CO_2Me	benzene, 60°C, 10h	**6o** (83%)
2a: $R^1 = R^4 = Bu^t$, $R^2 = R^3$ = H, **3f**: X = H, Y = CO_2Et	benzene, 60°C, 16h	**6r** (40%)
2a: $R^1 = R^4 = Bu^t$, $R^2 = R^3$ = H, **3d**: X = COPh, Y = CO_2Me	benzene, 80°C, 36h	**6s** (23%)
2a: $R^1 = R^4 = Bu^t$, **3e**: $R^2 = R^3$ = COPh	benzene, 80°C, 21h	**6t** (13%)
2b: R1 - R4 = Me, **3g**: X = H, Y = Ph	**3g** as solvent, 100°C, 24h	**6u** (40%)
2c: R1 - R4 = Me, **3h**: X = Y = Ph	$CHCl_3$, 70°C, 24 h or solvent-less 21 h	**6v** (nr)

While dibenzothiophene *S*-oxides[14] in their reactivity may be viewed as sulfoxy bridged biphenylenes rather than dibenzo-annelated thiophene *S*-oxides, benzothiophene *S*-oxides still possess chemical reactivity partly reminiscent of the non-annelated thiophene *S*-oxides. The study of 2-methylbenzo[*b*]thiophene *S*-oxide (**8**)[8] and of a number of aryl-substituted benzothiophene *S*-oxides showed that these molecules can also be subjected to cycloaddition reactions with alkynes and also alkenes, albeit at higher temperatures and under long reaction times. Reaction products are naphthalenes in the case of the reactions with alkynes and phthalimidodihydronaphthalenes in the case of the reaction with *N*-phenylmaleimide. Again, deoxygenation of the benzothiophene *S*-oxide to the benzothiophenes **10** is the main side-reaction (Scheme 6). Other cycloaddition reactions of this sort with the aromatic ring system providing part of the diene system have only been infrequently reported. Examples have come from cycloaddition reactions of methylindenes[16] and of phenaleno[1,9-*bc*]furan[17] with dimethyl acetylenedicarboxylate.

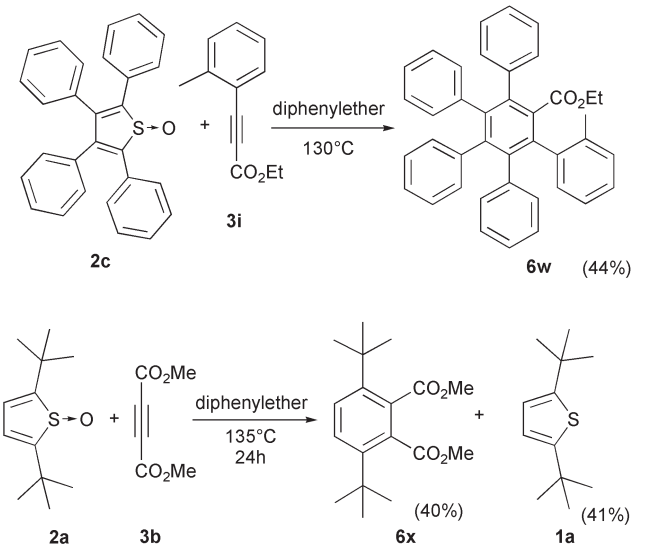
Cycloaddition of thiophene *S*-oxides with allenes

Reactions of thiophene *S*-oxides such as **2b** with alkylidenecyclopropanes have already been carried out by the authors[6c] and cycloadducts had been obtained as a single diastereoisomer in relatively good yield.[6c] Due to the oxidizability of the strained olefin, some thiophene *S*-oxide was lost at the time due to deoxygenation. Taking the reaction one step further, from ethyl acrylate *via* ethyl cyclopropylideneacetate, the authors decided to look at the reactivity of the thiophene *S*-oxides towards allenes **11** (Scheme 7), such as towards ethyl propadienoate (**11b**). When comparing **11b** and ethyl cyclopropylideneacetate,[6c] it is evident that the olefinic moiety in **11b** possesses less strain energy than that of the methylenecyclopropane, nevertheless, mono-substituted **11b** is sterically less exacting than cyclopropylideneacetate.

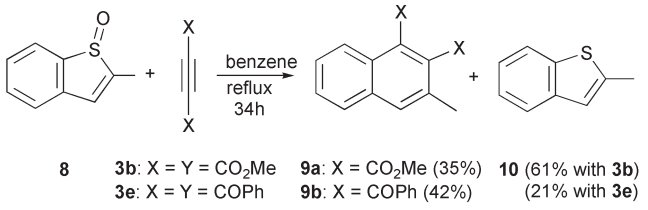
On the other hand, cycloaddition of **11b** to thiophene *S*-oxides **2** would give bridged thiabicyclo[2.2.1]heptene *S*-oxides such as **13**, which additionally possess an *exo*-methylene function. It is known that the cycloaddition of methylenecyclopropanes results in the formation of a spirocyclopropane unit, which is quite stable under the conditions of its formation and suppresses the extrusion of the SO-bridge and the concurrent aromatisation of the molecules. On the other hand,



Scheme 4



Scheme 5 Reactions of thiophene *S*-oxides at elevated temperatures.

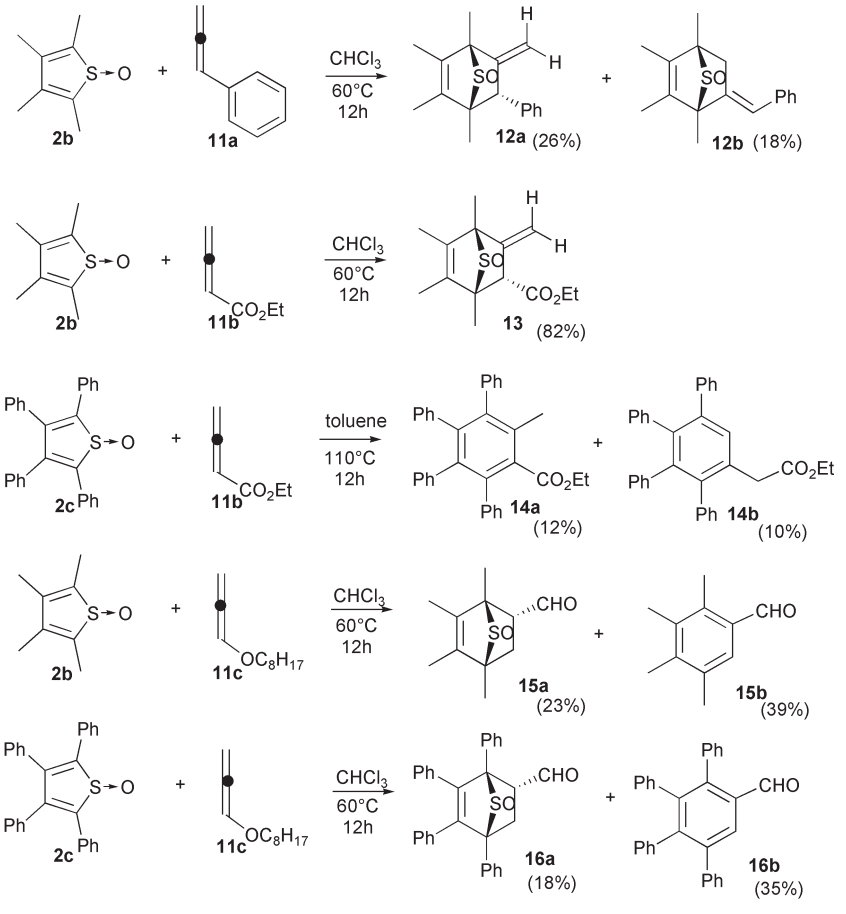


Scheme 6 Cycloaddition of 2-methylbenzothiophene *S*-oxide (**8**).

aromatisation is seen partly in the reaction of thiophene *S*-oxides with 1,2-disubstituted alkenes. Thus, some aromatisation was expected to occur in the case of the reaction of **2b** with ethyl propandienoate (**11b**) *via* isomerisation of the *exo*-olefin to an *endo*-olefin, which, as a thiabicyclo[2.2.1]heptadiene *S*-oxide, would spontaneously extrude the SO-bridge and would form a functionalized arene. Surprisingly, when **2b** was heated with **11b** in chloroform at 60 °C for 12 h only the cycloadduct **13** could be observed. The yield is very close to that found for the same reaction of a thiophene *S*-oxide with ethyl cyclopropylidene acetate.[6c] Pertinent ^{13}C NMR data of the compound **13** (Fig. 1) are the chemical shifts, $\delta_C = 69/75$ ppm, of the two quaternary carbons, which are indicative for the bridge head carbons of the sulfoxy bridge; also informative are the absorptions of the carbons of the *exo*-methylene functionality with the methylene carbon at $\delta_C = 111$ ppm and the quaternary carbon at $\delta_C = 147$ ppm. **13** is formed as one isomer only. Because of the evidence collected from cycloadducts of thiophene *S*-oxides with alkenes both by the authors as well as by others, it can be inferred that the stereochemistry of **13** is *endo* with the lone pair of the electron pair on sulfur pointing towards the newly formed double bond within the carbocyclic framework. The stereoselective formation of the chiral centre at the sulfur is explained by a π-selectivity in the cycloaddition due to the "*Cieplak*-effect", an effect first proposed by Cieplak[18] to account for the directing effects of remote substituents in addition reactions to substituted cyclohexanones. Cycloadditions of thiophene *S*-monoxides have been predicted to occur *anti* to the lone electron-pair on the sulfur, which is the better hyperconjugative donor when compared to the oxygen of the sulfoxy-moiety. The lone-pair electron orbital at the sulfur will stabilize the vacant σ^*-orbitals of the developing incipient σ-bonds better than would any orbital associated with the oxygen. The activation barriers of both *syn*- and *anti*-addition have been calculated previously by semi-empirical methods[19] for dimethylthiophene *S*-oxide and maleic anhydride as well as at the RHG/6-31G* level for thiophene *S*-oxide and ethylene, where the barrier for the *syn*-addition was found to be lower by 9 kcal mol^{-1} than that for the *anti*-addition.[6d]

Interestingly, in the reaction of the tetraphenylthiophene *S*-oxide (**2c**) and allene **11b** only the aromatized products **14a** and **14b** could be isolated. This seems to indicate that the steric factor is important for the non-selectivity of the attack, *i.e.* both olefinic moieties of the allene react equally; while one is favored electronically, as can be seen in the reaction of **2b** with **11b**, the other is favored sterically. Also the aromatisation of the primary cycloadduct decreases some steric congestion.

As the appended phenyl substituents are not in full conjugation to the aromatic core, due to out of plane rotation, stabilisation through conjugation with the phenyl substituents may not necessarily play an important role in the release of the sulfoxy bridge, when one compares the situation with that of the reaction of **2c** with **11c**, where cycloadduct **16a** can be isolated, although also here a larger amount of aromatized **16b** is formed.



Scheme 7 Cycloaddition reactions of thiophene *S*-oxides with allenes.

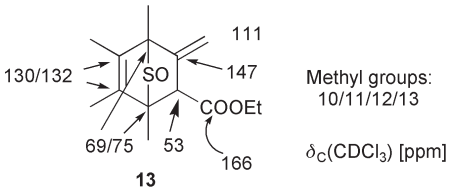
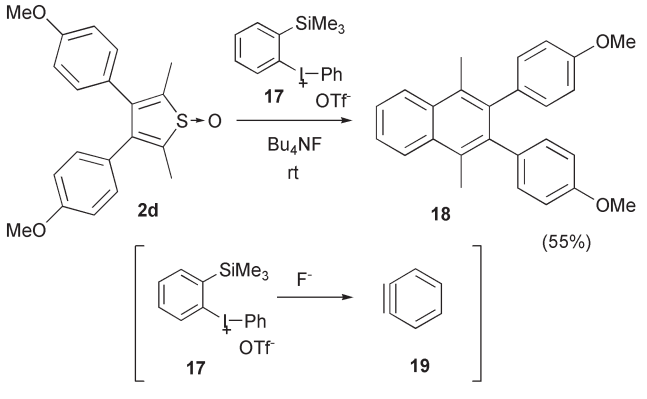


Fig. 1 Typical ^{13}C-NMR data of methylenethiabicyclo[2,2,1]heptene *S*-oxides.

Reaction of tetramethylthiophene *S*-oxide (**2b**) and phenylallene (**11a**) again leads to two products, **12a** and **12b**, stemming from comparative reactivity of the two olefinic moities of the allene. Here, the phenyl substituted olefinic moiety is not as favored electronically as in **11b** and thus a greater reactivity balance is found between the sterically less exacting, non-substituted olefinic moiety and the phenyl substituted moiety. No aromatized products have been isolated from this reaction. With the donor substituent allene **11c**, tetramethylthiophene *S*-oxide (**2b**) and tetraphenylthiophene *S*-oxide (**2c**) show comparative reactivity. Both react at the non-substituted side. In both cases similar yields are found and similar amounts of aromatized product are observed. The initially formed enol ethers, which can be observed by ^{1}H NMR spectroscopy before the work up, albeit not in a pure state, are hydrolysed during work up to the corresponding aldehydes **15a/b** and **16a/b**.

Cycloaddition of thiophene *S*-oxide to benzyne

In their study of the reactivity of substituted thiophene *S*-oxides as diene components in Diels–Alder type reactions, the authors have also recently employed benzyne (**19**) as the ene-component. While there are a number of methods[20] towards the preparation of benzyne, in this case it was important to use a procedure under mild, non-reductive and not too basic conditions. This is offered by the method of T. Kitamura *et al.*[21] from *o*-(trimethylsilyl)phenyl(phenyl)iodonium triflate (**17**), which can be prepared from *o*-dichlorobenzene in two steps. When tetrabutylammonium fluoride is added to **17**[22] in THF, benzyne is formed *in situ*. It can be reacted with thiophene *S*-oxides. When a 1:1 mixture of thiophene *S*-oxide **2d**[6c] and **19** (*i.e.*, *in situ* derived from **17**) were reacted accordingly, the cycloadduct **18** was obtained in 55% yield (Scheme 8). The reaction of 5 eq. of tetraphenylthiophene *S*-oxide (**2c**) with **17** at rt gave the respective cycloadduct in quantitative yield, as calculated on **2c**. A very good indication that from their chemical behavior, dibenzothiophene *S*-oxides should not be viewed as annelated thiophene *S*-oxides but rather as sulfoxy-bridged diaryls can be obtained from the fact that dibenzothiophene *S*-oxide is totally unreactive towards benzyne (**29**) under the conditions described above. When one compares the outcome of the cycloaddition of thiophene *S*-oxide to benzyne with published cycloaddition reactions of benzyne with thiophene



Scheme 8 Reaction of a thiophene *S*-oxide with benzyne.

S,*S*-dioxides,[23] the yield of the former is better, most likely due to the lower reaction temperature used.

Conclusions

In conclusion, thiophene *S*-oxides react as diene component with alkynes, where the best yields are obtained when the thiophene *S*-oxides are donor, the alkynes are acceptor substituted. While strongly electron-acceptor substituted thiophene *S*-oxides have not yet been isolated in pure form, the correspondingly substituted thiophenes can be made to undergo oxidative cycloaddition reactions with alkynes under forcing conditions. The reaction of thiophene *S*-oxides with allenes furnishes in part thiabicyclo[2.2.1]heptene *S*-oxides with an *exo*-methylene unit. Thiophene *S*-oxides also react with benzyne, formed *in situ*.

Experimental

General methods and materials

Melting points were measured on a Yanaco microscopic hot-stage and are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines.^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Partly the interpretation of the ^{13}C-NMR data was aided by DEPT (Distortionless Enhancement by Polarisation Transfer) experiments: (+) denotes primary and tertiary, (−) secondary and C_{quat} quaternary carbons. Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV). Column chromatography was carried out on Wakogel 300. All experiments were purged with argon at the start.

Dibenzoylacetylene (**3e**) was prepared from 1,2-dibenzoylethene by a bromination/dehydrobromination [(a) Br_2, CCl_4; (b) Et_3N, benzene, 80 °C] procedure. **3d** was synthesized from glyoxylic acid monohydrate *via* Wittig reaction with carbomethoxymethylidenetriphenylphosphorane, addition of bromine to the ensuing olefin (Br_2, CCl_4), methylation of the carboxylic acid (diazomethane) and dehydrobromination (Et_3N, benzene, 80 °C). Allenes **11a**, **11b**, and **11c** were prepared by known methods.[24] Phenylallene [phenylpropadiene] (**11a**) was synthesized in a two step procedure *via* Skattebøl rearrangement of 1,1-dibromo-2-phenylcyclopropane (MeLi, ether).[24a] 1,1-Dibromo-2-phenylcyclopropane itself was prepared by dibromocarbene addition to styrene, where the reaction was run as a two-phase reaction under PTC-conditions (bromoform, triethylbenzylammonium bromide, 50% aq. NaOH, styrene)[24b] Allene **11b** was prepared by Wittig olefination of acetyl chloride with ethoxycarbonylmethylidenetriphenylphosphorane (Et_3N, CH_2Cl_2).[24c] Octyloxyallene (**11c**) was obtained in a two step procedure from propargyl bromide by etherification with *n*-octanol to octylpropargyl ether and subsequent base induced alkyne–allene isomerisation.[24d]

Thiophene *S*-oxides **2a**,[7] **2b**,[6a] **2c**[5] and **2d**[6c] and dibenzothiophene *S*-oxide were prepared by oxidation of the corresponding thiophenes and of dibenzothiophene, respectively. Also, 2-methylbenzothiophene *S*-oxide (**8**)[15] was synthesized by oxidation of 2-methylbenzothiophene (**10**) (*m*-CPBA, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −18 °C, 72%).

Transformations - representative examples[25,26]

***In situ* reaction of an electron-acceptor substituted thiophene with an alkyne. Oxidative cycloaddition of methyl 4,5-dimethylthiophenecarboxylate (1f) with dimethyl acetylenedicarboxylate (3b).** A solution of methyl 4,5-dimethylthiophenecarboxylate (**1f**) (222 mg, 1.30 mmol), dimethyl

acetylenedicarboxylate (**3b**) (927 mg, 6.53 mmol) and *m*-CPBA (675 mg, 70 wt%, 2.74 mmol) was stirred under reflux for 85 h. The cooled reaction mixture was poured into 10 wt% aq. Na_2CO_3. The mixture was stirred for 15 min. and then the layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gave trimethyl 4,5-dimethylbenzene-1,2,3-tricarboxylate (**6g**) as a colorless solid (55 mg, 0.20 mmol, 15%) R_f 0.2 (hexane/ether 1:1) mp 92–93 °C; IR (KBr) *v* 2996, 2952, 2848, 1726, 1436, 1283, 1247, 1195, 1030, 1001, 961 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.31 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.88 (s, 3H, $COOCH_3$), 3.89 (s, 3H, $COOCH_3$), 3.90 (s, 3H, $COOCH_3$), 7.73 (s, 1H) ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 16.95, 20.31, 52.58, 52.74, 127.19, 130.89, 132.06, 133.01, 139.14, 139.89, 166.36, 168.17, 168.26; MS (70 eV) *m*/*z* (%) 280 (M^+, 4.0), 249 ($M^+ - CH_3O$, 100), 248 ($M^+ - CH_4O$, 70). Anal. Calcd. for $C_{14}H_{16}O_6$ (280.31): C, 59.99; H, 5.76. Found: C, 60.12; H, 5.87%.

Cycloaddition of an isolated thiophene *S*-oxide with an alkyne. Preparation of methyl 2-benzoyl-3,6-bis(*tert*-butyl)-benzoate (6s). A solution of 2,5-di-*tert*-butylthiophene *S*-oxide (**2a**) (106 mg, 0.5 mmol) and methyl 3-benzoylpropiolate (**3d**) (94 mg, 0.5 mmol) in benzene (2 mL) was kept at 80 °C for 36 h. Thereafter, the mixture was separated by column chromatography on silica gel (benzene) to give methyl 2-benzoyl-3,6-bis-(*tert*-butyl)benzoate (**6s**) (40 mg, 23%) IR (neat) *v* 3064, 2960, 2870, 1733, 1675, 1450, 1362, 1283, 1260, 1241, 1204, 1170, 1107, 713, 653 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.26 (s, 9H, Bu^t), 1.35 (s, 9H, Bu^t), 3.28 (s, 3H, $COOCH_3$), 7.32–8.25 (m, partially broad, 7H) ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 35.81, 36.23, 51.61, 127.83, 128.12, 128.33, 128.68, 128.96, 129.34, 131.12, 133.33, 136.98, 138.18, 136.98, 144.62, 145.37, 170.40, 199.62; MS (70 eV) *m*/*z* (%) 352 (M^+, 1.4), 105 ($C_6H_5CO^+$, 100), 77 ($C_6H^+_5$, 59). HRMS Found: 352.2032. Calcd. for $C_{23}H_{28}O_3$: 352.2038.

Cycloaddition of a thiophene *S*-oxide with an alkyne at an elevated temperature. Synthesis of ethyl 2-(*o*-tolyl)-3,4,5,6-tetraphenylbenzoate (6w). A mixture of ethyl *o*-tolylpropiolate (**3i**) (47 mg, 0.25 mmol) and tetraphenylthiophene *S*-oxide (**2c**) (50 mg, 0.125 mmol) in diphenyl ether (800 mg) was heated under argon at 130 °C for 10 h. Column chromatography on silica gel (hexane/ether 10:1) gave ethyl 2-(*o*-tolyl)-3,4,5,6-tetraphenylbenzoate (**6w**) (30 mg, 44%) as a colorless solid: IR (KBr) *v* 3054, 3024, 2978, 2924, 1730, 1601, 1495, 1441, 1406, 1327, 1229, 1158, 1063, 697 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.67 (t, 3H, ^3J 7.2 Hz), 2.11 (s, 3H, CH_3), 3.61 (q, 2H, ^3J 7.2 Hz), 6.71–7.31 (m, 24H) ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.31, 20.49, 60.45, 124.33, 125.44, 125.53, 125.66, 126.36, 126.57, 126.61, 126.66, 127.22, 127.27, 129.16, 129.97, 130.17, 130.33, 130.72, 131.12, 131.25, 131.34, 131.44, 136.55, 137.77, 138.29, 139.17, 139.21, 139.42, 139.89, 140.29, 140.36, 142.05, 168.66; MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 545 (MH^+, 18), 544 (M^+, 16), 499 ($M^+ - C_2H_5O$, 14)

Comparative cycloaddition of tetraphenylcyclopentadienone [tetracyclone] (7) and of tetraphenylthiophene *S*-oxide (2c). Synthesis of dimethyl 3,4,5,6-tetraphenylbenzene-1,2-dicarboxylate (6i). Method A: A mixture of tetracyclone (**7**) (100 mg, 0.26 mmol) and dimethyl acetylenedicarboxylate (**3b**) (140 mg) in chloroform (2 mL) was kept at 70 °C for 9 h. Thereafter, the mixture was subjected to column chromatography on silica gel to give the starting material, tetracyclone (**7**), (11 mg, 11%) and **6i** (140 mg, 80%). Method B: A mixture of tetraphenylthiophene *S*-oxide (**2c**) (100 mg, 0.247 mmol) and dimethyl acetylenedicarboxylate (**3b**) (140 mg, 1.0 mmol) in chloroform (2 mL) was kept at 70 °C for 10 h. Column chromatography on silica gel gave **6i** (87 mg, 71%). MS (FAB, 3-nitrobenzylalcohol) *m*/*z* (%) 498 (M^+, 32), 467 ($M^+ - CH_3O$, 53). Calcd. for: $C_{44}H_{30}O_2$: C, 89.46; H, 5.12. Found: C. 89.16; H, 5.17%.

Cycloaddition of 2-methylbenzo[*b*]thiophene *S*-oxide (8) with dimethyl acetylenedicarboxylate (3b). A solution of 2-methylbenzo[*b*]thiophene *S*-oxide (**8**) (82 mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (**3b**) (172 mg, 1.0 mmol) in benzene (2 mL) was held at 80 °C for 34 h. Thereafter, the cooled reaction mixture was concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/ether 3:1) gave 2-methylbenzo[*b*]thiophene (**10**) (50 mg, 61%) and dimethyl 3-methylnaphthalene-1,2-dicarboxylate (**9a**) (45 mg, 35%): IR (KBr) *v* 2950, 2924, 2850, 1732, 1438, 1276, 1236, 1203, 1179, 1136, 1068 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.56 (s, 3H, CH_3), 3.94 (s, 3H, $COOCH_3$), 3.99 (s, 3H, $COOCH_3$), 7.51–7.56 (m, 2H), 7.77 (m, 2H), 8.07–8.12 (m, 1H) ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 20.47 (+, CH_3), 52.51 (+, $COOCH_3$), 52.69 (+, $COOCH_3$), 125.71 (+, CH), 127.13 (+, CH), 127.53 (+, CH), 127.74 (+, CH), 128.17 (C_{quat}), 130.49 (C_{quat}), 131.28 (C_{quat}), 131.71 (+, CH), 132.36 (C_{quat}), 134.07 (C_{quat}), 168.37 (C_{quat}, C=O), 168.68 (C_{quat}, C=O) MS (70 eV) *m*/*z* (%) 258 (M^+, 60), 227 (96), 226 (96), 168 (100). HRMS Found: 258.0894. Calcd. for $C_{15}H_{14}O_4$: 258.0892.

Cycloaddition reaction of a thiophene *S*-oxide with an allene. A mixture of phenylpropadiene (**11a**) (100 mg, 0.86 mmol) and tetramethylthiophene *S*-oxide (**2b**) (134 mg, 0.86 mmol) in chloroform (1 mL) was placed into a pressure tube and deaerated. Then, the mixture was stirred at 60 °C for 12 h. The products were separated by column chromatography on silica gel and by TLC plate to give **12a** (60 mg, 26%) and **12b** (41 mg, 18%). (**12a**): IR (KBr) *v* 3056, 3030, 2970, 2924, 1642, 1598, 1492, 1449, 1376, 1090, 1063, 913, 768, 705 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.30 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 4.12 (m, 1H)**, 5.05 (d, 1H, ^2J 2.3 Hz), 5.18 (d, 1H, ^2J, 2.3 Hz), 6.98–7.02 (m, 2H, phenyl-H), 7.23–7.27 (m, 3H, phenyl-H) ^{13}C NMR (67.8 MHz, DEPT 90, DEPT 135) δ 10.57 (+, CH_3), 10.98 (+, CH_3), 12.29 (+, CH_3), 12.64 (+, CH_3), 53.53 (+, CH), 70.91 (C_{quat}), 75.54 (C_{quat}), 111.57 (−), 127.06 (+, CH), 128.12 (+, CH), 129.42 (+, CH), 130.69 (C_{quat}), 131.68 (C_{quat}), 139.23 (C_{quat}), 152.24 (C_{quat}) (**12b**): ^1H NMR (270 MHz, $CDCl_3$) δ 1.52 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.61 (dd, 1H, ^2J 16.2 Hz, ^4J 2.0 Hz), 3.09 (dd, 1H, ^2J 16.2 Hz, ^4J 1.8 Hz), 6.31 (dd, ^4J 2.0 Hz, ^4J 1.8 Hz), 7.20–7.42 (m, 5H) ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 11.00 (+, CH_3), 11.50 (+, CH_3), 13.64 (+, CH_3), 15.24 (+, CH_3), 37.38 (−), 67.64 (C_{quat}), 77.70 (C_{quat}), 124.60 (+, CH), 126.92 (+, CH), 128.24 (+, CH), 129.45 (+, CH), 131.50 (C_{quat}), 132.60 (C_{quat}), 137.34 (C_{quat}), 141.04 (C_{quat}). *The assignment of the C-signals has been aided by DEPT experiments (DEPT = Distortionless Enhancement of Polarisation Transfer), where (+) denotes primary and tertiary carbons, (−) secondary carbons and (C_{quat}) quaternary carbons. **^1H–^1H COSY experiment shows that in **12a** there is a long-range coupling between the methine proton on the carbocycle adjacent to the phenyl substituent and both *exo*-methylene protons; from the 270 MHz ^1H NMR spectrum it has not been possible to obtain the coupling constants for either of the couplings.

1,4-Dimethyl-2,3-bis(*p*-methoxyphenyl)naphthalene (18). reaction of a thiophene *S*-oxide with benzyne, formed *in situ*. At 0 °C and within 10 min, a solution of tetra-*n*-butylammonium fluoride (TBAF) (78 mg, 0.3 mmol) in THF (0.5 mL) was slowly added to a mixture of **2d** (68 mg, 0.2 mmol) and **17** (100 mg, 0.2 mmol) in CH_2Cl_2 (1 mL). The resulting solution was stirred for 1 h at rt. Then, water (5 mL) was added

and the reaction mixture was extracted with CH_2Cl_2 (3×5 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel to give **18** (40 mg, 55%) as colorless needles: IR (KBr) ν 3064, 2992, 2920, 1610, 1513, 1286, 1035, 759 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.43 (s, 6H, 2 CH_3), 3.75 (s, 6H, 2 OCH_3), 6.70 (d, 2H, ^3J 8.7 Hz), 6.87 (d, 2H, ^3J 8.7 Hz), 7.56 (m, 2H), 8.12 (m, 2H) ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135)* δ 16.87 (2C, 2 CH_3), 55.07 (2C, 2 OCH_3), 125.01 (2C, CH), 125.62 (2C, CH), 129.77 (2C, C_{quat}), 131.37 (4C, CH), 132.02 (2C, C_{quat}), 134.30 (2C, C_{quat}), 139.44 (2C, C_{quat}), 157.52 (2C, C_{quat}) MS (70 eV) m/z (%) 368 (M^+, 100). HRMS Found: 368.1779. Calcd. for $C_{26}H_{24}O_2$: 368.1776 (M^+).

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25 All compounds were analysed by ^1H and ^{13}C NMR IR and MS. All new compounds gave correct analytical and/or HRMS data. A number of compounds had been synthesized before by alternative routes. For **6h** and **6j** see: W. Ried and K. Boenninghausen, *Ann.*, 1961, **639**, 61. For **6m** see:D. CriegeeP. Ludwig, *Chem. Ber.*, 1961, 94, 2038. For **6n** see: J. Mueller andA. Huth, *Tetrahedron Lett.*, 1972, 1035. For **6u**, see: J. Novrocik, M. Novrocikova and J. Foniok, *Collect. Czech Chem Commun.*, 1984, **49**, 218.

26 Selected spectroscopic data: **6e**: IR (KBr) ν 2924, 1724, 1679, 1253 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.57 (s, 3H, $COOCH_3$), 7.35–7.58 (m, 8H), 7.65 (dd, 1H, ^3J 7.0 Hz, ^4J 1.4 Hz), 7.73 (1H, dd, ^3J 7.3 Hz, ^4J 1.7 Hz), 7.83 (d, 1H, ^3J 8.5 Hz), 8.02 (d, 1H, ^3J 8.5 Hz) ^{13}C NMR (67.9 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 52.47 ($COOCH_3$), 124.86 (C_{quat}), 128.47 (CH), 128.64 (CH), 129.00 (CH), 130.02 (CH), 131.73 (CH), 133.37 (CH), 133.85 (CH), 134.03 (CH), 136.10 (2C, C_{quat}), 137.21 (C_{quat}), 140.61 (C_{quat}), 141.69 (C_{quat}), 165.15 (C_{quat}, $COOCH_3$), 194.55 (C_{quat}, CO), 194.75 (C_{quat}, CO) MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 425 ($^{81}BrMH^+$, 7.2), 423 ($^{79}BrMH^+$, 7.2). **6f**:IR (neat) ν 3004, 2954, 2848, 1734, 1575, 1439, 1257 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.90 (s, 6H, 2 $COOCH_3$), 3.94 (s, 3H, $COOCH_3$), 7.75 (d 1H, ^3J 8.2 Hz), 7.81 (d, 1H, ^3J 8.2 Hz) ^{13}C NMR (69.7

MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 52.94, 53.10, 53.15, 124.46 (C_{quat}), 128.77 (C_{quat}), 128.91 (C_{quat}), 133.46 (CH), 134.65 (2C, CH and C_{quat}), 165.35, 165.95, 165.56; MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 333 ($^{81}BrMH^+$, 4.9), 331 ($^{79}BrMH^+$, 3.3), 301 ($^{81}BrMH^+ - CH_3O$, 100), 299 ($^{79}BrMH^+ - CH_3O$, 99.8). **6r**: IR (neat) ν 2962, 1726, 1466, 1364, 1303, 1284, 1272, 1240, 1113, 1061 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.30 (s, 9H, Bu^t), 1.39 (s, 9H, Bu^t), 1.40 (t, 3H, ^3J 7.3 Hz), 4.37 (q, 2H, ^3J 7.3 Hz), 7.27 (d, 1H, ^4J 2.0 Hz), 7.37 (dd, 1H, ^3J 8.2 Hz, ^4J 2.0 Hz) 7.40 (d, 1H, ^3J 8.2 Hz) ^{13}C NMR (67.8 MHz) δ 14.07, 31.14, 31.37, 34.21, 35.47, 61.35, 125.30, 126.75, 126.83, 132.59, 144.27, 148.12, 172.59; MS (70 eV) m/z (%) 352 (M^+, 1.5), 337 ($M^+ - CH_3$, 4.5), 305 (14), 105 (100), 77 (59). HRMS Calcd. for $C_{23}H_{28}O_3$: 352.2038. Found: 352.2023. **6t**: IR (KBr) ν 3060, 2962, 1673, 1597, 1450, 1261, 1240 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21 (s, 18H, $2Bu^t$), 7.62 (s, 2H) 7.34–8.15 (m, 10H) ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 32.43, 36.30, 127.94, 128.15, 129.81, 132.24, 136.58, 139.28, 144.88, 199.91; MS (70 eV) m/z (%) 398 (M^+, 37), 383 ($M^+ - CH_3$, 73). HRMS Calcd. for $C_{28}H_{30}O_2$: 398.2246. Found: 398.2246. **6x**: 3006, 2950, 2866, 1728, 1436, 1293, 1244, 1204, 1164, 1121, 1090, 983, 826, 787, 703, 669 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.36 (s, 18H, 2 Bu^t), 3.84 (s, 6H, 2 $COOCH_3$), 7.47 (s, 2H) ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 31.27, 35.70, 52.36, 128.32, 131.37, 144.76, 170.99; MS (70 eV) m/z (%) 306 (M^+, 32), 291 ($M^+ - CH_3$, 69), 275 (32), 259 (100), 243 (18), 227 (26). HRMS Calcd. for $C_{18}H_{26}O_4$: 306.1831. Found: 306.1827.