

# **SUPPORTING INFORMATION**

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Manuscript Title:

**PHOTOOXIDATION PRODUCTS OF POLYCYCLIC AROMATIC COMPOUNDS  
CONTAINING SULFUR**

## **Summary**

51 pages

70 figures

0 tables

## **Table of Contents**

HPLC Chromatograms and Mass Balance

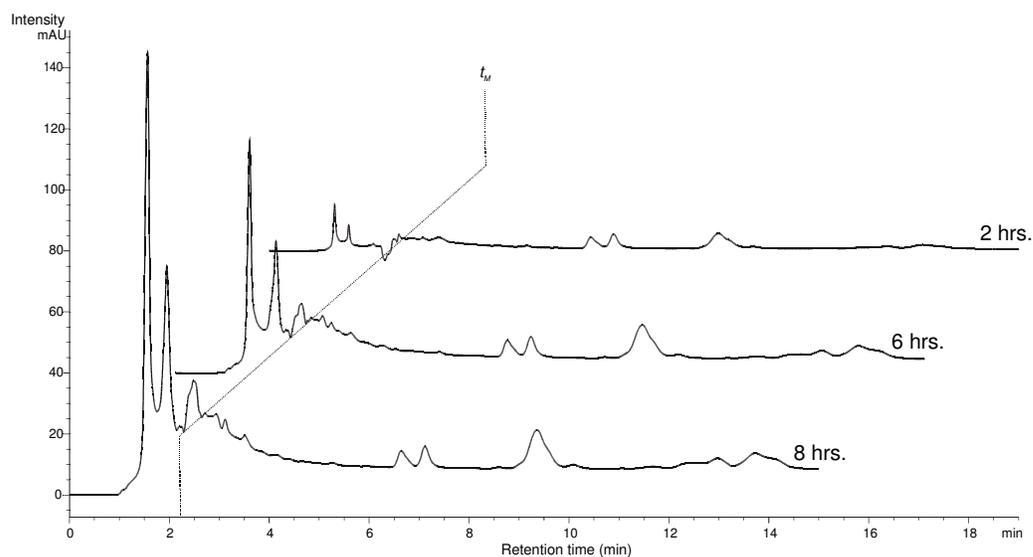
Photooxidation Products

Synthetic Methods of Educts

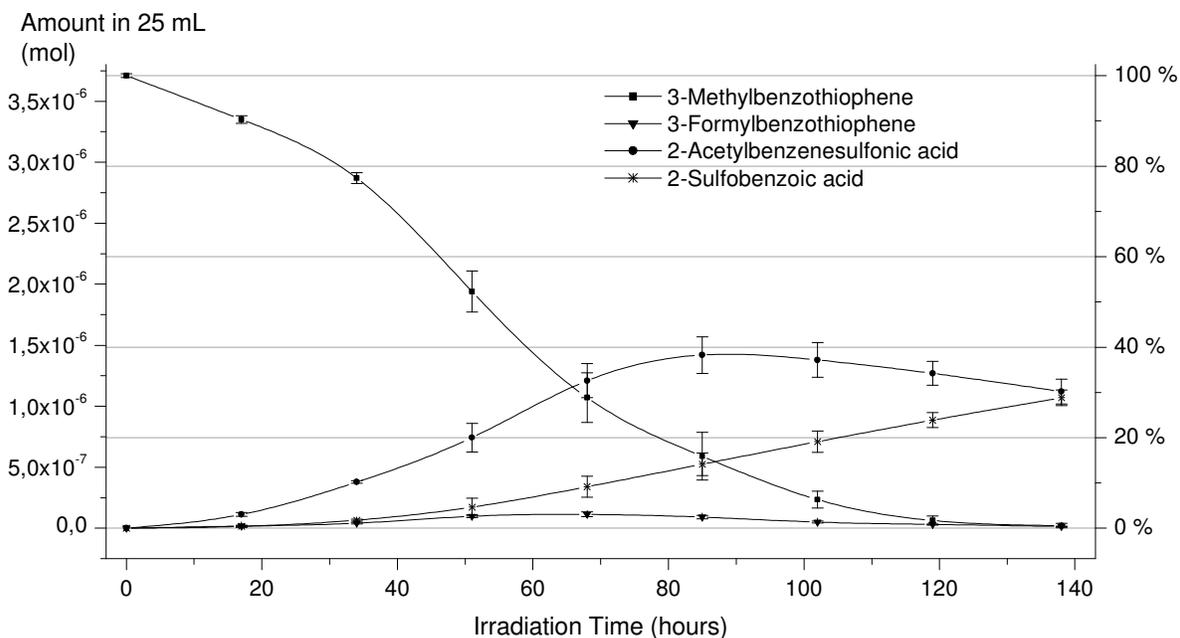
Synthetic Methods of Reference Compounds

Non-Synthesized Compounds

## HPLC Chromatograms and Mass Balance



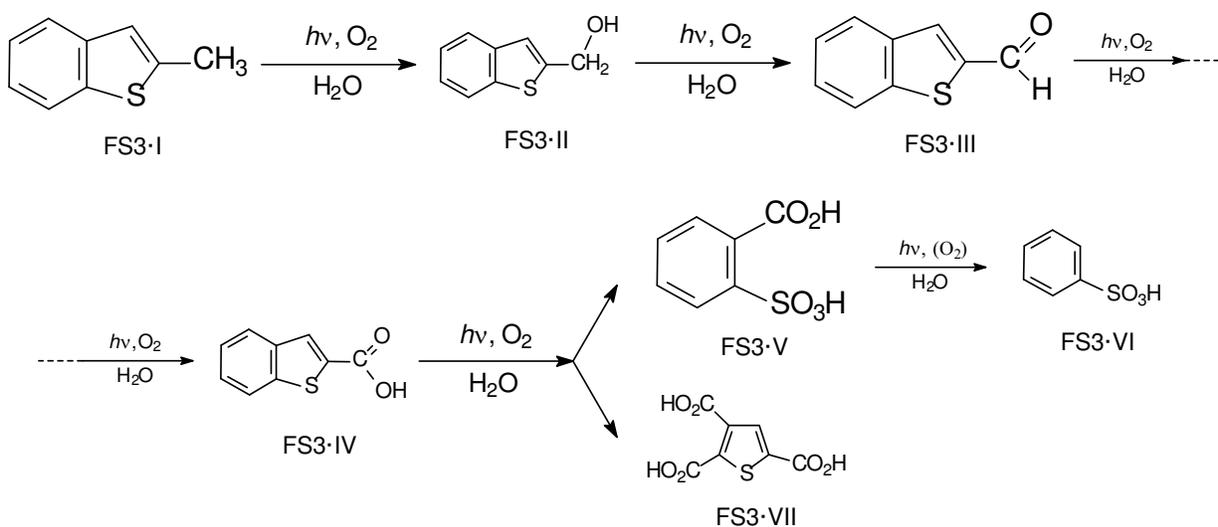
**Figure S1** Photooxidation of a *Kirkuk* crude oil floating on water. HPLC chromatograms after 2, 6 and 8 hours of irradiation with lamp light. Conditions: C-18 column, 75/25 methanol/water, detection wavelength: 0-2.2 min 210 nm, 2-15 min 225 nm. Hold-up time  $t_M$  2.3 min.



**Figure S2** Estimated kinetic and mass balance during the photooxidation of 3-methylbenzothiophene. Shown is the average of four irradiated solutions, measured by RP-HPLC and ion-pair chromatography.

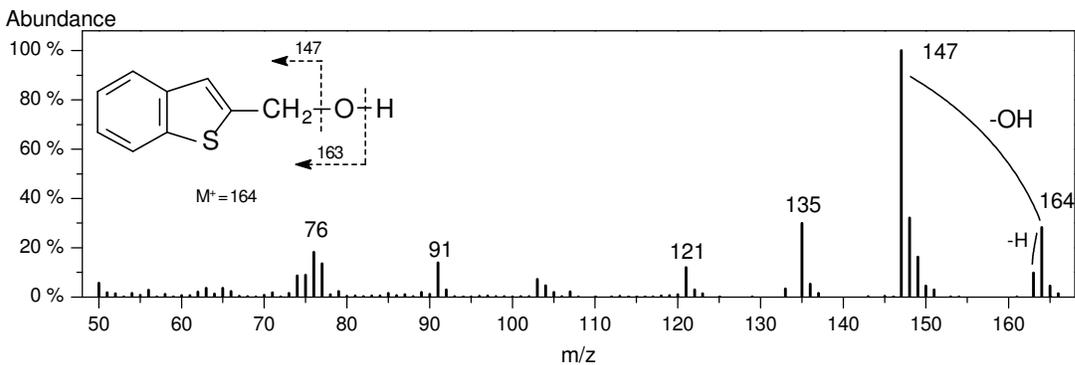
In this SUPPORTING INFORMATION we include data on several monomethylbenzothiophenes although their photolysis is not reported in this work. However, the spectral data of these compounds proved to be invaluable for the assignment of structures to the higher substituted benzothiophenes reported here.

### Photooxidation Products of 2-Methylbenzothiophene



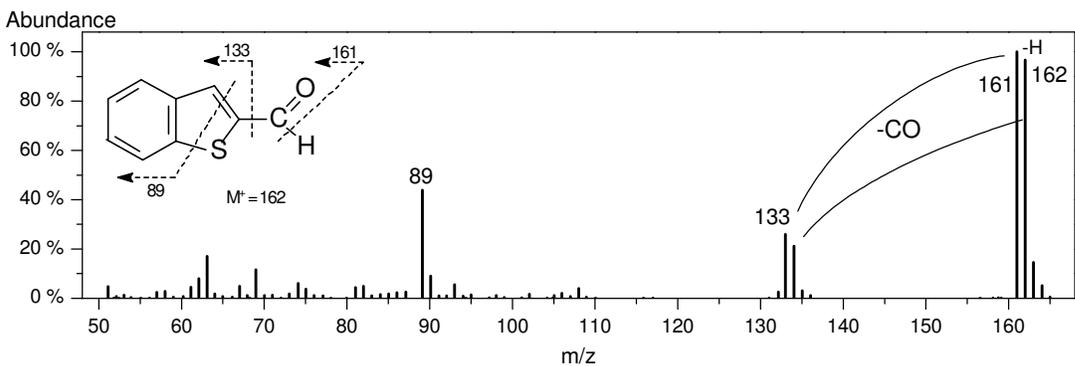
**Figure S3** Postulated reaction scheme of the photooxidation of 2-methylbenzothiophene (FS3-I).

## 2-Hydroxymethylbenzothiophene (FS3-II)



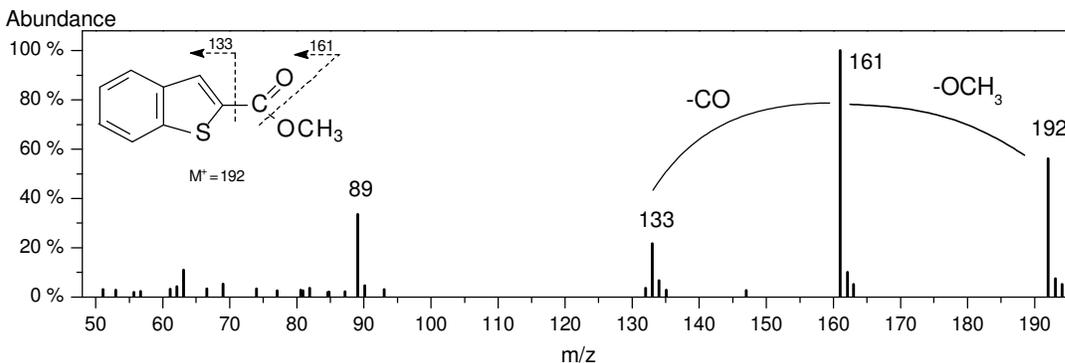
**Figure S4** Mass spectrum of 2-hydroxymethylbenzothiophene, formed through photooxidation of 2-methylbenzothiophene.

## 2-Formylbenzothiophene (FS3-III)



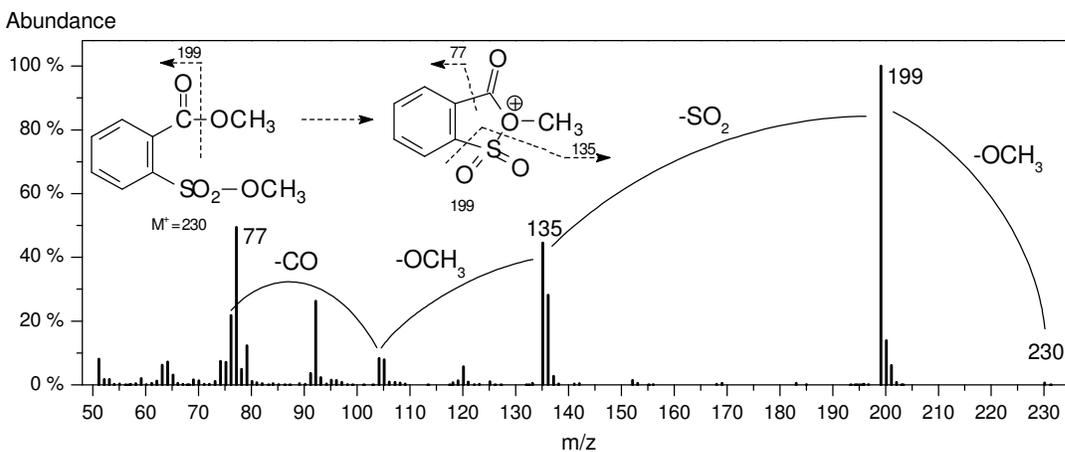
**Figure S5** Mass spectrum of 2-formylbenzothiophene, formed through photooxidation of 2-methylbenzothiophene.

## Benzothiophene-2-carboxylic acid (FS3-IV)



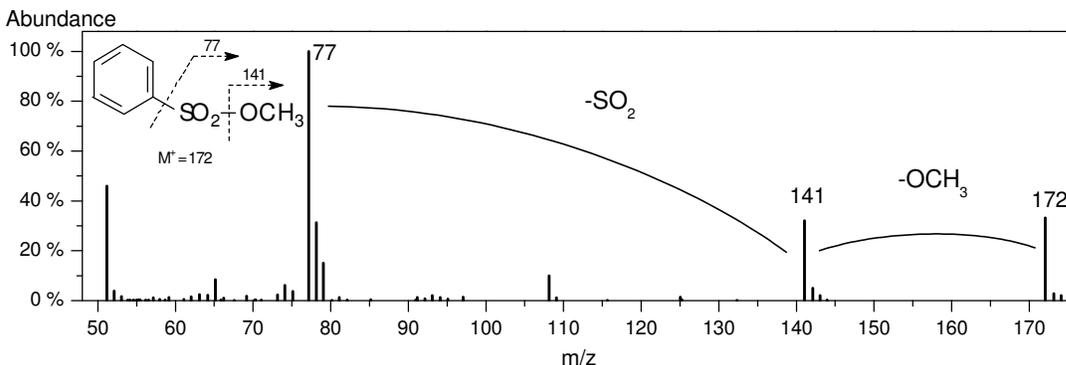
**Figure S6** Mass spectrum of benzothiophene-2-carboxylic acid methyl ester, formed through photooxidation of 2-methylbenzothiophene. The acid is shown as the methyl ester since the sample was treated with diazomethane.

## 2-Sulfobenzoic acid (FS3-V)



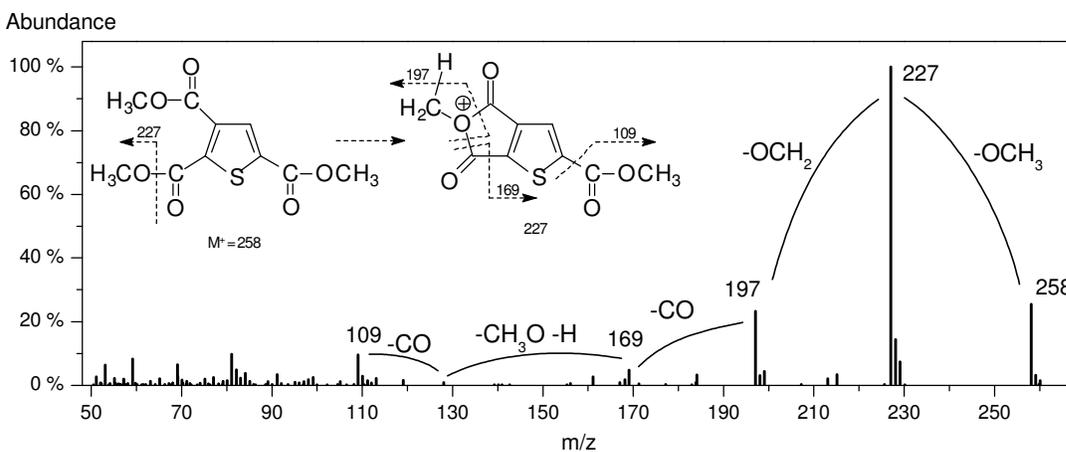
**Figure S7** Mass spectrum of 2-sulfobenzoic acid dimethyl ester, formed through photooxidation of 2-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

## Benzenesulfonic acid (FS3·VI)



**Figure S8** Mass spectrum of benzenesulfonic acid methyl ester, formed through photooxidation of 2-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

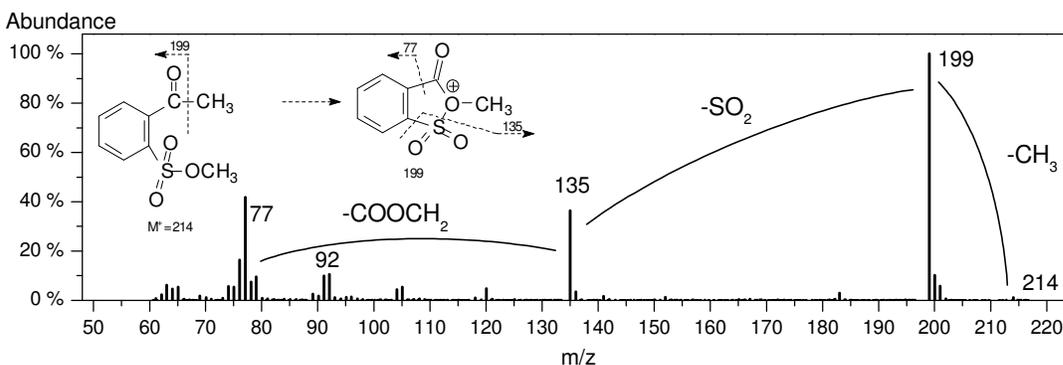
## 2,3,5-Thiophenetricarboxylic acid (FS3·VII)



**Figure S9** Mass spectrum of 2,3,5-thiophenetricarboxylic acid trimethyl ester, formed through photooxidation of 2-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

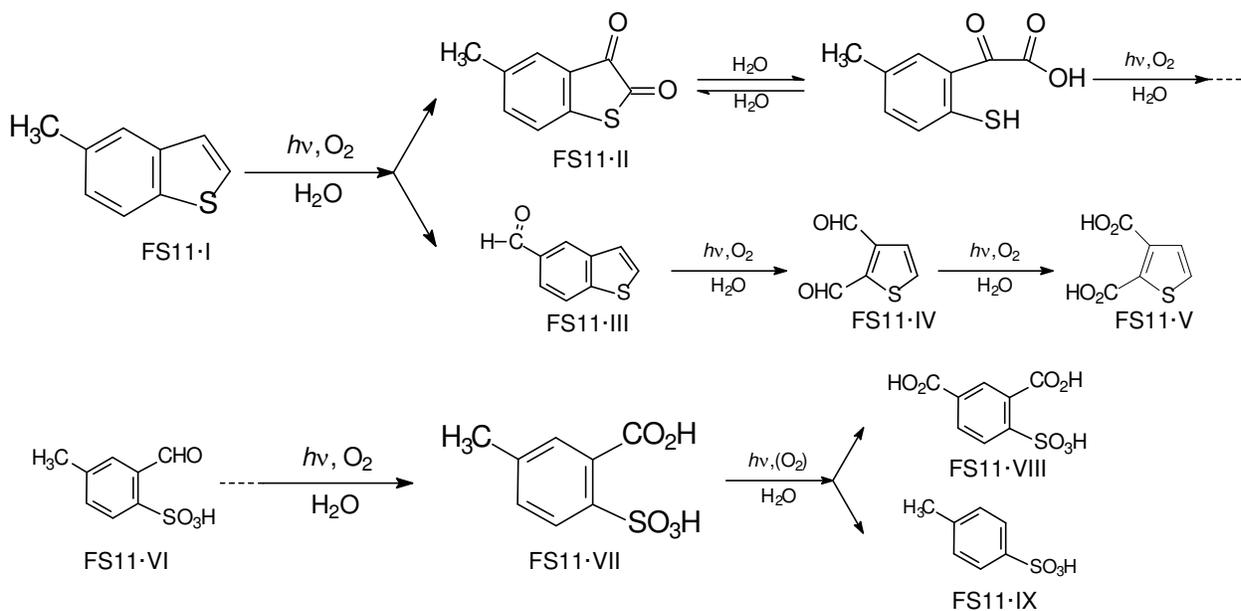
## Photooxidation Products of 3-Methylbenzothiophene

### 2-Acetylbenzenesulfonic acid



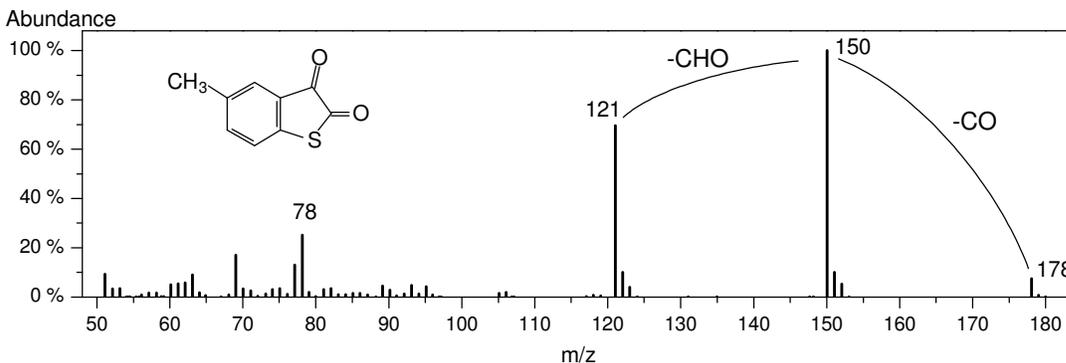
**Figure S10** Mass spectrum of 2-acetylbenzenesulfonic acid methyl ester, formed through photooxidation of 3-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

## Photooxidation Products of 5-Methylbenzothiophene



**Figure S11** Postulated reaction scheme of the photooxidation of 5-methylbenzothiophene (FS11-I).

### 5-Methylbenzothiophene-2,3-quinone (FS11-II)



**Figure S12** Mass spectrum of 5-methylbenzothiophene-2,3-quinone, formed through photooxidation of 5-methylbenzothiophene.

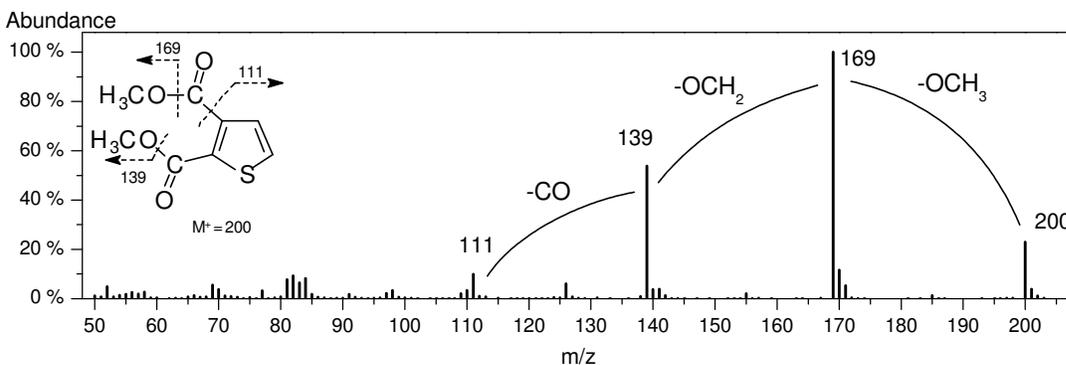
### 5-Formylbenzothiophene (FS11-III)

Mass spectrum is similar to that of 2-formylbenzothiophene shown in Figure S5.

### 2,3-Diformylthiophene (FS11-IV)

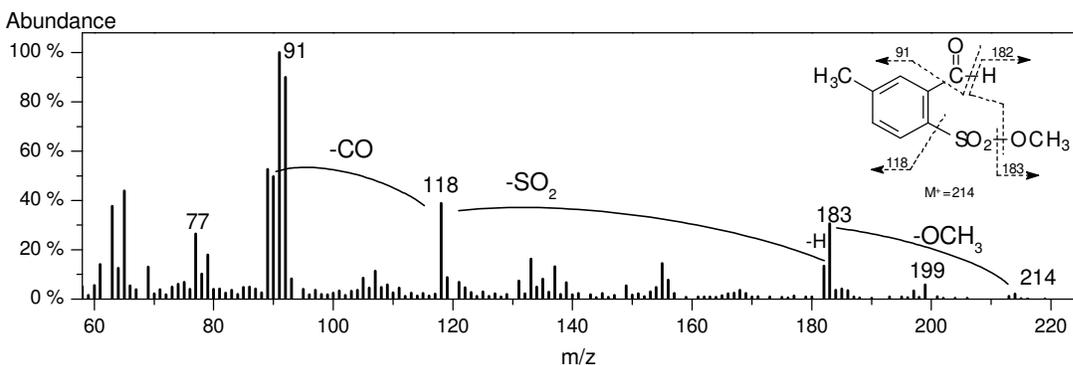
$m/z = 140$  ( $M^+$ ; 30%),  $139$  ( $[M-H]^+$ ; 17%),  $111$  ( $[M-H-CO]^+$ ; 100%),  
 $83$  ( $[M-H-CO-CO]^+$ ; 15%).

### 2,3-Thiophenedicarboxylic acid (FS11-V)



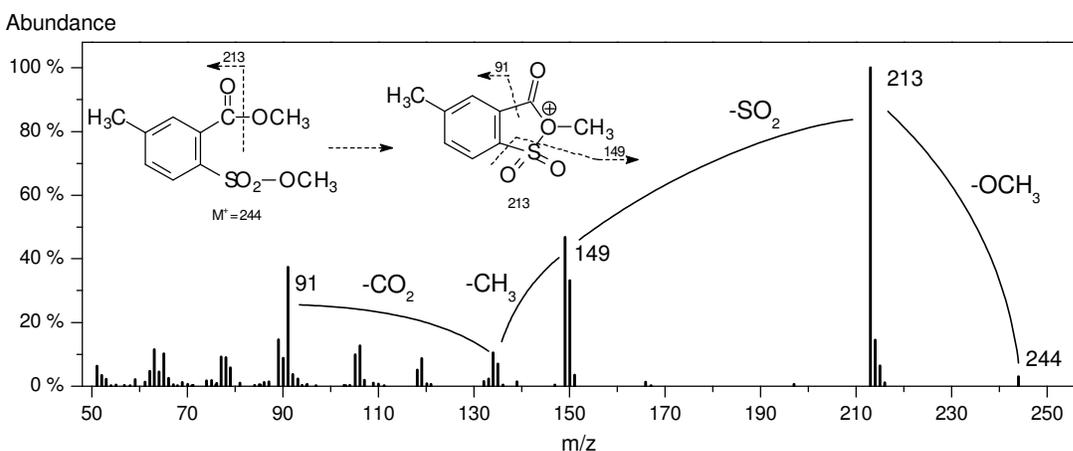
**Figure S13** Mass spectrum of 2,3-thiophenedicarboxylic acid dimethyl ester, formed through photooxidation of 5-methylbenzothiophene. The acid is shown as methyl ester because sample was treated with diazomethane.

## 2-Formyl-4-methylbenzenesulfonic acid (FS11·VI)



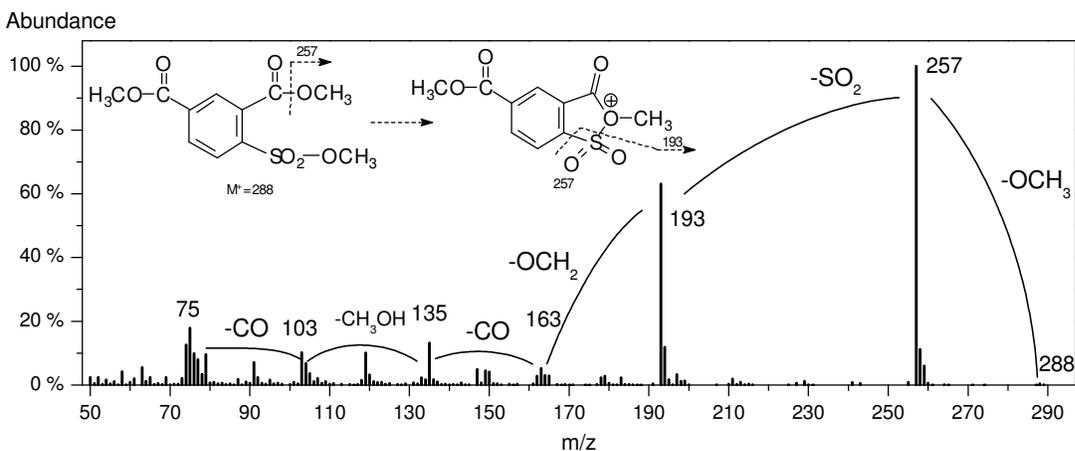
**Figure S14** Mass spectrum of 2-formyl-4-methylbenzenesulfonic acid dimethyl ester, formed through photooxidation of 5-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

## 5-Methyl-2-sulfobenzoic acid (FS11·VII)



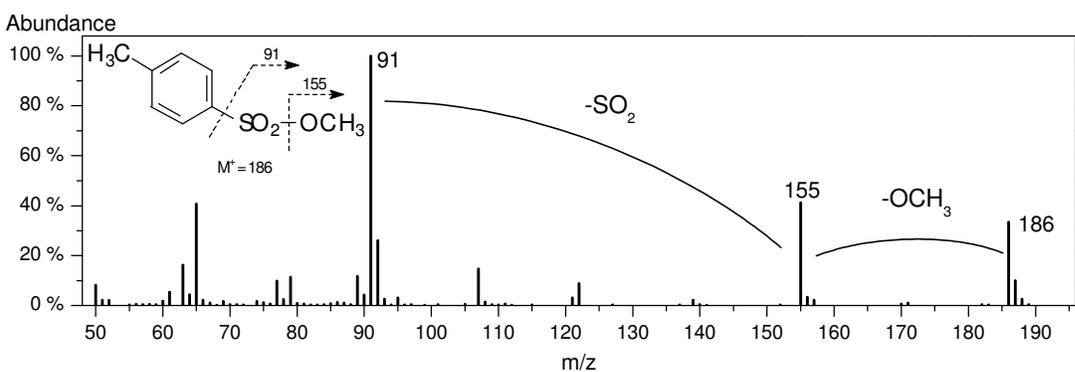
**Figure S15** Mass spectrum of 5-methyl-2-sulfobenzoic acid dimethyl ester, formed through photooxidation of 5-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

#### 4-Sulfoisophthalic acid (FS11·VIII)



**Figure S16** Mass spectrum of 4-sulfoisophthalic acid trimethyl ester, formed through photooxidation of 5-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

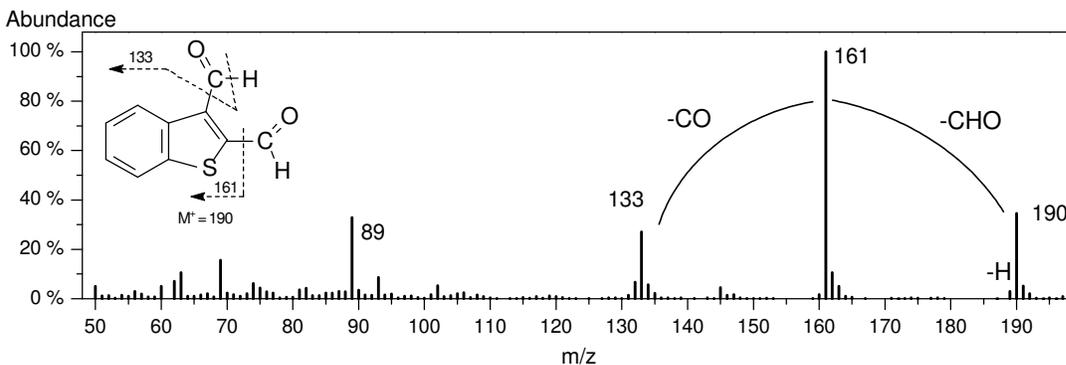
#### 4-Toluenesulfonic acid (FS11·IX)



**Figure S17** Mass spectrum of 4-toluenesulfonic acid methyl ester, formed through photooxidation of 5-methylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

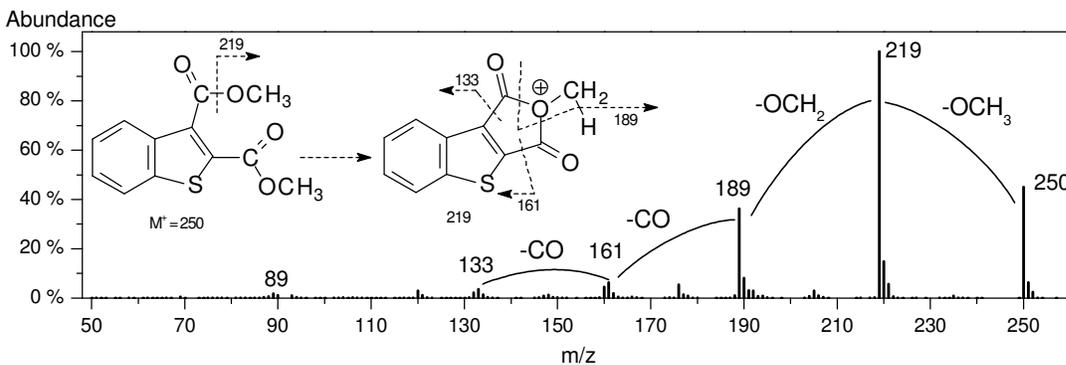
# Photooxidation Products of 2,3-Dimethylbenzothiophene

## 2,3-Diformylbenzothiophene



**Figure S18** Mass spectrum of 2,3-diformylbenzothiophene, formed through photooxidation of 2,3-dimethylbenzothiophene.

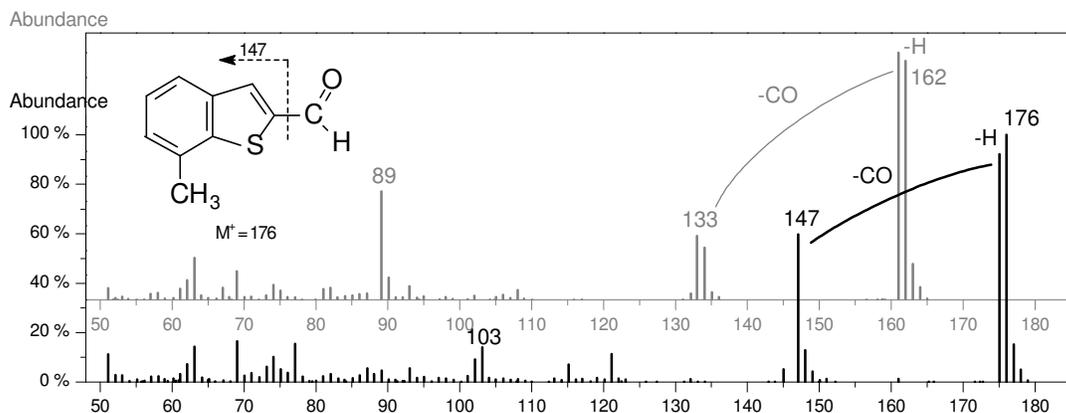
## Benzothiophene-2,3-dicarboxylic acid



**Figure S19** Mass spectrum of benzothiophene-2,3-dicarboxylic acid dimethyl ester, formed through photooxidation of 2,3-dimethylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

## Photooxidation Products of 2,7-Dimethylbenzothiophene

### 2-Formyl-7-methylbenzothiophene (F1·II)

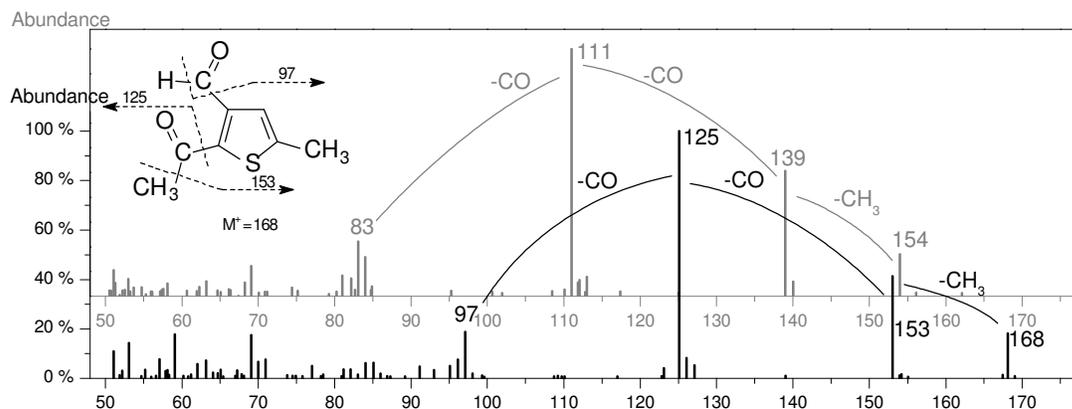


**Figure S20** Mass spectrum of 2-formyl-7-methylbenzothiophene (lower MS), formed through photooxidation of 2,7-dimethylbenzothiophene. The mass spectrum of 2-formylbenzothiophene (upper MS in gray), formed through photooxidation of 2-methylbenzothiophene is helpful in the identification and is shown for comparison.

### 7-Methylbenzothiophene-2-carboxylic acid (F1·III)

Mass spectrum of the methyl ester is similar to that of benzothiophene-2-carboxylic acid methyl ester shown in Figure S6 but at 14 mass units higher.

## 2-Acetyl-3-formyl-5-methylthiophene (F1·IV)



**Figure S21** Mass spectrum of 2-acetyl-3-formyl-5-methylthiophene (lower MS), formed through photooxidation of 2,7-dimethylbenzothiophene. The mass spectrum of 2-acetyl-3-formylthiophene (upper MS in gray), formed through photooxidation of 7-methylbenzothiophene is helpful in the identification and is shown for comparison.

## 2,3,5-Thiophenetricarboxylic acid (F1·V)

Mass spectrum of the trimethyl ester is shown in Figure S9.

## 2-Formyl-6-methylbenzenesulfonic acid (F1·VI)

Mass spectrum of the methyl ester is similar to that of 2-formyl-4-methylbenzenesulfonic acid methyl ester shown in Figure S14.

## 3-Methyl-2-sulfobenzoic acid (F1·VII)

Mass spectrum of the dimethyl ester is similar to that of 5-methyl-2-sulfobenzoic acid dimethyl ester shown in Figure S15.

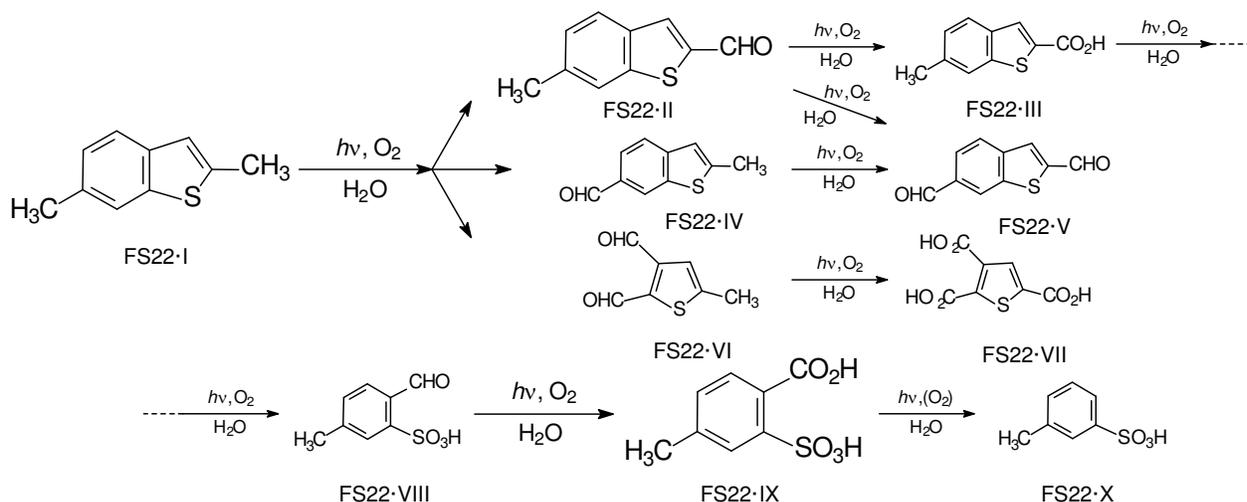
## 2-Sulfoisophthalic acid (F1·VIII)

Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16.

## 2-Toluenesulfonic acid (F1·IX)

Mass spectrum of the methyl ester is similar to that of 4-toluenesulfonic acid methyl ester shown in Figure S17.

## Photooxidation Products of 2,6-Dimethylbenzothiophene



**Figure S22** Postulated reaction scheme of the photooxidation of 2,6-dimethylbenzothiophene (FS22·I).

### 2-Formyl-6-methylbenzothiophene (FS22·II)

Mass spectrum is similar to that of 2-formyl-7-methylbenzothiophene shown in Figure S20.

### 6-Methylbenzothiophene-2-carboxylic acid (FS22·III)

Mass spectrum of the methyl ester is similar to that of benzothiophene-2-carboxylic acid methyl ester shown in Figure S6 but at 14 mass units higher.

### 6-Formyl-2-methylbenzothiophene (FS22·IV)

Mass spectrum is similar to that of 2-formylbenzothiophene shown in Figure S5 but at 14 mass units higher.

### 2,6-Diformylbenzothiophene (FS22·V)

Mass spectrum is similar to that of 2,3-diformylbenzothiophene shown in Figure S18.

### 2,3-Diformyl-5-methylthiophene (FS22·VI)

Mass spectrum is similar to that of 2,3-diformylthiophene shown as FS11·IV but at 14 mass units higher.

### 2,3,5-Thiophenetricarboxylic acid (FS22·VII)

Mass spectrum of the trimethyl ester is shown in Figure S9.

### 2-Formyl-5-methylbenzenesulfonic acid (FS22·VIII)

Mass spectrum of the methyl ester is similar to that of 2-formyl-4-methylbenzenesulfonic acid methyl ester shown in Figure S14.

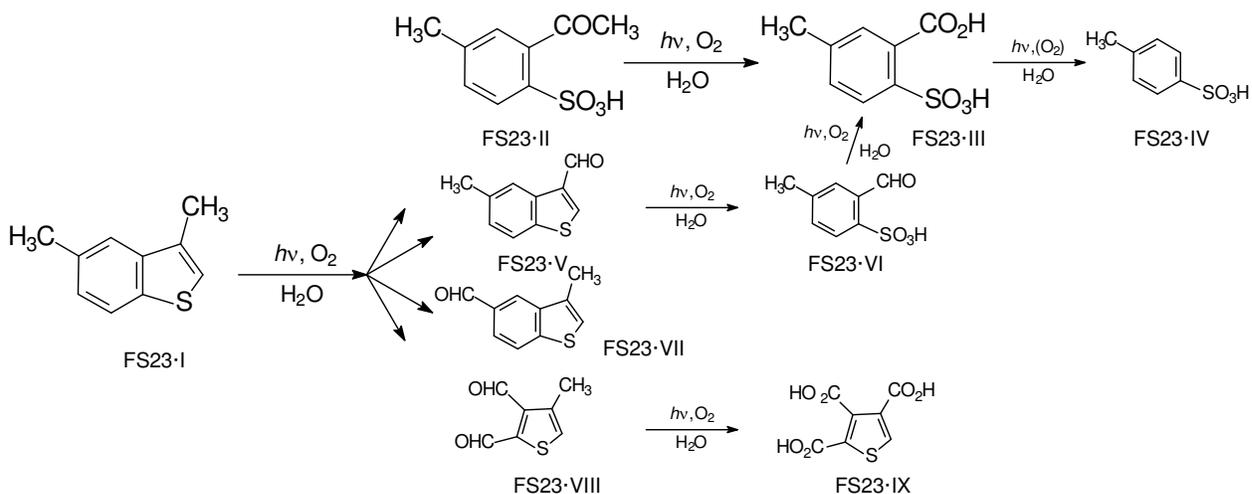
#### 4-Methyl-2-sulfobenzoic acid (FS22-IX)

Mass spectrum of the dimethyl ester is shown in Figure S24 (upper MS in gray).

#### 3-Toluenesulfonic acid (F22-X)

Mass spectrum of the methyl ester is similar to that of 4-toluenesulfonic acid methyl ester shown in Figure S17.

### Photooxidation Products of 3,5-Dimethylbenzothiophene



**Figure S23** Postulated reaction scheme of the photooxidation of 3,5-dimethylbenzothiophene (FS23-I).

#### 2-Acetyl-4-methylbenzenesulfonic acid (FS23-II)

Mass spectrum of the methyl ester is similar to that of 2-acetylbenzenesulfonic acid methyl ester shown in Figure S10 but at 14 mass units higher.

#### 5-Methyl-2-sulfobenzoic acid (FS23-III)

Mass spectrum of the dimethyl ester is shown in Figure S15.

#### 4-Toluenesulfonic acid (F23-IV)

Mass spectrum of the methyl ester is shown in Figure S17.

#### 5-Methyl-3-formylbenzothiophene (FS23-V)

Mass spectrum is similar to that of 2-formylbenzothiophene shown in Figure S5 but at 14 mass units higher.

#### 2-Formyl-4-methylbenzenesulfonic acid (FS23-VI)

Mass spectrum of the methyl ester is shown in Figure S14.

### **3-Methyl-5-formylbenzothiophene (FS23·VII)**

Mass spectrum is similar to that of 2-formylbenzothiophene shown in Figure S5 but at 14 mass units higher.

### **2,3-Diformyl-4-methylthiophene (FS23·VIII)**

Mass spectrum is similar to that of 2,3-diformylthiophene shown as FS11·IV but at 14 mass units higher.

### **2,3,4-Thiophenetricarboxylic acid (FS23·IX)**

Mass spectrum of the trimethyl ester is similar to that of 2,3,5-thiophenetricarboxylic acid trimethyl ester shown in Figure S9.

## **Photooxidation Products of 4,6-Dimethylbenzothiophene**

### **4,6-Dimethylbenzothiophene-2,3-quinone (F2·II)**

Mass spectrum is similar to that of 5-methylbenzothiophene-2,3-quinone shown in Figure S12 but at 14 mass units higher.

### **6-Formyl-4-methylbenzothiophene (F2·III)**

Mass spectrum is similar to that of 2-formylbenzothiophene shown in Figure S5 but at 14 mass units higher.

### **3-Acetyl-2-formylthiophene (F2·IV)**

Mass spectrum is similar to that of 2-acetyl-3-formylthiophene shown in Figure S21 (upper MS in gray).

### **4-Formyl-6-methylbenzothiophene (F2·V)**

Mass spectrum is similar to that of 2-formylbenzothiophene shown in Figure S5 but at 14 mass units higher.

### **2,3-Diformylthiophene (F2·VI)**

$m/z = 140$  ( $M^+$ ; 30 %),  $139$  ( $[M-H]^+$ ; 17 %),  $111$  ( $[M-H-CO]^+$ ; 100 %),  
 $83$  ( $[M-H-CO-CO]^+$ ; 15%).

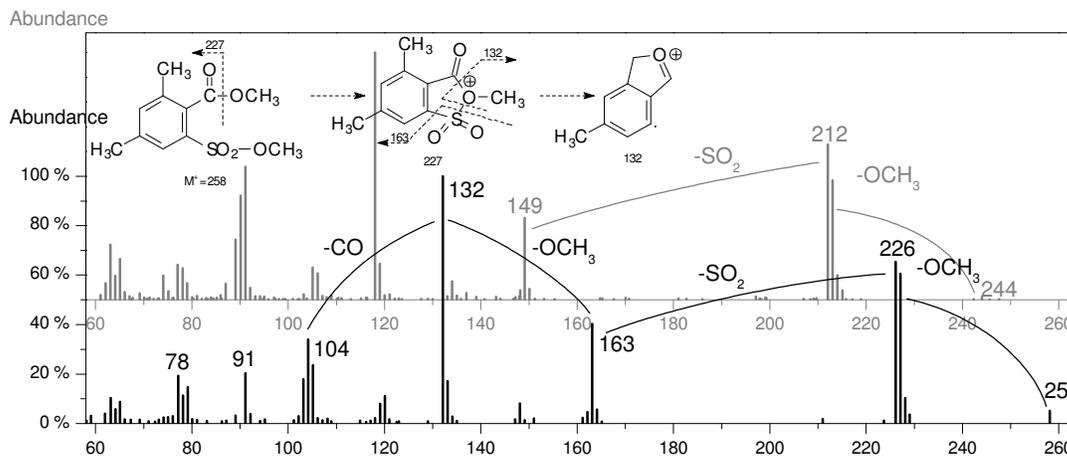
### **2,3-Thiophenedicarboxylic acid (F2·VII)**

Mass spectrum of the dimethyl ester is shown in Figure S13.

### **2-Formyl-3,5-dimethylbenzenesulfonic acid (F2·VIII)**

Mass spectrum of the methyl ester is similar to that of 2-formyl-4-methylbenzenesulfonic acid methyl ester shown in Figure S14 but at 14 mass units higher.

## 2,4-Dimethyl-6-sulfobenzoic acid (F2·IX)



**Figure S24** Mass spectrum of 2,4-dimethyl-6-sulfobenzoic acid dimethyl ester (lower MS), formed through photooxidation of 4,6-dimethylbenzothiophene. The mass spectrum of 4-methyl-2-sulfobenzoic acid dimethyl ester (upper MS in gray), formed through photooxidation of 6-methylbenzothiophene is helpful in the identification and is shown for comparison. All acids are shown as methyl esters since sample was treated with diazomethane.

## 2-Methyl-6-sulfoterephthalic acid (F2·X)

Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16 but at 14 mass units higher.

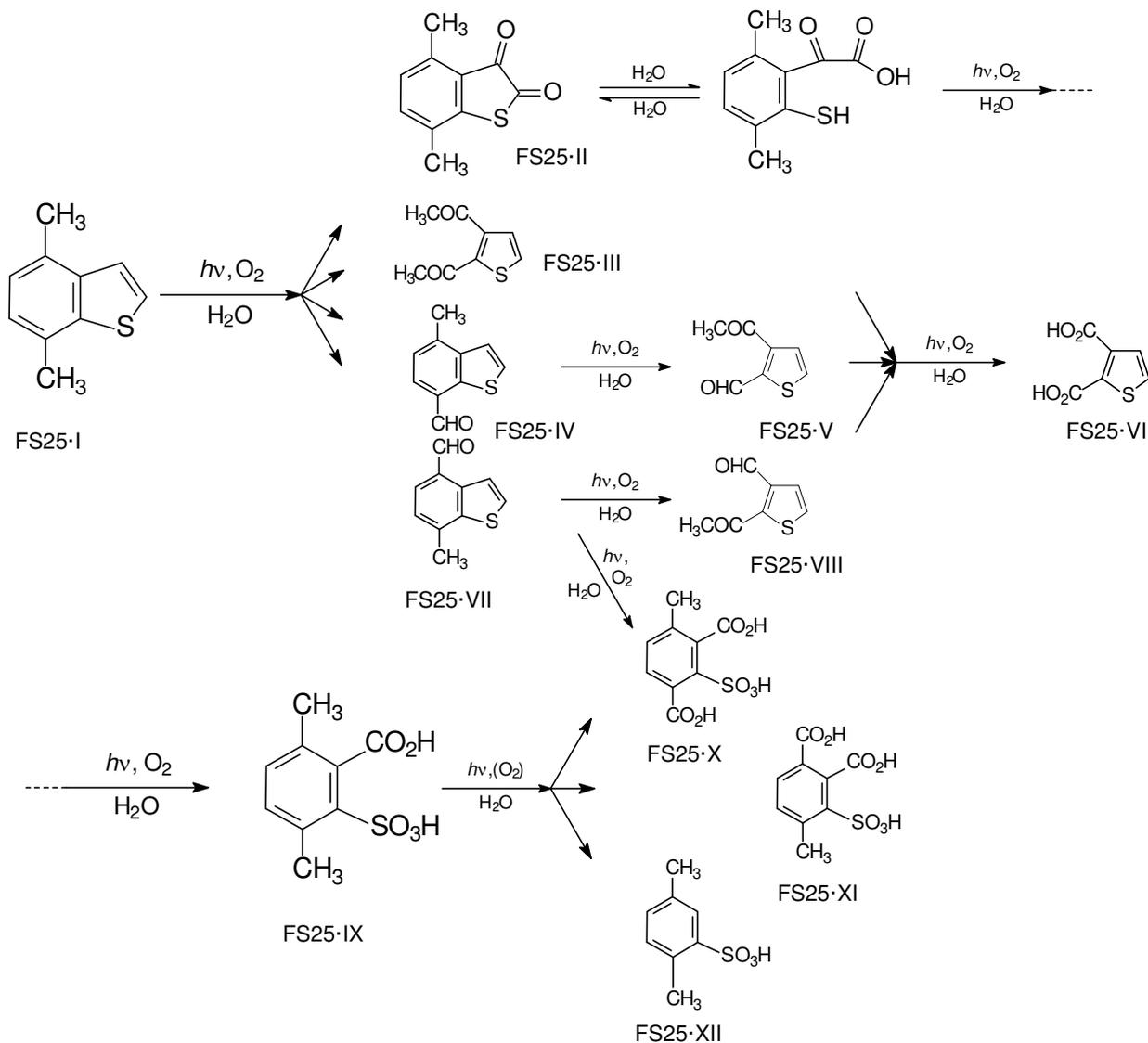
## 4-Methyl-6-sulfophthalic acid (F2·XI)

Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16 but at 14 mass units higher.

## 3,5-Dimethylbenzenesulfonic acid (F2·XII)

Mass spectrum of the methyl ester is similar to that of 2,3-dimethylbenzenesulfonic acid methyl ester in Figure S27.

## Photooxidation Products of 4,7-Dimethylbenzothiophene



**Figure S25** Postulated reaction scheme of the photooxidation of 4,7-dimethylbenzothiophene (FS25-I).

### 4,6-Dimethylbenzothiophene-2,3-quinone (FS25-II)

Mass spectrum is similar to that of 5-methylbenzothiophene-2,3-quinone shown in Figure S12 but at 14 mass units higher.

### 2,3-Diacetylthiophene (FS25-III)

$m/z = 168$  ( $M^+$ ; 60 %),  $153$  ( $[M-CH_3]^+$ ; 82 %),  $111$  ( $[M-CH_3-COCH_2]^+$ ; 100 %),  $83$  ( $C_4H_3S^+$ ; 23 %)

**7-Formyl-4-methylbenzothiophene (FS25·IV)**

Mass spectrum is similar to that of 2-formyl-7-methylbenzothiophene shown in Figure S20.

**3-Acetyl-2-formylthiophene (FS25·V)**

Mass spectrum is similar to that of 2-acetyl-3-formylthiophene shown in Figure S21 (upper MS in gray).

**2,3-Thiophenedicarboxylic acid (FS25·VI)**

Mass spectrum of the dimethyl ester is shown in Figure S13.

**4-Formyl-7-methylbenzothiophene (FS25·VII)**

Mass spectrum is similar to that of 2-formyl-7-methylbenzothiophene shown in Figure S20.

**2-Acetyl-3-formylthiophene (FS25·VIII)**

Mass spectrum is shown in Figure S21 (upper MS in gray).

**3,6-Dimethyl-2-sulfobenzoic acid (FS25·IX)**

Mass spectrum of the dimethyl ester is similar to that of 2,4-dimethyl-6-sulfobenzoic acid dimethyl ester shown in Figure S24.

**2-Methyl-6-sulfoisophthalic acid (FS25·X)**

Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16 but at 14 mass units higher.

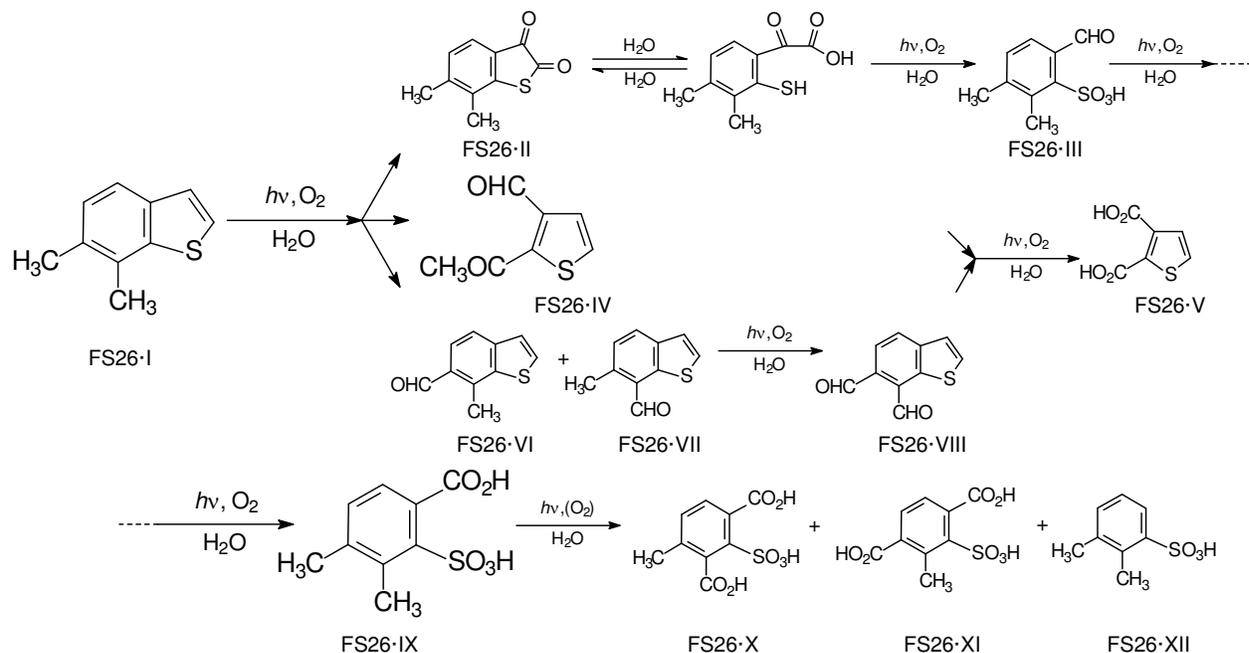
**4-Methyl-3-sulfophthalic acid (FS25·XI)**

Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16 but at 14 mass units higher.

**2,5-Dimethylbenzenesulfonic acid (FS25·XII)**

Mass spectrum of the methyl ester is similar to that of 2,3-dimethylbenzenesulfonic acid methyl ester in Figure S27.

## Photooxidation Products of 6,7-Dimethylbenzothiophene



**Figure S26** Postulated reaction scheme of the photooxidation of 6,7-dimethylbenzothiophene (FS26-I).

### 6,7-Dimethylbenzothiophene-2,3-quinone (FS26-II)

Mass spectrum is similar to that of 5-methylbenzothiophene-2,3-quinone shown in Figure S12 but at 14 mass units higher.

### 2-Formyl-5,6-dimethylbenzenesulfonic acid (FS26-III)

Mass spectrum of the methyl ester is similar to that of 2-formyl-4-methylbenzenesulfonic acid methyl ester shown in Figure S14 but at 14 mass units higher.

### 2-Acetyl-3-formylthiophene (FS26-IV)

Mass spectrum is shown in Figure S21 (upper MS in gray).

### 2,3-Thiophenedicarboxylic acid (FS26-V)

Mass spectrum of the dimethyl ester is shown in Figure S13.

### 6-Formyl-7-methylbenzothiophene (FS26-VI)

Mass spectrum is similar to that of 2-formyl-7-methylbenzothiophene shown in Figure S20.

### 7-Formyl-6-methylbenzothiophene (FS26-VII)

Mass spectrum is similar to that of 2-formyl-7-methylbenzothiophene shown in Figure S20.

### 6,7-Diformylbenzothiophene (FS26·VIII)

Mass spectrum is similar to that of 2,3-diformylbenzothiophene shown in Figure S18.

### 3,4-Dimethyl-2-sulfobenzoic acid (FS26·IX)

Mass spectrum of the dimethyl ester is similar to that of 2,4-dimethyl-6-sulfobenzoic acid dimethyl ester shown in Figure S24.

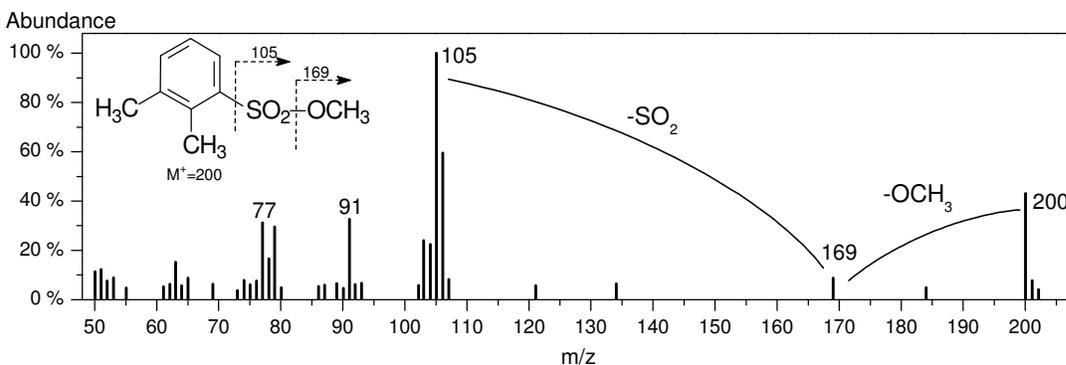
### 2-Methyl-6-sulfoisophthalic acid (FS26·X)

Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16 but at 14 mass units higher.

### 2-Methyl-3-sulfoterephthalic acid (FS26·XI)

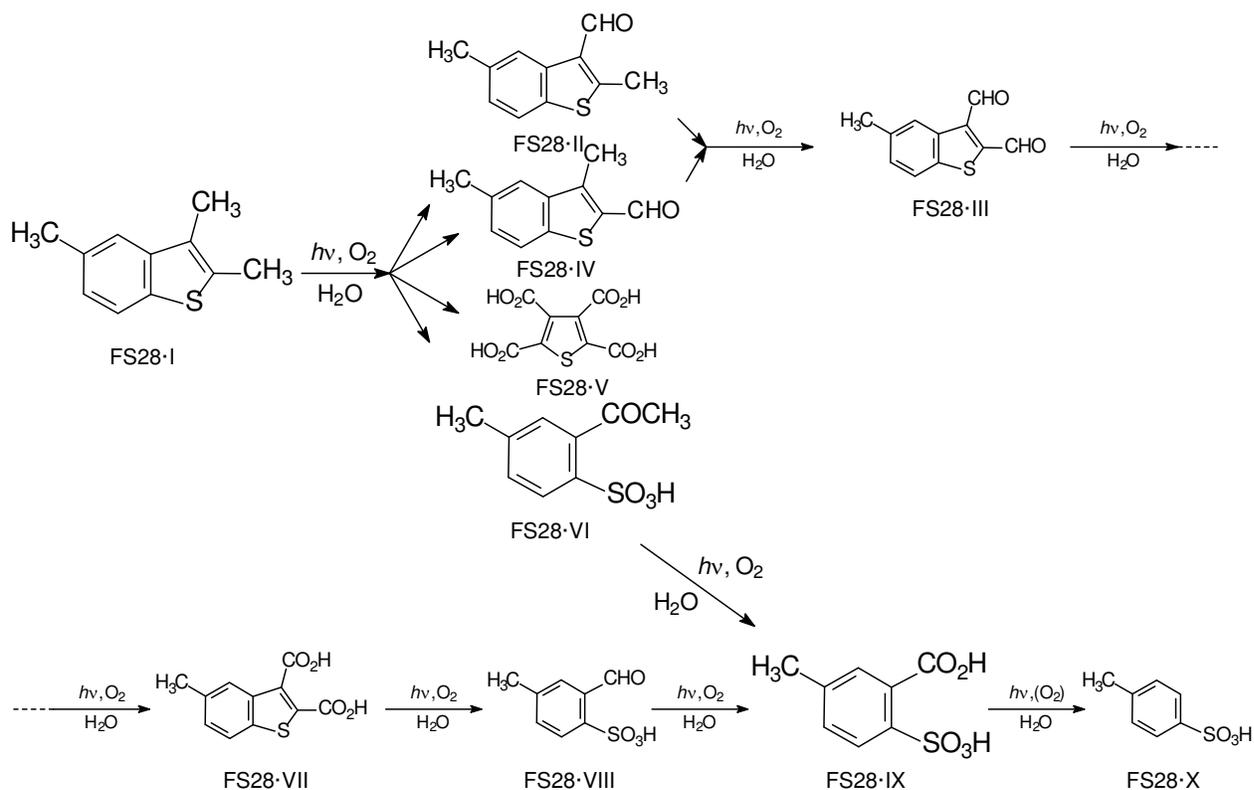
Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16 but at 14 mass units higher.

### 2,3-Dimethylbenzenesulfonic acid (FS26·XII)



**Figure S27** Mass spectrum of methyl ester of 2,3-dimethylbenzenesulfonic acid methyl ester, formed through photooxidation of 6,7-dimethylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

## Photooxidation Products of 2,3,5-Trimethylbenzothiophene



**Figure S28** Postulated reaction scheme of the photooxidation of 2,3,5-trimethylbenzothiophene (FS28-I).

### 3-Formyl-2,5-dimethylbenzothiophene (FS28-II)

Mass spectrum is similar to that of 2-formyl-7-methylbenzothiophene shown in Figure S20 but at 14 mass units higher.

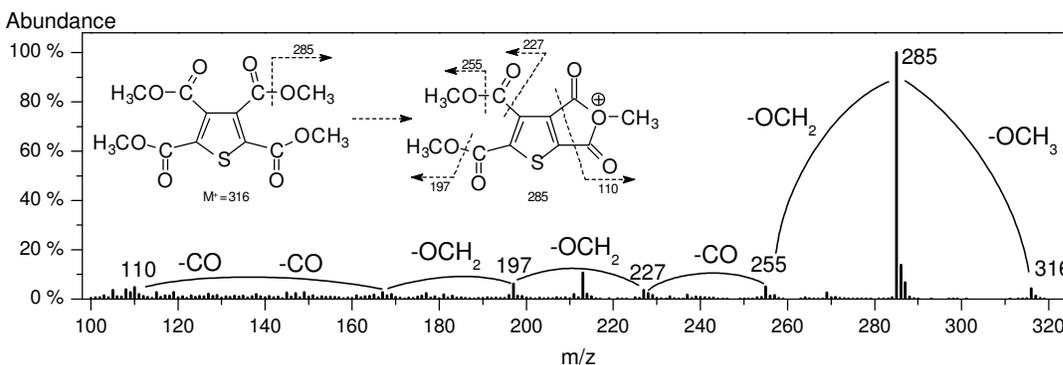
### 2,3-Diformyl-5-methylbenzothiophene (FS28-III)

Mass spectrum is similar to that of 2,3-diformyl-7-methylbenzothiophene shown in Figure S33 (upper MS in gray).

### 2-Formyl-3,5-dimethylbenzothiophene (FS28-IV)

Mass spectrum is similar to that of 2-formyl-7-methylbenzothiophene shown in Figure S20 but at 14 mass units higher.

## 2,3,4,5-Thiophenetetracarboxylic acid (FS28·V)



**Figure S29** Mass spectrum of 2,3,4,5-thiophenetetracarboxylic acid tetramethyl ester, formed through photooxidation of 2,3,5-trimethylbenzothiophene. The acid is shown as the methyl ester since sample was treated with diazomethane.

## 2-Acetyl-4-methylbenzenesulfonic acid (FS28·VI)

Mass spectrum of the methyl ester is shown in Figure S34 (upper MS in gray).

## 5-Methylbenzothiophene-2,3-dicarboxylic acid (FS28·VII)

Mass spectrum of the dimethyl ester is similar to that of benzothiophene-2,3-dicarboxylic acid dimethyl ester shown in Figure S19 but at 14 mass units higher.

## 2-Formyl-4-methylbenzenesulfonic acid (FS28·VIII)

Mass spectrum of the methyl ester is shown in Figure S14.

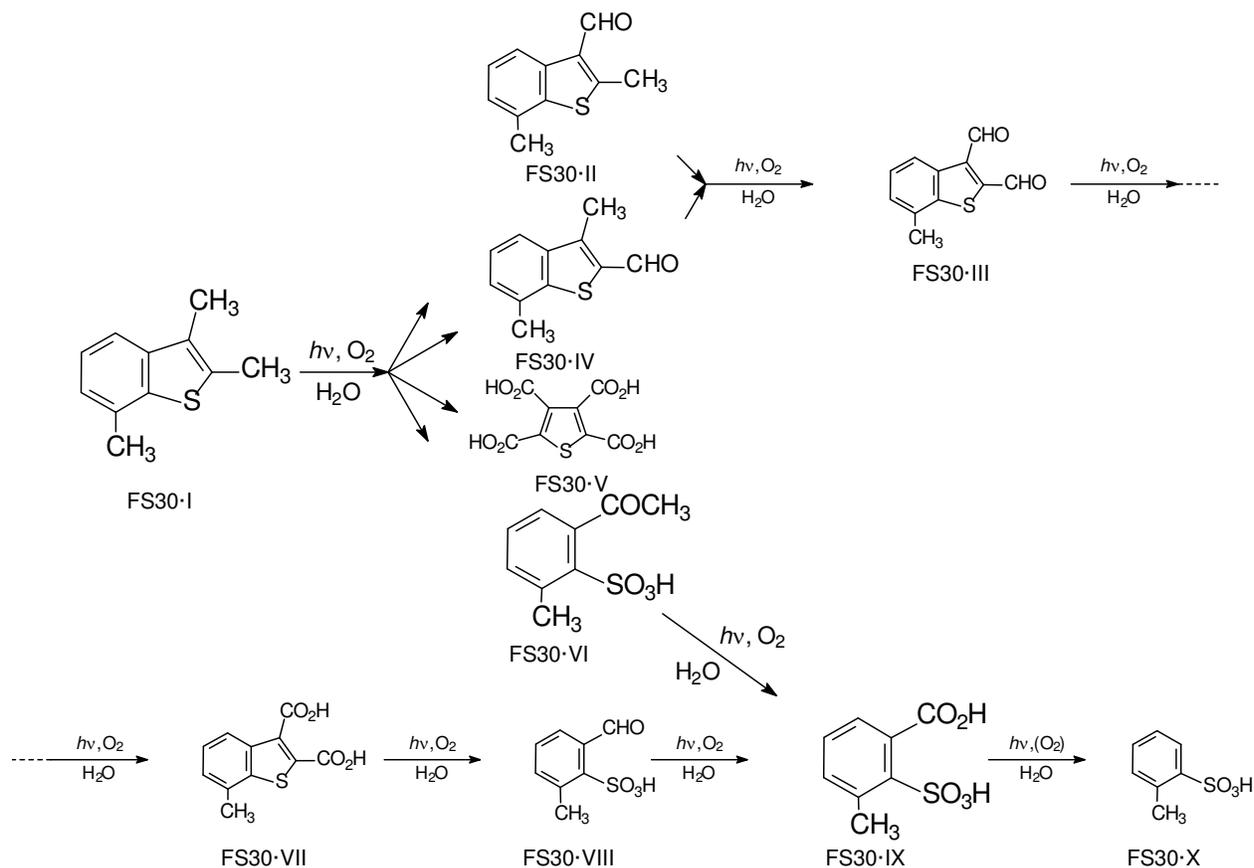
## 5-Methyl-2-sulfobenzoic acid (FS28·IX)

Mass spectrum of the dimethyl ester is shown in Figure S15.

## 4-Toluenesulfonic acid (FS28·X)

Mass spectrum of the methyl ester is shown in Figure S17.

## Photooxidation Products of 2,3,7-Trimethylbenzothiophene



**Figure S30** Postulated reaction scheme of the photooxidation of 2,3,7-trimethylbenzothiophene (FS30-I).

### 3-Formyl-2,7-dimethylbenzothiophene (FS30-II)

Mass spectrum is shown in Figure S32 (upper MS in gray).

### 2,3-Diformyl-7-methylbenzothiophene (FS30-III)

Mass spectrum is shown in Figure S33 (upper MS in gray).

### 2-Formyl-3,7-dimethylbenzothiophene (FS30-IV)

Mass spectrum is shown in Figure S32 (upper MS in gray).

### 2,3,4,5-Thiophenetetracarboxylic acid (FS30-V)

Mass spectrum of the tetramethyl ester is shown in Figure S29.

### 2-Acetyl-6-methylbenzenesulfonic acid (FS30-VI)

Mass spectrum of the methyl ester is similar to that of 2-acetylbenzenesulfonic acid methyl ester shown in Figure S10 but at 14 mass units higher.

**7-Methylbenzothiophene-2,3-dicarboxylic acid (FS30·VII)**

Mass spectrum of the dimethyl ester is similar to that of benzothiophene-2,3-dicarboxylic acid dimethyl ester shown in Figure S19 but at 14 mass units higher.

**2-Formyl-6-methylbenzenesulfonic acid (FS30·VIII)**

Mass spectrum of the methyl ester is similar to that of 2-formyl-4-methylbenzenesulfonic acid methyl ester shown in Figure S14.

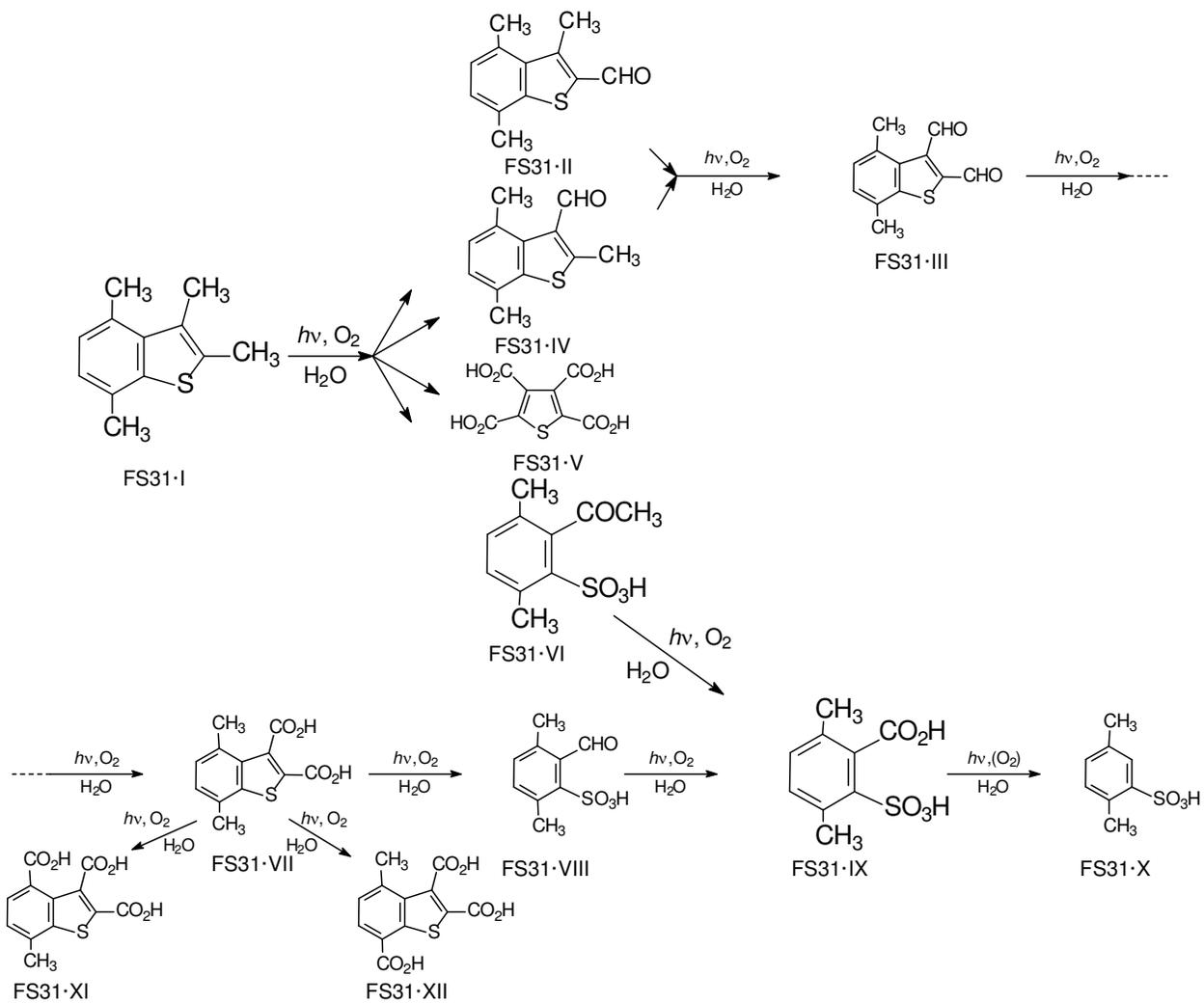
**3-Methyl-2-sulfobenzoic acid (FS30·IX)**

Mass spectrum of the dimethyl ester is similar to that of 5-methyl-2-sulfobenzoic acid dimethyl ester shown in Figure S15.

**2-Toluenesulfonic acid (FS30·X)**

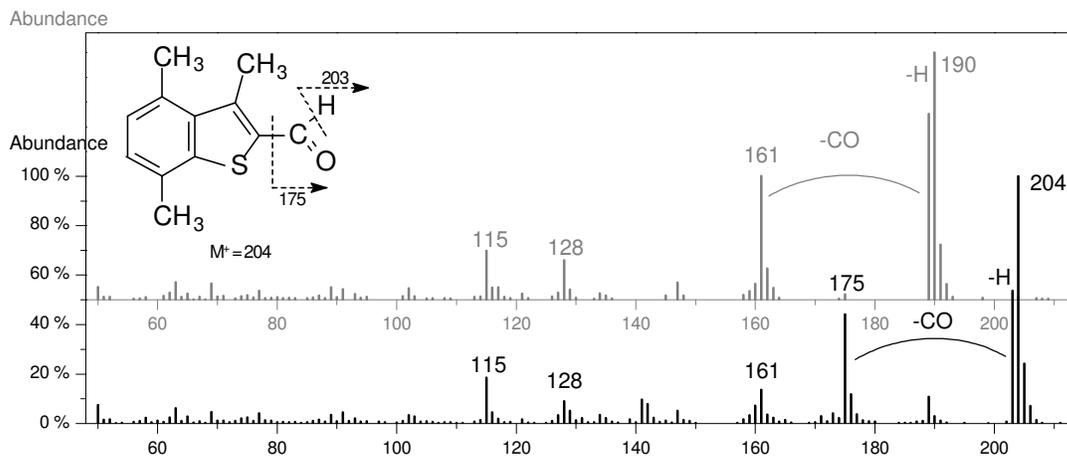
Mass spectrum of the methyl ester is similar to that of 4-toluenesulfonic acid methyl ester shown in Figure S17.

## Photooxidation Products of 2,3,4,7-Tetramethylbenzothiophene



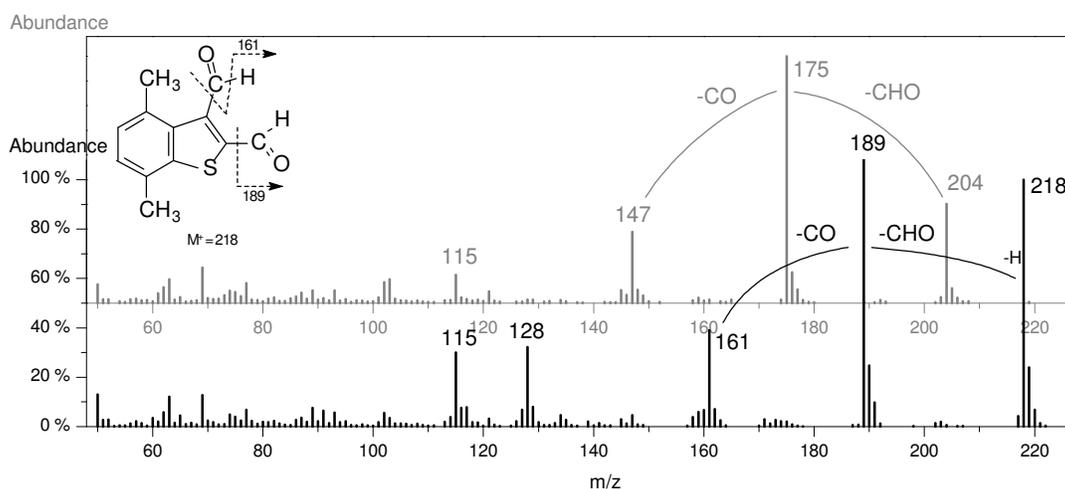
**Figure S31** Postulated reaction scheme of the photooxidation of 2,3,4,7-tetramethylbenzothiophene (FS31-I).

## 2-Formyl-3,4,7-trimethylbenzothiophene (FS31-II)



**Figure S32** Mass spectrum of 2-formyl-3,4,7-trimethylbenzothiophene (lower MS), formed through photooxidation of 2,3,4,7-tetramethylbenzothiophene. The known mass spectrum of 2-formyl-3,7-dimethylbenzothiophene (upper MS in gray), formed through photooxidation of 2,3,7-trimethylbenzothiophene is helpful in the identification and is shown for comparison. The isomer 3-formyl-2,4,7-trimethylbenzothiophene was also found so an exact assignment is impossible.

## 2,3-Diformyl-4,7-dimethylbenzothiophene (FS31-III)



**Figure S33** Mass spectrum of 2,3-diformyl-4,7-dimethylbenzothiophene (lower MS), formed through photooxidation of 2,3,4,7-tetramethylbenzothiophene. The known mass spectrum of 2,3-diformyl-7-methylbenzothiophene (upper MS in gray), formed through photooxidation of 2,3,7-trimethylbenzothiophene is helpful in the identification and is shown for comparison.

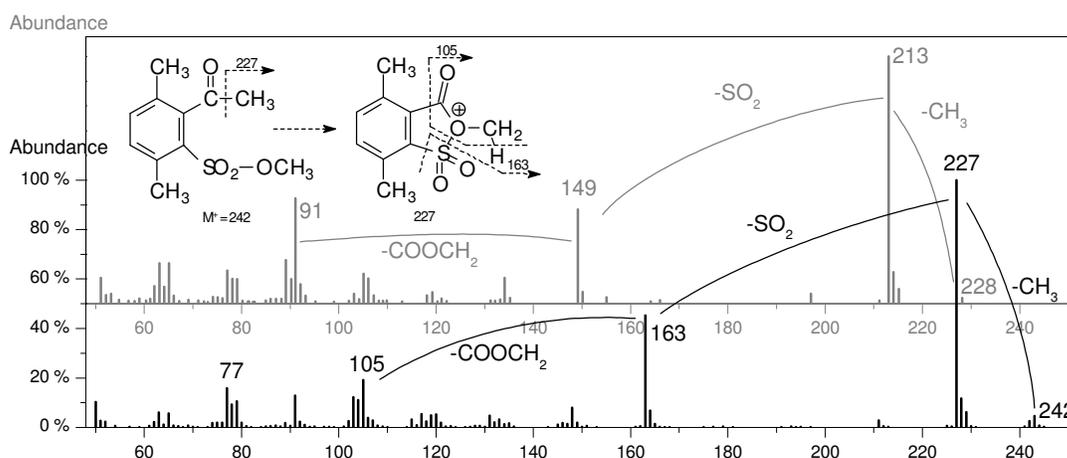
### 3-Formyl-2,4,7-trimethylbenzothiophene (FS31·IV)

Mass spectrum is similar to that of 2-formyl-3,4,7-trimethylbenzothiophene shown in Figure S32.

### 2,3,4,5-Thiophenetetracarboxylic acid (FS31·V)

Mass spectrum of the tetramethyl ester is shown in Figure S29.

### 2-Acetyl-3,6-dimethylbenzenesulfonic acid (FS31·VI)



**Figure S34** Mass spectrum of 2-acetyl-3,6-dimethylbenzenesulfonic acid methyl ester (lower MS), formed through photooxidation of 2,3,4,7-tetramethylbenzothiophene. The known mass spectrum of 2-acetyl-4-methylbenzenesulfonic acid methyl ester (upper MS in gray), formed through photooxidation of 2,3,5-trimethylbenzothiophene is helpful in the identification and is shown for comparison. The acid is shown as the methyl ester since the sample was treated with diazomethane.

### 4,7-Dimethylbenzothiophene-2,3-dicarboxylic acid (FS31·VII)

Mass spectrum of the dimethyl ester is similar to that of benzothiophene-2,3-dicarboxylic acid dimethyl ester shown in Figure S19 but at 28 mass units higher.

### 2-Formyl-3,6-dimethylbenzenesulfonic acid (FS31·VIII)

Mass spectrum of the methyl ester is similar to that of 2-formyl-4-methylbenzenesulfonic acid methyl ester shown in Figure S14 but at 14 mass units higher.

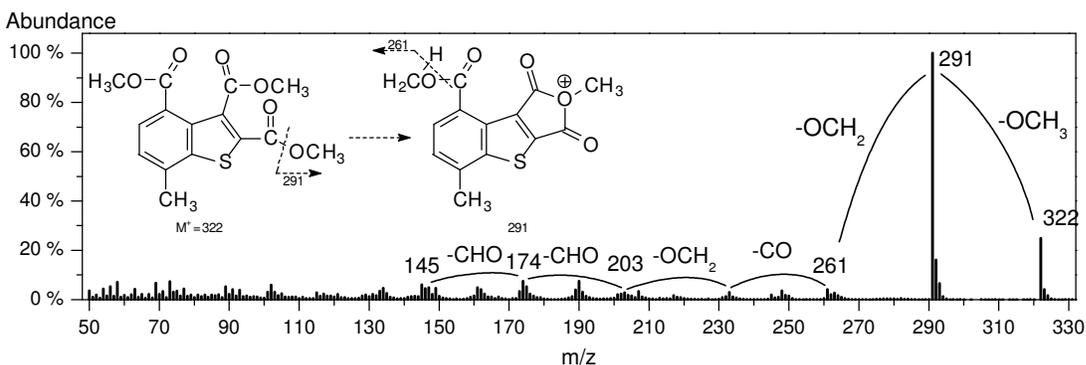
### 3,6-Dimethyl-2-sulfobenzoic acid (FS31·IX)

Mass spectrum of the dimethyl ester is similar to that of 2,4-dimethyl-6-sulfobenzoic acid dimethyl ester shown in Figure S24.

### 2,5-Dimethylbenzenesulfonic acid (FS31·X)

Mass spectrum of the methyl ester is similar to that of 2,3-dimethylbenzenesulfonic acid methyl ester in Figure S27.

### 7-Methyl-2,3,4-benzothiophenetricarboxylic acid (FS31·XI)

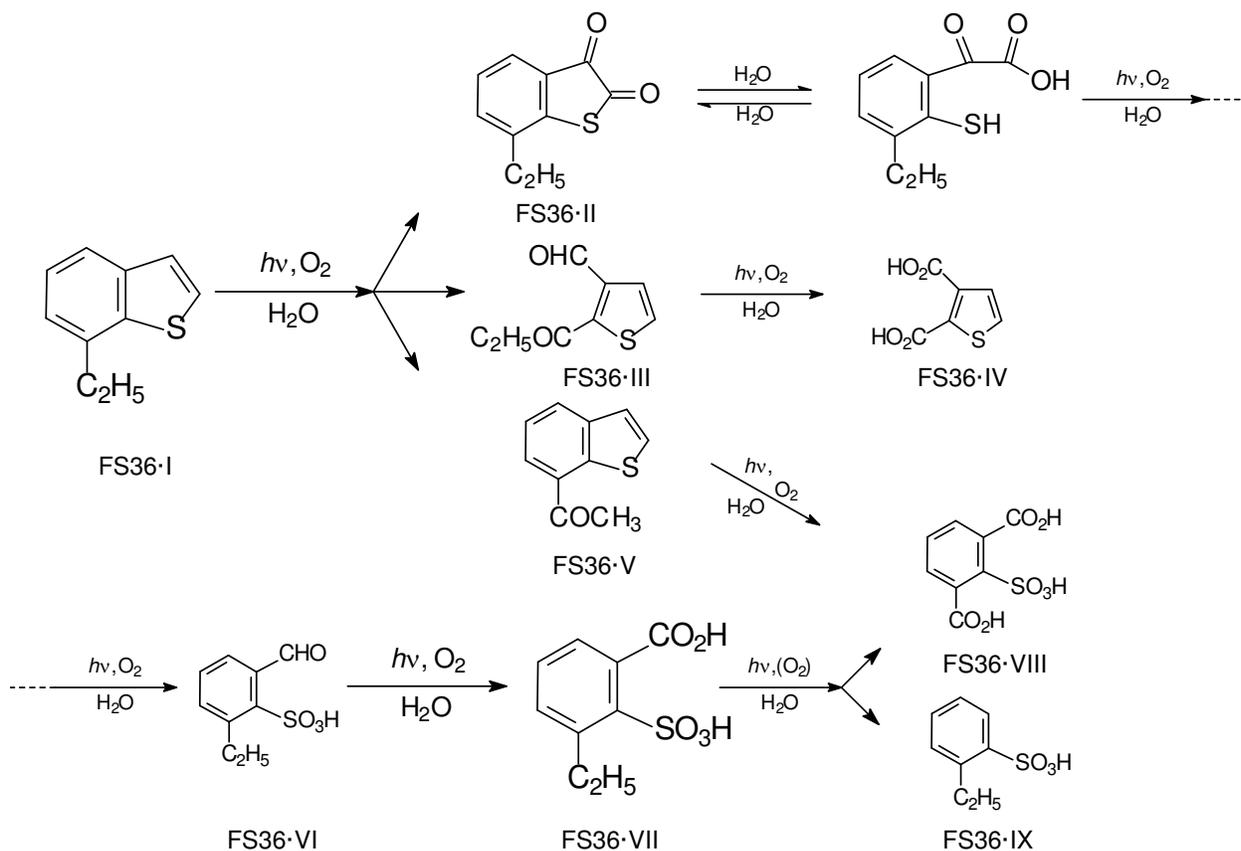


**Figure S35** Mass spectrum of 7-methyl-2,3,4-benzothiophenetricarboxylic acid trimethyl ester, formed through photooxidation of 2,3,4,7-tetramethylbenzothiophene. The isomer 4-methyl-2,3,7-benzothiophenetricarboxylic acid trimethyl ester was also found so an exact assignment is impossible. The acid is shown as methyl ester because sample was treated with diazomethane.

### 4-Methyl-2,3,7-benzothiophenetricarboxylic acid (FS31·XII)

Mass spectrum of the trimethyl ester is similar to that of 7-methyl-2,3,4-benzothiophenetricarboxylic acid trimethyl ester shown in Figure S35.

## Photooxidation Products of 7-Ethylbenzothiophene

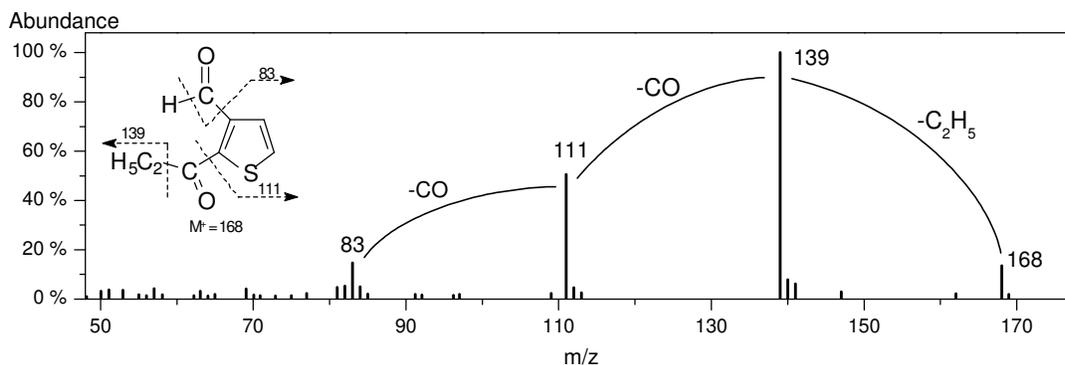


**Figure S36** Postulated reaction scheme of the photooxidation of 7-ethylbenzothiophene (FS36-I).

### 7-Ethylbenzothiophene-2,3-quinone (FS36-II)

Mass spectrum is similar to that of 5-methylbenzothiophene-2,3-quinone shown in Figure S12 but at 14 mass units higher.

### 2-Propionyl-3-formylthiophene (FS36-III)

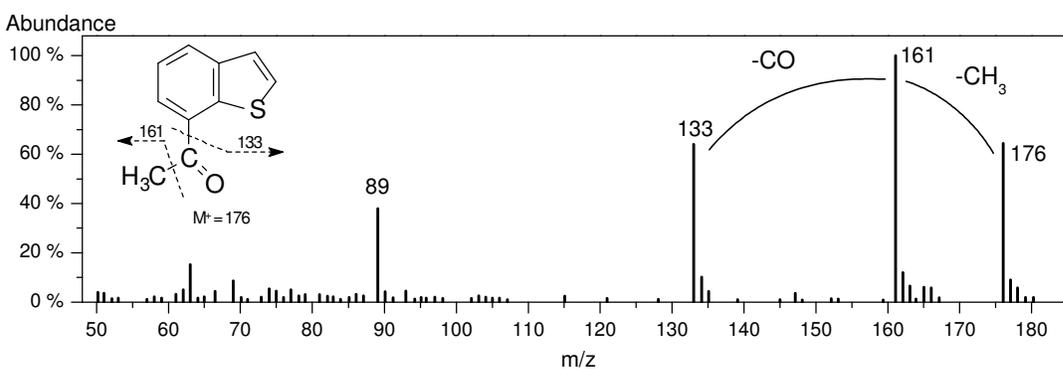


**Figure S37** Mass spectrum of 2-propionyl-3-formylthiophene, formed through photooxidation of 7-ethylbenzothiophene.

### 2,3-Thiophenedicarboxylic acid (FS36-IV)

Mass spectrum of the dimethyl ester is shown in Figure S13.

### 7-Acetylbenzothiophene (FS36-V)



**Figure S38** Mass spectrum of 7-acetylbenzothiophene, formed through photooxidation of 7-ethylbenzothiophene.

### 2-Formyl-6-ethylbenzenesulfonic acid (FS36-VI)

Mass spectrum of the methyl ester is similar to that of 2-formyl-4-methylbenzenesulfonic acid methyl ester shown in Figure S14 but at 14 mass units higher.

### 3-Ethyl-2-sulfobenzoic acid (FS36·VII)

Mass spectrum of the dimethyl ester is similar to that of 2,4-dimethyl-6-sulfobenzoic acid dimethyl ester shown in Figure S24.

### 2-Sulfoisophthalic acid (FS36·VIII)

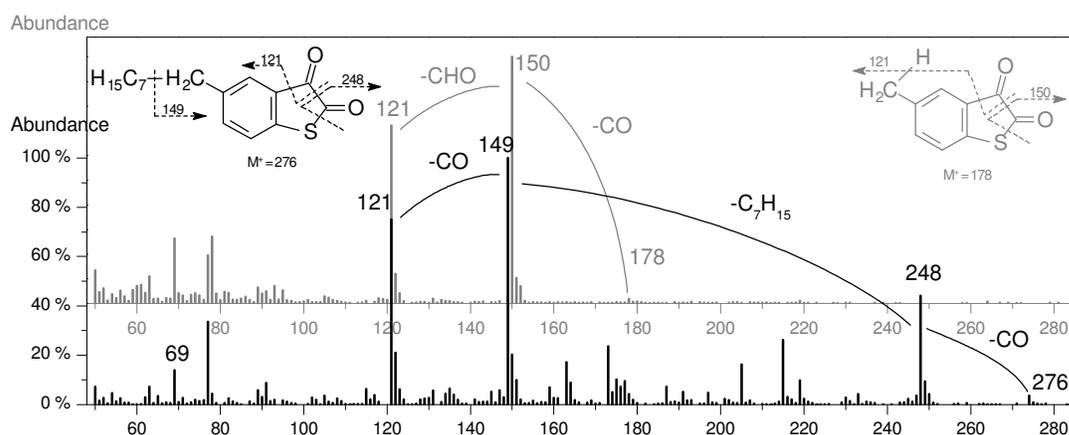
Mass spectrum of the trimethyl ester is similar to that of 4-sulfoisophthalic acid trimethyl ester shown in Figure S16.

### 2-Ethylbenzenesulfonic acid (FS36·IX)

Mass spectrum of the methyl ester is similar to that of 2,3-dimethylbenzenesulfonic acid methyl ester shown in Figure S27.

## Photooxidation Products of 5-Octylbenzothiophene

### 5-Octylbenzothiophene-2,3-quinone (F3·II)



**Figure S39** Mass spectrum of 5-octylbenzothiophene-2,3-quinone (lower MS), formed through photooxidation of 5-octylbenzothiophene. The known mass spectrum of 5-methylbenzothiophene-2,3-quinone (upper MS in gray), formed through photooxidation of 5-methylbenzothiophene is helpful in the identification and is shown for comparison.

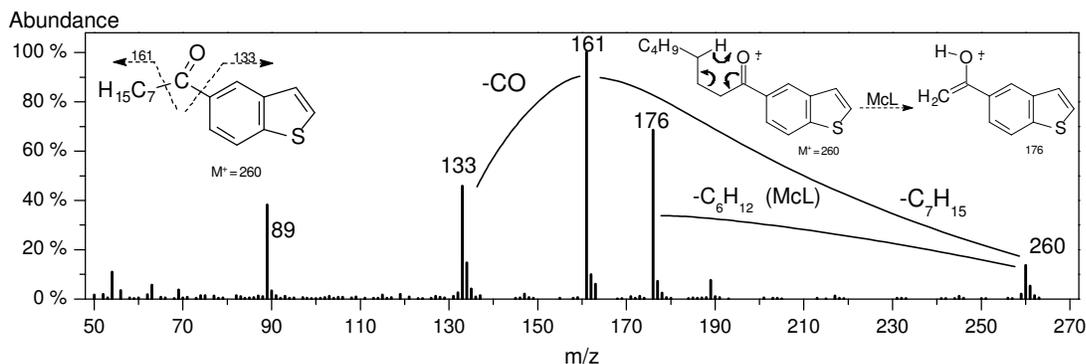
### 2,3-Diformylthiophene (F3·III)

$m/z = 140$  ( $M^+$ ; 30 %),  $139$  ( $[M-H]^+$ ; 17 %),  $111$  ( $[M-H-CO]^+$ ; 100 %),  
 $83$  ( $[M-H-CO-CO]^+$ ; 15%).

### 2,3-Thiophenedicarboxylic acid (F3·IV)

Mass spectrum of the dimethyl ester is shown in Figure S13.

### 5-Octanoylbenzothiophene (F3·V)

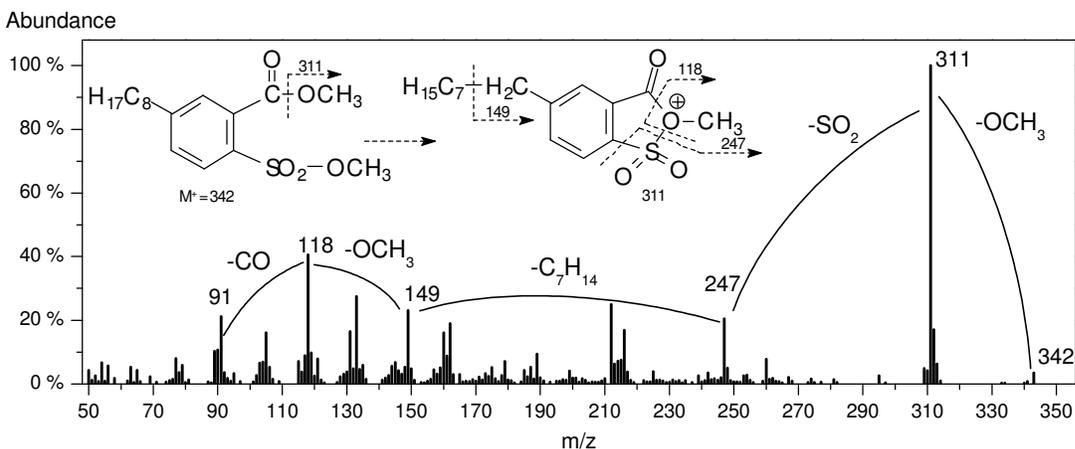


**Figure S40** Mass spectrum of 5-octanoylbenzothiophene, formed through photooxidation of 5-octylbenzothiophene.

### 2-Formyl-4-octylbenzenesulfonic acid (F3·VI)

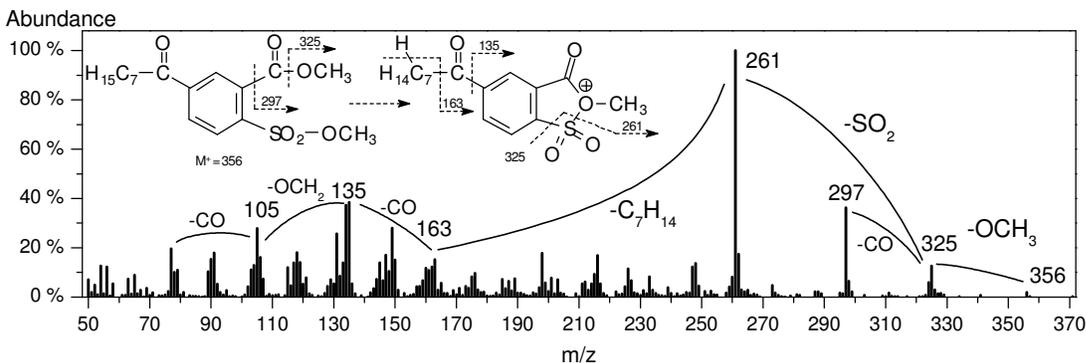
Mass spectrum of the dimethyl ester is similar to that of 5-octyl-2-sulfobenzoic acid dimethyl ester shown in Figure S41 but M<sup>+</sup> is 312 m/z instead of 342 m/z.

### 5-Octyl-2-sulfobenzoic acid (F3·VII)



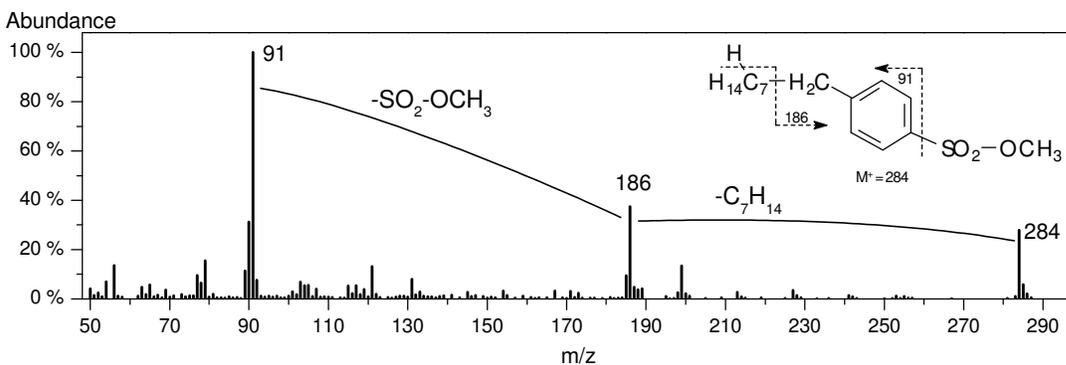
**Figure S41** Mass spectrum of 5-octyl-2-sulfobenzoic acid dimethyl ester, formed through photooxidation of 5-octylbenzothiophene. The acid is shown as the methyl ester since the sample was treated with diazomethane.

### 5-Octanoyl-2-sulfobenzoic acid (F3·VIII)



**Figure S42** Mass spectrum of 5-octanoyl-2-sulfobenzoic acid dimethyl ester, formed through photooxidation of 5-octylbenzothiophene. The acid is shown as the methyl ester since the sample was treated with diazomethane.

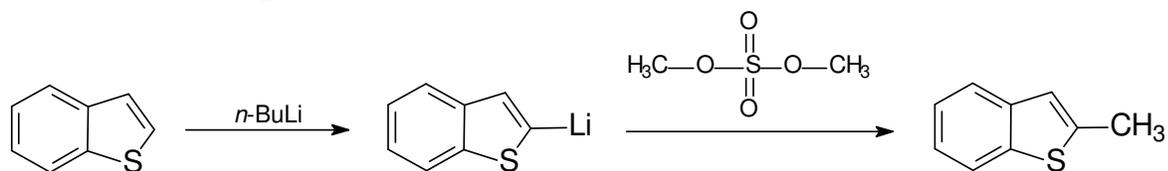
### 4-Octylbenzenesulfonic acid (F3·IX)



**Figure S43** Mass spectrum of 4-octylbenzenesulfonic acid methyl ester, formed through photooxidation of 5-octylbenzothiophene. The acid is shown as the methyl ester since the sample was treated with diazomethane.

## Synthetic Methods of Educts

### 2-Methylbenzothiophene



**Figure S44** Synthesis of 2-methylbenzothiophene

Reference: [S1]; melting point: 52 °C; purity: 98.5 % (GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

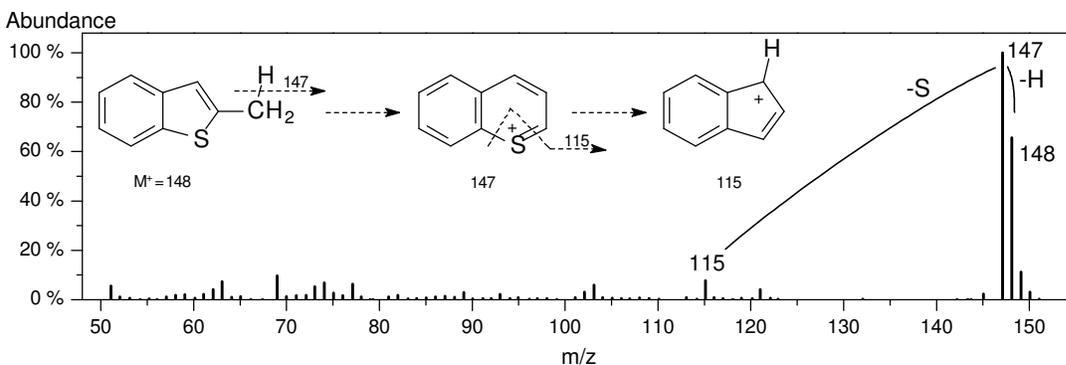
$\delta/\text{ppm}$  = 16,11 ( $\text{C}^2\text{-CH}_3$ ); 121,56 ( $\underline{\text{CH}}$ ); 121,97 ( $\underline{\text{CH}}$ ); 122,5 ( $\underline{\text{CH}}$ ); 123,3 ( $\underline{\text{CH}}$ ); 124,02 ( $\underline{\text{CH}}$ ); 139,65 ( $\underline{\text{C}}_q$ ); 140,43 ( $\underline{\text{C}}_q$ ); 140,82 ( $\underline{\text{C}}_q$ )

$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm}$  = 2,58 (s, 3 H,  $\text{C}^2\text{-CH}_3$ ); 6,96 (s, 1 H,  $\text{H}^3$ ); 7,26 (qi, 2 H,  $\text{H}^{5,6}$ ); 7,63 (d, 1 H,  $\text{H}^4$ ); 7,73 (d, 1 H,  $\text{H}^7$ )

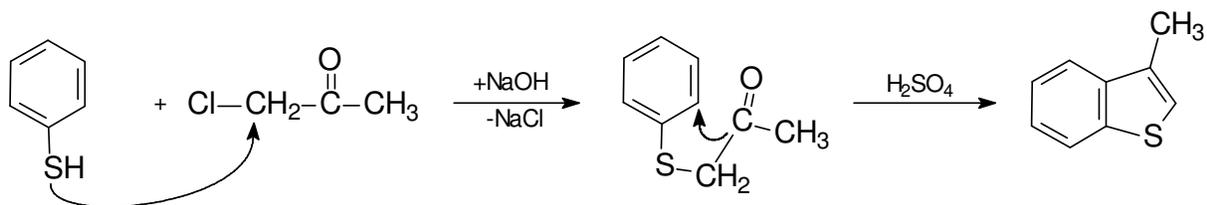
Mass spectrum:

$m/z$  = 148 (66 %), 147 (100 %), 115 (8 %)



**Figure S45** Mass spectrum of 2-methylbenzothiophene

### 3-Methylbenzothiophene



**Figure S46** Synthesis of 3-methylbenzothiophene

Reference: [S2, S3, S4] modified; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

<sup>13</sup>C-NMR (CDCl<sub>3</sub>/TMS):

δ/ppm = 13,74 (C<sup>3</sup>-CH<sub>3</sub>); 121,38 (CH); 121,57 (CH); 122,5 (CH); 123,69 (CH); 123,96 (CH); 131,95 (C<sub>q</sub>); 139,55 (C<sub>q</sub>); 140,18 (C<sub>q</sub>)

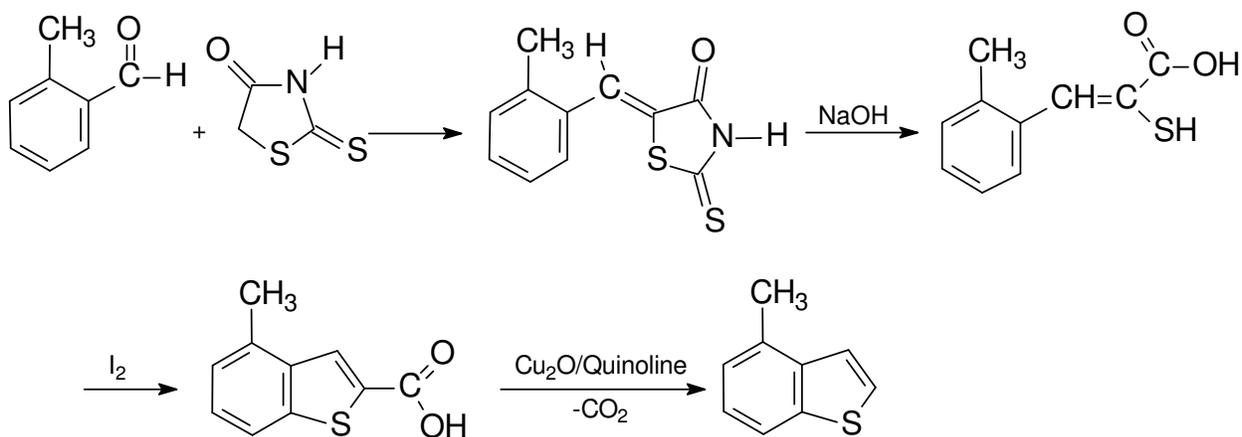
<sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS)

δ/ppm = 2,35 (s, 3 H, C<sup>3</sup>-CH<sub>3</sub>); 6,96 (s, 1 H, H<sup>2</sup>); 7,23 (t, 1 H, H<sup>5</sup>); 7,29 (t, 1 H, H<sup>6</sup>); 7,63 (d, 1 H, H<sup>4</sup>); 7,78 (d, 1 H, H<sup>7</sup>)

Mass spectrum:

m/z = 148 (67 %), 147 (100 %), 115 (8 %)

### 4-Methylbenzothiophene



**Figure S47** Synthesis of 4-methylbenzothiophene

Reference: [S5, S6]; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 19,52 (\text{C}^4\text{-CH}_3)$ ; 119,93 ( $\underline{\text{CH}}$ ); 121,89 ( $\underline{\text{CH}}$ ); 124,19 ( $\underline{\text{CH}}$ ); 124,53 ( $\underline{\text{CH}}$ ); 125,55 ( $\underline{\text{CH}}$ ); 132,70 ( $\underline{\text{C}}_q$ ); 139,05 ( $\underline{\text{C}}_q$ ); 139,57 ( $\underline{\text{C}}_q$ )

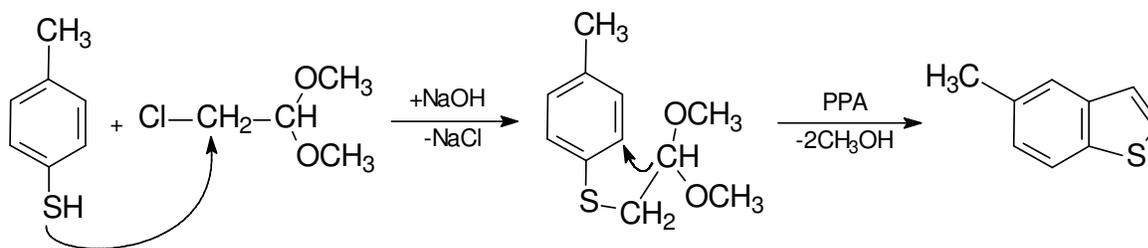
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,52 (\text{s}, 3 \text{ H}, \text{C}^4\text{-CH}_3)$ ; 7,05 (d, 1 H,  $\text{H}^5$ ); 7,16 (t, 1 H,  $\text{H}^6$ ); 7,28 (s, 2 H,  $\text{H}^{2,3}$ ); 7,64 (d, 1 H,  $\text{H}^7$ )

Mass spectrum:

$m/z = 148 (80 \%)$ , 147 (100 %), 121 (11 %), 115 (7 %)

### 5-Methylbenzothiophene



**Figure S48** Synthesis of 5-methylbenzothiophene

Reference: [S4, S6, S7, S8, S9, S10] modified; melting point 35 °C; purity: 99 % (purified with RP-HPLC, measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 21,35 (\text{C}^5\text{-CH}_3)$ ; 122,05 ( $\underline{\text{CH}}$ ); 123,46 ( $\underline{\text{CH}}$ ); 123,51 ( $\underline{\text{CH}}$ ); 125,96 ( $\underline{\text{CH}}$ ); 126,35 ( $\underline{\text{CH}}$ ); 133,81 ( $\underline{\text{C}}_q$ ); 136,86 ( $\underline{\text{C}}_q$ ); 139,93 ( $\underline{\text{C}}_q$ )

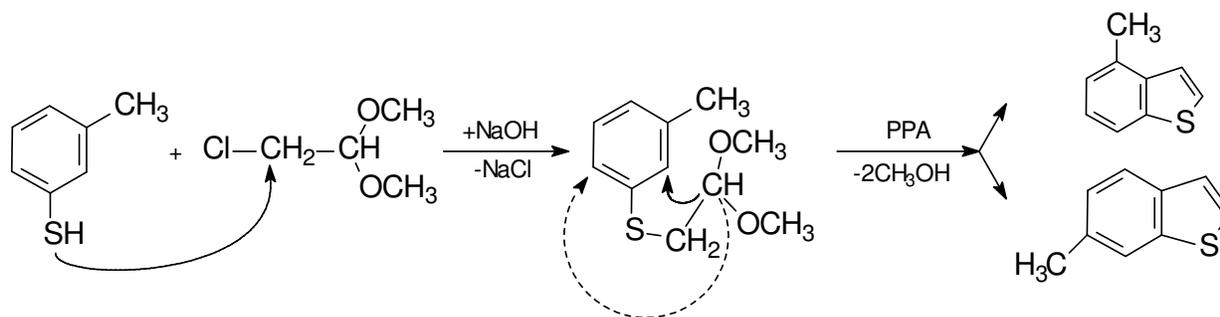
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,45 (\text{s}, 3 \text{ H}, \text{C}^5\text{-CH}_3)$ ; 7,15 (d, 1 H,  $\text{H}^6$ ); 7,22 (d, 1 H,  $\text{H}^3$ ); 7,37 (d, 1 H,  $\text{H}^2$ ); 7,60 (s, 1 H,  $\text{H}^4$ ); 7,73 (d, 1 H,  $\text{H}^7$ )

Mass spectrum:

$m/z = 148 (81 \%)$ , 147 (100 %), 121 (9 %), 115 (5 %)

## 6-Methylbenzothiophene



**Figure S49** Synthesis of 4- and 6-methylbenzothiophene (product ratio 1:2)

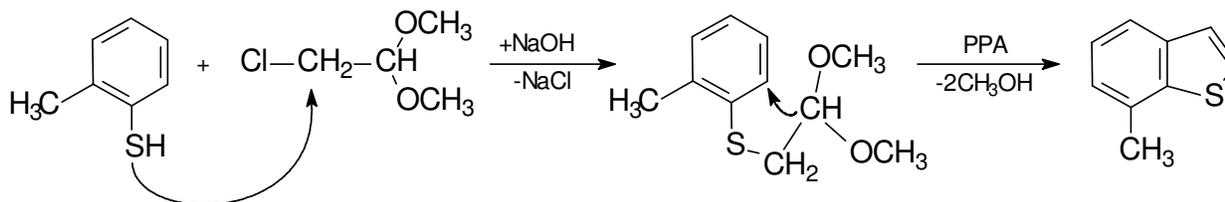
Reference: [S4, S6, S7, S8, S9, S10] modified; purity: 99 % (purified with RP-HPLC where both products coelute, measured as sum of two peaks by GC-FID/FPD)

<sup>13</sup>C-NMR (CDCl<sub>3</sub>/TMS) corrected by eliminating 4-methylbenzothiophene peaks:  
δ/ppm = 21,24 (C<sup>6</sup>-CH<sub>3</sub>); 122,11 (CH); 123,23 (CH); 123,41 (CH); 125,85 (CH); 126,17 (CH);  
133,96 (C<sub>q</sub>); 137,79 (C<sub>q</sub>); 139,98 (C<sub>q</sub>)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS) is not available since a mixture of 4- and 6-methylbenzothiophene was used and the individual signals could not be differentiated

Mass spectrum (4- and 6-methylbenzothiophene baseline separated on the GC column used):  
m/z = 148 (82 %), 147 (100 %), 121 (9 %), 115 (5 %)

## 7-Methylbenzothiophene



**Figure S50** Synthesis of 7-methylbenzothiophene

Reference: [S4, S6, S7, S8, S9, S10] modified; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

<sup>13</sup>C-NMR (CDCl<sub>3</sub>/TMS):  
δ/ppm = 20,64 (C<sup>7</sup>-CH<sub>3</sub>); 122,08 (CH); 123,68 (CH); 124,51 (CH); 125,36 (CH); 126,19 (CH);  
131,84 (C<sub>q</sub>); 139,41 (C<sub>q</sub>); 139,75 (C<sub>q</sub>)

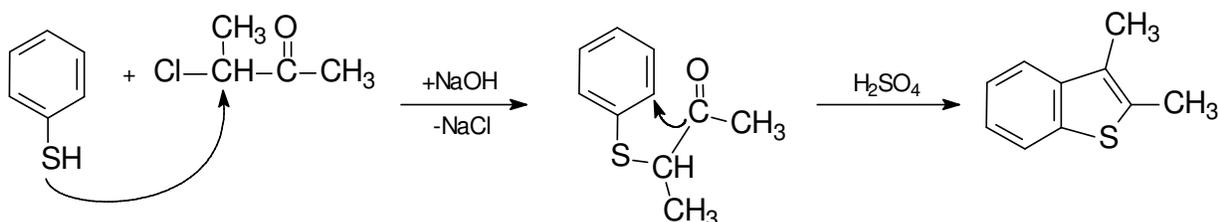
$^1\text{H-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,55$  (s, 3 H,  $\text{C}^7\text{-CH}_3$ ); 7,14 (d, 1 H,  $\text{H}^6$ ); 7,31 (m, 3 H,  $\text{H}^{2,3,5}$ ); 7,60 (d, 1 H,  $\text{H}^4$ )

Mass spectrum:

$m/z = 148$  (87 %), 147 (100 %), 121 (12 %), 115 (6 %)

### 2,3-Dimethylbenzothiophene



**Figure S51** Synthesis of 2,3-dimethylbenzothiophene

Reference: [S2, S3, S4]; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 10,95$  ( $\text{C}^3\text{-CH}_3$ ); 13,60 ( $\text{C}^2\text{-CH}_3$ ); 120,93 ( $\text{CH}$ ); 121,68 ( $\text{CH}$ ); 123,21 ( $\text{CH}$ ); 123,63 ( $\text{CH}$ ); 126,49 ( $\text{C}_q$ ); 133,43 ( $\text{C}_q$ ); 137,91 ( $\text{C}_q$ ); 140,57 ( $\text{C}_q$ )

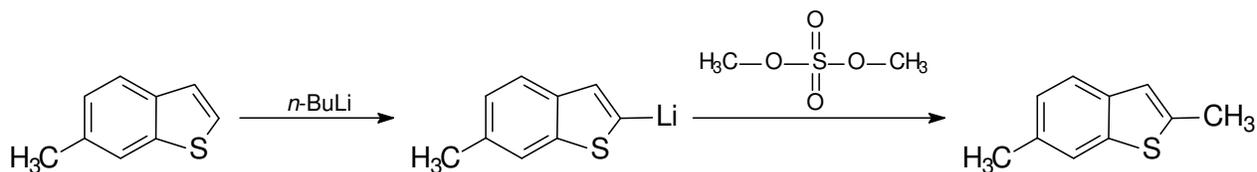
$^1\text{H-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,39$  (s, 3 H,  $\text{C}^3\text{-CH}_3$ ); 2,53 (s, 3 H,  $\text{C}^2\text{-CH}_3$ ); 7,04 (t, 1 H,  $\text{H}^5$ ); 7,18 (t, 1 H,  $\text{H}^6$ ); 7,38 (d, 1 H,  $\text{H}^4$ ); 7,57 (d, 1 H,  $\text{H}^7$ )

Mass spectrum:

$m/z = 162$  (62 %), 161 (29 %), 147 (100 %), 128 (18 %), 115 (12 %)

### 2,6-Dimethylbenzothiophene



**Figure S52** Synthesis of 2,6-dimethylbenzothiophene

Reference: [S1]; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 16,07 (\text{C}^2\text{-CH}_3)$ ;  $21,44 (\text{C}^6\text{-CH}_3)$ ;  $121,25 (\underline{\text{CH}})$ ;  $121,77 (\underline{\text{CH}})$ ;  $121,85 (\underline{\text{CH}})$ ;  $122,11 (\underline{\text{C}}_q)$ ;  $125,68 (\underline{\text{C}}_q)$ ;  $133,11 (\underline{\text{C}}_q)$ ;  $139,53 (\underline{\text{C}}_q)$ ;  $139,96 (\underline{\text{C}}_q)$

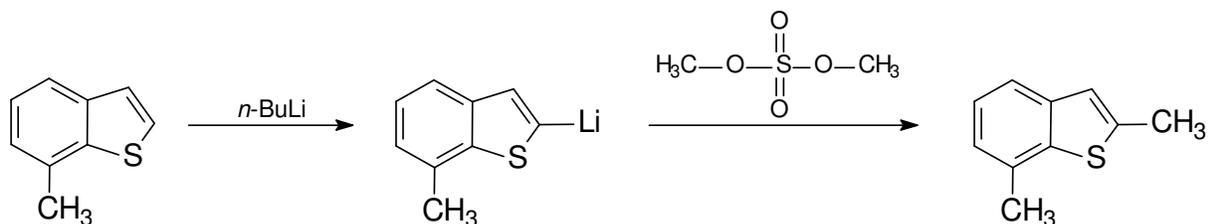
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,44 (\text{s}, 3 \text{ H}, \text{C}^6\text{-CH}_3)$ ;  $2,56 (\text{s}, 3 \text{ H}, \text{C}^2\text{-CH}_3)$ ;  $6,91 (\text{s}, 1 \text{ H}, \text{H}^3)$ ;  $7,11 (\text{d}, 1 \text{ H}, \text{H}^5)$ ;  $7,24 (\text{s}, 1 \text{ H}, \text{H}^7)$ ;  $7,52 (\text{d}, 1 \text{ H}, \text{H}^4)$

Mass spectrum:

$m/z = 162 (90 \%)$ ,  $161 (100 \%)$ ,  $147 (35 \%)$ ,  $128 (14 \%)$ ,  $115 (11 \%)$

## 2,7-Dimethylbenzothiophene



**Figure S53** Synthesis of 2,7-dimethylbenzothiophene

Reference: [S1]; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 15,93 (\text{C}^2\text{-CH}_3)$ ;  $20,04 (\text{C}^7\text{-CH}_3)$ ;  $121,42 (\underline{\text{CH}})$ ;  $122,35 (\underline{\text{CH}})$ ;  $124,11 (\underline{\text{CH}})$ ;  $125,68 (\underline{\text{C}}_q)$ ;  $132,11 (\underline{\text{C}}_q)$ ;  $138,51 (\underline{\text{C}}_q)$ ;  $139,53 (\underline{\text{C}}_q)$ ;  $141,06 (\underline{\text{C}}_q)$

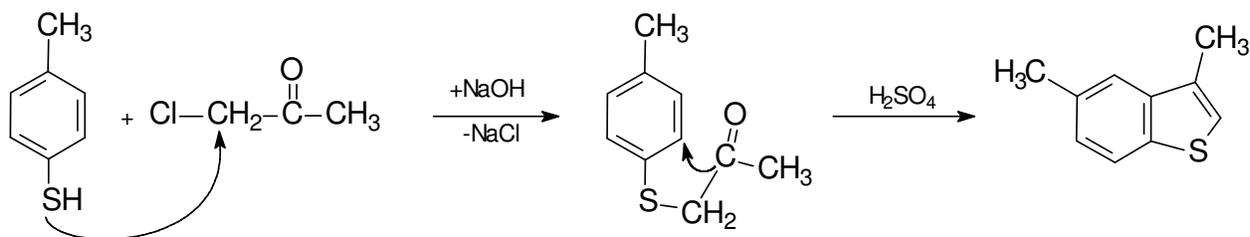
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,49 (\text{s}, 3 \text{ H}, \text{C}^2\text{-CH}_3)$ ;  $2,53 (\text{s}, 3 \text{ H}, \text{C}^7\text{-CH}_3)$ ;  $6,69 (\text{s}, 1 \text{ H}, \text{H}^3)$ ;  $6,98 (\text{d}, 1 \text{ H}, \text{H}^6)$ ;  $7,16 (\text{t}, 1 \text{ H}, \text{H}^5)$ ;  $7,37 (\text{d}, 1 \text{ H}, \text{H}^4)$

Mass spectrum:

$m/z = 162 (90 \%)$ ,  $161 (100 \%)$ ,  $147 (32 \%)$ ,  $128 (15 \%)$ ,  $115 (12 \%)$

### 3,5-Dimethylbenzothiophene



**Figure S54** Synthesis of 3,5-dimethylbenzothiophene

Reference: [S2, S3, S4]; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 13,68 (\text{C}^3-\text{CH}_3)$ ;  $21,34 (\text{C}^5-\text{CH}_3)$ ;  $121,50 (\text{CH})$ ;  $121,57 (\text{CH})$ ;  $122,21 (\text{CH})$ ;  $125,67 (\text{CH})$ ;  $131,50 (\text{C}_q)$ ;  $133,26 (\text{C}_q)$ ;  $137,34 (\text{C}_q)$ ;  $139,81 (\text{C}_q)$

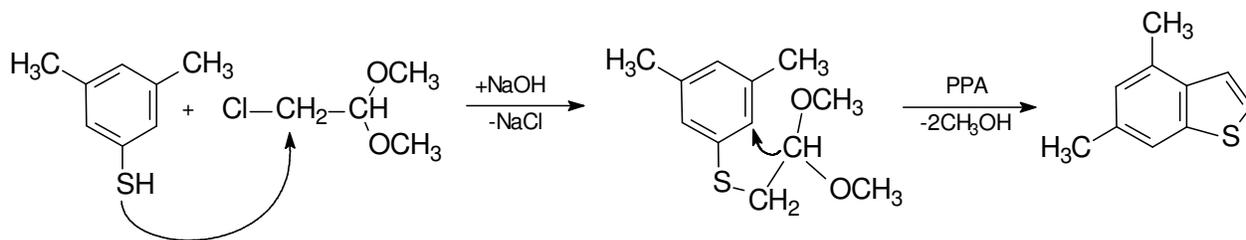
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,60 (\text{s}, 3 \text{ H}, \text{C}^5-\text{CH}_3)$ ;  $2,71 (\text{s}, 3 \text{ H}, \text{C}^3-\text{CH}_3)$ ;  $7,19 (\text{s}, 1 \text{ H}, \text{H}^4)$ ;  $7,37 (\text{d}, 1 \text{ H}, \text{H}^6)$ ;  $7,73 (\text{s}, 1 \text{ H}, \text{H}^2)$ ;  $7,93 (\text{d}, 1 \text{ H}, \text{H}^7)$

Mass spectrum:

$m/z = 162 (83 \%)$ ,  $161 (100 \%)$ ,  $147 (31 \%)$ ,  $128 (13 \%)$ ,  $115 (15 \%)$

### 4,6-Dimethylbenzothiophene



**Figure S55** Synthesis of 4,6-dimethylbenzothiophene

Reference: [S2, S4, S6, S7, S8, S9, S10] modified; purity: 99 % (purified by RP-HPLC, measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 19,95 (\text{C}^4-\text{CH}_3)$ ;  $20,74 (\text{C}^6-\text{CH}_3)$ ;  $120,85 (\text{CH})$ ;  $123,18 (\text{CH})$ ;  $126,25 (\text{CH})$ ;  $127,91 (\text{CH})$ ;  $131,98 (\text{C}_q)$ ;  $133,89 (\text{C}_q)$ ;  $138,43 (\text{C}_q)$ ;  $139,56 (\text{C}_q)$

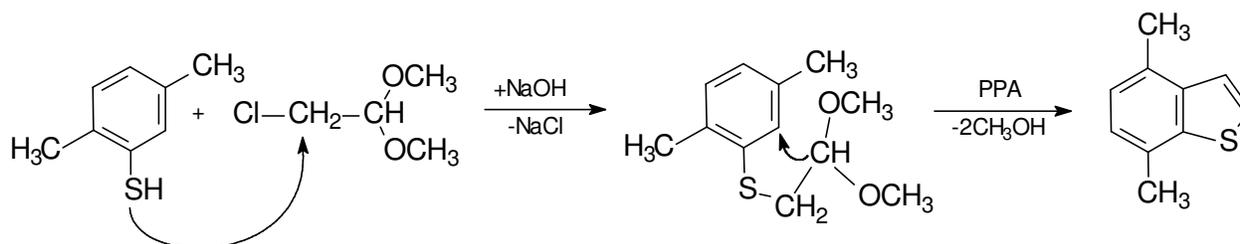
$^1\text{H-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,29$  (s, 3 H,  $\text{C}^6\text{-CH}_3$ ); 2,35 (s, 3 H,  $\text{C}^4\text{-CH}_3$ ); 6,91 (s, 1 H,  $\text{H}^5$ ); 7,12 (t, 2 H,  $\text{H}^{2,3}$ ); 7,42 (s, 1 H,  $\text{H}^7$ )

Mass spectrum:

$m/z = 162$  (95 %), 161 (51 %), 147 (100 %), 128 (13 %), 115 (14 %)

### 4,7-Dimethylbenzothiophene



**Figure S56** Synthesis of 4,7-dimethylbenzothiophene

Reference: [S2, S4, S6, S7, S8, S9, S10] modified; purity: 98 % (measured by GC-FID/FPD)

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 19,48$  ( $\text{C}^4\text{-CH}_3$ ); 20,68 ( $\text{C}^7\text{-CH}_3$ ); 123,69 ( $\underline{\text{CH}}$ ); 125,37 ( $\underline{\text{CH}}$ ); 126,02 ( $\underline{\text{CH}}$ ); 127,72 ( $\underline{\text{CH}}$ ); 131,53 ( $\underline{\text{C}}_q$ ); 133,16 ( $\underline{\text{C}}_q$ ); 138,56 ( $\underline{\text{C}}_q$ ); 139,19 ( $\underline{\text{C}}_q$ )

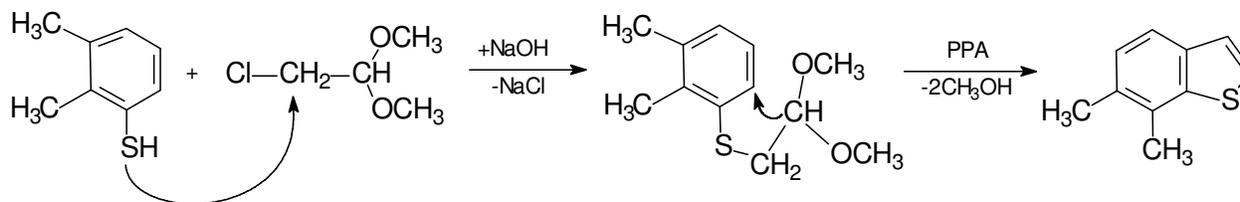
$^1\text{H-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,43$  (s, 3 H,  $\text{C}^4\text{-CH}_3$ ); 2,51 (s, 3 H,  $\text{C}^7\text{-CH}_3$ ); 6,95 (d, 1 H,  $\text{H}^5$ ); 7,16 (d, 1 H,  $\text{H}^6$ ); 7,34 (d, 1 H,  $\text{H}^3$ ); 7,40 (d, 1 H,  $\text{H}^2$ )

Mass spectrum:

$m/z = 162$  (91 %), 161 (52 %), 147 (100 %), 128 (14 %), 115 (15 %)

### 6,7-Dimethylbenzothiophene



**Figure S57** Synthesis of 6,7-dimethylbenzothiophene

Reference: [S2, S4, S6, S7, S8, S9, S10] modified; purity: 98.5 % (measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 17,34$  ( $\text{C}^7\text{-CH}_3$ );  $20,46$  ( $\text{C}^6\text{-CH}_3$ );  $122,85$  ( $\text{CH}$ );  $124,79$  ( $\text{CH}$ );  $126,24$  ( $\text{CH}$ );  $127,71$  ( $\text{CH}$ );  $133,98$  ( $\text{C}_q$ );  $138,61$  ( $\text{C}_q$ );  $139,63$  ( $\text{C}_q$ );  $140,36$  ( $\text{C}_q$ )

$\delta/\text{ppm} = 19,48$  ( $\text{C}^4\text{-CH}_3$ );  $20,68$  ( $\text{C}^7\text{-CH}_3$ );  $123,69$  ( $\text{CH}$ );  $125,37$  ( $\text{CH}$ );  $126,02$  ( $\text{CH}$ );  $127,72$  ( $\text{CH}$ );  $131,53$  ( $\text{C}_q$ );  $133,16$  ( $\text{C}_q$ );  $138,56$  ( $\text{C}_q$ );  $139,19$  ( $\text{C}_q$ )

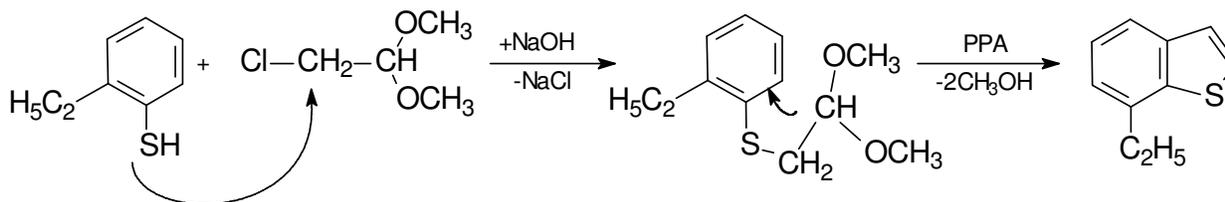
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,43$  (s, 3 H,  $\text{C}^4\text{-CH}_3$ );  $2,51$  (s, 3 H,  $\text{C}^7\text{-CH}_3$ );  $6,95$  (d, 1 H,  $\text{H}^5$ );  $7,16$  (d, 1 H,  $\text{H}^6$ );  $7,34$  (d, 1 H,  $\text{H}^3$ );  $7,40$  (d, 1 H,  $\text{H}^2$ )

Mass spectrum:

$m/z = 162$  (91 %),  $161$  (52 %),  $147$  (100 %),  $128$  (14 %),  $115$  (15 %)

### 7-Ethylbenzothiophene



**Figure S58** Synthesis of 7-ethylbenzothiophene

Reference: [S4, S6, S7, S8, S9, S10] modified; purity: 95 % (measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 15,12$  ( $\text{C}^7\text{-CH}_2\text{-CH}_3$ );  $28,53$  ( $\text{C}^7\text{-CH}_2\text{-CH}_3$ );  $122,31$  ( $\text{CH}$ );  $124,67$  ( $\text{CH}$ );  $125,04$  ( $\text{CH}$ );  $125,75$  ( $\text{CH}$ );  $126,24$  ( $\text{CH}$ );  $135,78$  ( $\text{C}_q$ );  $140,12$  ( $\text{C}_q$ );  $140,86$  ( $\text{C}_q$ )

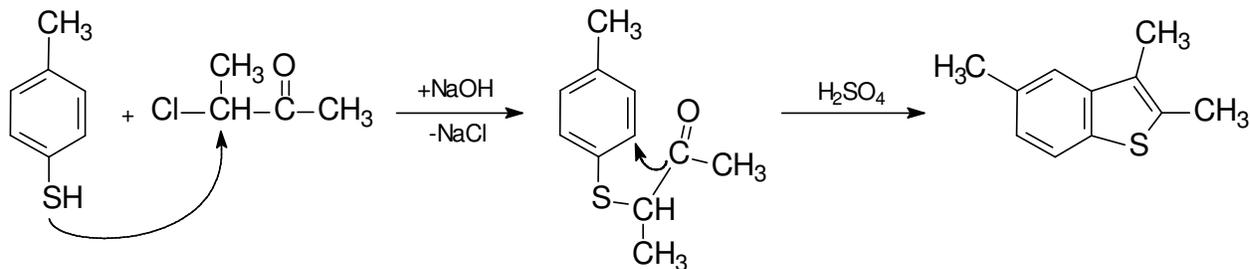
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 1,28$  (s, 3 H,  $\text{C}^7\text{-CH}_2\text{-CH}_3$ );  $2,71$  (s, 2 H,  $\text{C}^7\text{-CH}_2\text{-CH}_3$ );  $7,11$  (d, 1 H,  $\text{H}^3$ );  $7,16$  (t, 1 H,  $\text{H}^5$ );  $7,20$  (d, 1 H,  $\text{H}^6$ );  $7,29$  (d, 1 H,  $\text{H}^2$ );  $7,32$  (d, 1 H,  $\text{H}^4$ )

Mass spectrum:

$m/z = 162$  (39 %),  $147$  (100 %),  $134$  (6 %),  $115$  (6 %)

## 2,3,5-Trimethylbenzothiophene



**Figure S59** Synthesis of 2,3,5-dimethylbenzothiophene

Reference: [S2, S4]; melting point: 55.5 °C; purity: 99 % (measured by GC-FID/FPD)

<sup>13</sup>C-NMR (CDCl<sub>3</sub>/TMS):

δ/ppm = 11,41 (C<sup>3</sup>-CH<sub>3</sub>); 13,18 (C<sup>2</sup>-CH<sub>3</sub>); 20,45 (C<sup>5</sup>-CH<sub>3</sub>); 121,15 (CH); 121,45 (CH); 125,85 (CH); 126,46 (C<sub>q</sub>); 133,05 (C<sub>q</sub>); 133,58 (C<sub>q</sub>); 135,46 (C<sub>q</sub>); 140,96 (C<sub>q</sub>)

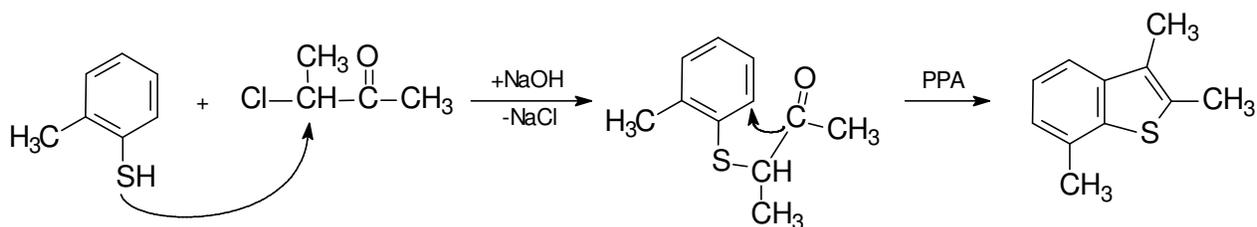
<sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS)

δ/ppm = 2,32 (s, 3 H, C<sup>5</sup>-CH<sub>3</sub>); 2,43 (s, 3 H, C<sup>3</sup>-CH<sub>3</sub>); 2,56 (s, 3 H, C<sup>2</sup>-CH<sub>3</sub>); 7,17 (d, 1 H, H<sup>6</sup>); 7,36 (s, 1 H, H<sup>4</sup>); 7,57 (d, 1 H, H<sup>7</sup>)

Mass spectrum:

m/z = 176 (83 %), 175 (37 %), 161 (100 %), 142 (8 %), 128 (11 %), 115 (7 %)

## 2,3,7-Trimethylbenzothiophene



**Figure S60** Synthesis of 2,3,7-dimethylbenzothiophene

Reference: [S2, S4, S6, S9, S10]; melting point: 61.5 °C; purity: 99 % (measured by GC-FID/FPD)

<sup>13</sup>C-NMR (CDCl<sub>3</sub>/TMS):

δ/ppm = 11,27 (C<sup>3</sup>-CH<sub>3</sub>); 13,48 (C<sup>2</sup>-CH<sub>3</sub>); 20,03 (C<sup>7</sup>-CH<sub>3</sub>); 123,15 (CH); 124,16 (CH); 124,75 (CH); 127,48 (C<sub>q</sub>); 131,09 (C<sub>q</sub>); 132,98 (C<sub>q</sub>); 139,16 (C<sub>q</sub>); 140,84 (C<sub>q</sub>)

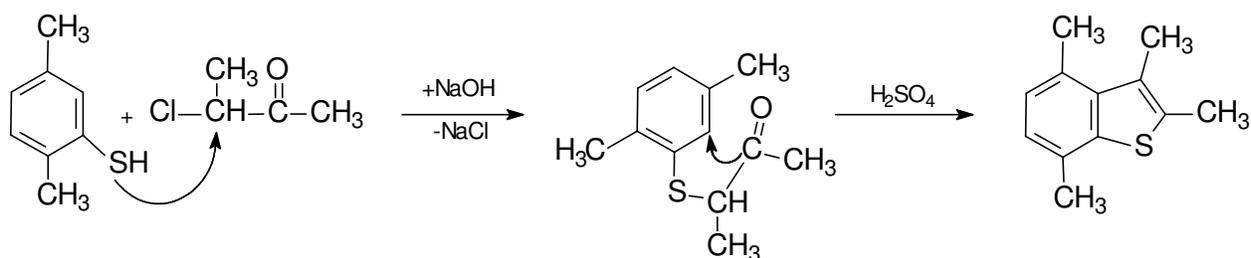
$^1\text{H-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,46$  (s, 3 H,  $\text{C}^3\text{-CH}_3$ );  $2,54$  (s, 3 H,  $\text{C}^2\text{-CH}_3$ );  $2,58$  (s, 3 H,  $\text{C}^7\text{-CH}_3$ );  $6,84$  (t, 1 H,  $\text{H}^5$ );  $6,91$  (d, 1 H,  $\text{H}^6$ );  $6,98$  (d, 1 H,  $\text{H}^4$ )

Mass spectrum:

$m/z = 176$  (72 %),  $175$  (26 %),  $161$  (100 %),  $147$  (7 %),  $128$  (13 %),  $115$  (17 %)

### 2,3,5,7-Tetramethylbenzothiophene



**Figure S61** Synthesis of 2,3,5,7-tetramethylbenzothiophene

Reference: [S2, S4]; melting point:  $65.5\text{ }^\circ\text{C}$ ; purity: 98.5 % (measured by GC-FID/FPD)

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 12,18$  ( $\text{C}^3\text{-CH}_3$ );  $13,59$  ( $\text{C}^2\text{-CH}_3$ );  $20,03$  ( $\text{C}^4\text{-CH}_3$ );  $20,48$  ( $\text{C}^7\text{-CH}_3$ );  $125,26$  ( $\text{CH}$ );  $127,82$  ( $\text{CH}$ );  $129,32$  ( $\text{C}_q$ );  $132,06$  ( $\text{C}_q$ );  $132,58$  ( $\text{C}_q$ );  $134,04$  ( $\text{C}_q$ );  $135,64$  ( $\text{C}_q$ );  $140,73$  ( $\text{C}_q$ )

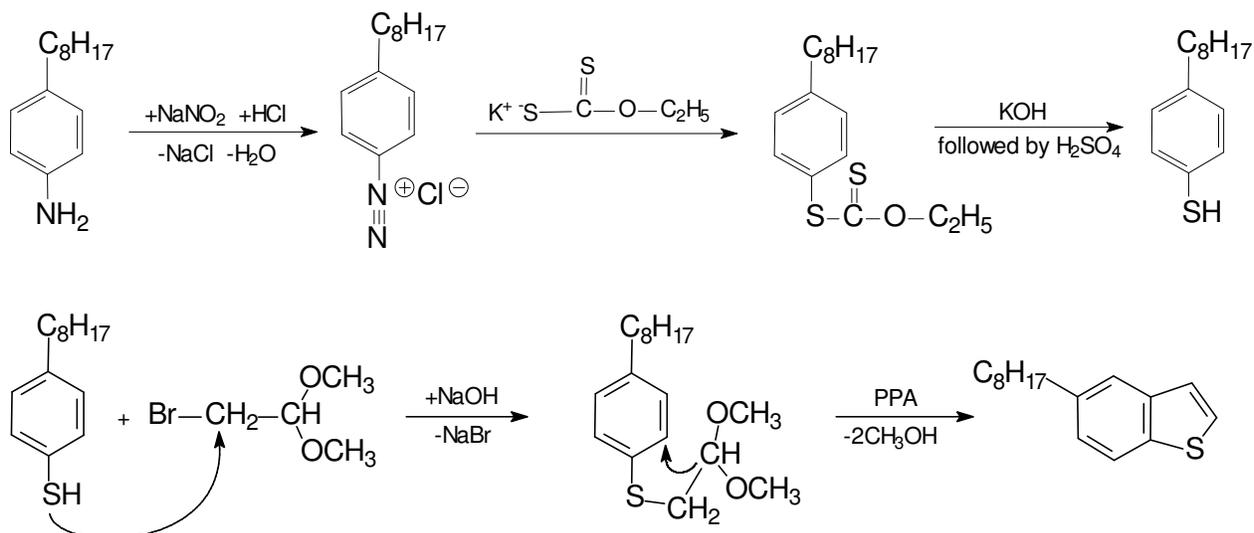
$^1\text{H-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 2,41$  (s, 3 H,  $\text{C}^3\text{-CH}_3$ );  $2,46$  (s, 3 H,  $\text{C}^4\text{-CH}_3$ );  $2,56$  (s, 3 H,  $\text{C}^2\text{-CH}_3$ );  $2,57$  (s, 3 H,  $\text{C}^7\text{-CH}_3$ );  $6,65$  (d, 1 H,  $\text{H}^6$ );  $6,88$  (d, 1 H,  $\text{H}^5$ )

Mass spectrum:

$m/z = 190$  (82 %),  $189$  (33 %),  $175$  (100 %),  $161$  (100 %),  $142$  (8 %),  $141$  (7 %),  $115$  (5 %)

## 5-Octylbenzothiophene



**Figure S62** Synthesis of 5-octylbenzothiophene

Reference: [S6, S7, S9, S10, S11] modified; purity: 98 % (measured by GC-AED)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

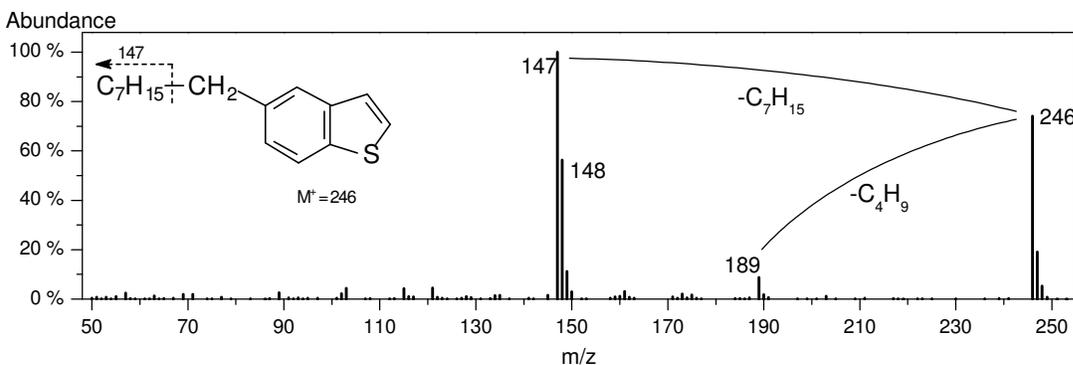
$\delta/\text{ppm} = 14,09$  ( $\text{C}^5\text{-}\underline{\text{C}}^8\text{H}_3$ ); 22,57 ( $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2$ ); 29,24 ( $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2$ ); 29,47 ( $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2$ ); 29,51 ( $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2$ ); 31,30 ( $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2$ ); 31,89 ( $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2$ ); 35,87 ( $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2$ ); 121,99 ( $\underline{\text{C}}\text{H}$ ); 122,83 ( $\underline{\text{C}}\text{H}$ ); 123,49 ( $\underline{\text{C}}\text{H}$ ); 125,31 ( $\underline{\text{C}}\text{H}$ ); 126,14 ( $\underline{\text{C}}\text{H}$ ); 137,07 ( $\underline{\text{C}}_q$ ); 137,65 ( $\underline{\text{C}}_q$ ); 139,84 ( $\underline{\text{C}}_q$ )

$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 0,87$  (t, 3 H,  $\text{C}^5\text{-}\underline{\text{C}}^8\text{H}_3$ ); 1,25 (m, 12H,  $\text{C}^5\text{-}\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}^{2-7}\text{H}_2$ ); 2,66 (t, 2 H,  $\text{C}^2\text{-}\underline{\text{C}}^1\text{H}_2$ ); 7,08 (d, 1 H,  $\text{H}^5$ ); 7,20 (d, 1 H,  $\text{H}^2$ ); 7,26 (d, 1 H,  $\text{H}^3$ ); 7,54 (s, 1 H,  $\text{H}^4$ ); 7,69 (d, 1 H,  $\text{H}^7$ )

Mass spectrum:

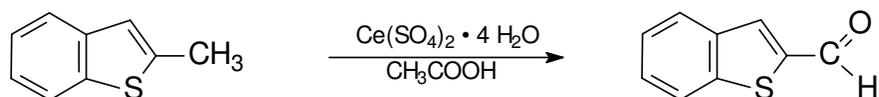
$m/z = 246$  (74 %), 189 (9 %), 148 (56 %), 147 (100 %), 142 (8 %), 128 (11 %), 115 (7 %)



**Figure S63** Mass spectrum of 5-octylbenzothiophene

## Synthetic Methods of Reference Compounds

### 2-Formylbenzothiophene



**Figure S64** Synthesis of 2-formylbenzothiophene

Reference: [S12]; melting point: 34 °C; purity: 99 % (measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm} = 123,27$  ( $\underline{\text{CH}}$ ); 125,23 ( $\underline{\text{CH}}$ ); 126,24 ( $\underline{\text{CH}}$ ); 128,14 ( $\underline{\text{CH}}$ ); 134,47 ( $\underline{\text{C}}_q$ ); 138,49 ( $\underline{\text{C}}_q$ ); 142,64 ( $\underline{\text{C}}_q$ ); 143,29 ( $\underline{\text{CH}}$ ); 184,66 ( $\text{C}^2$ - $\underline{\text{CHO}}$ )

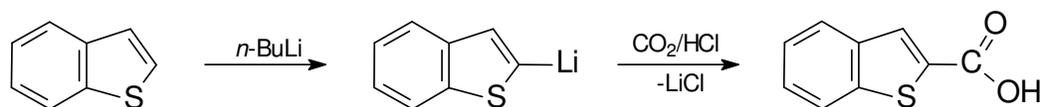
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 7,45$  (qi, 2 H,  $\text{H}^{5,6}$ ); 7,91 (t, 2 H,  $\text{H}^{4,7}$ ); 8,02 (s, 1 H,  $\text{H}^3$ ); 10,10 (s, 1 H,  $\text{C}^2$ - $\underline{\text{CHO}}$ )

Mass spectrum:

$m/z = 162$  (97 %), 161 (100 %), 134 (21 %), 133 (26 %), 89 (44 %), 69 (12 %), 63 (17 %)

### Benzothiophene-2-carboxylic acid



**Figure S65** Synthesis of benzothiophene-2-carboxylic acid

Reference: [S13]; melting point: 239 °C; purity: 97 % (measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

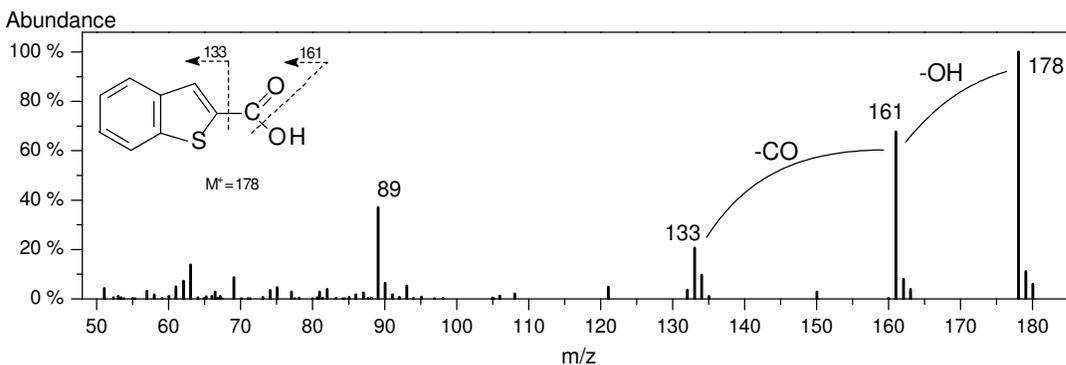
$\delta/\text{ppm} = 122,67$  ( $\underline{\text{CH}}$ ); 124,16 ( $\underline{\text{CH}}$ ); 124,74 ( $\underline{\text{CH}}$ ); 125,44 ( $\underline{\text{CH}}$ ); 126,79 ( $\underline{\text{CH}}$ ); 130,74 ( $\underline{\text{C}}_q$ ); 138,77 ( $\underline{\text{C}}_q$ ); 142,35 ( $\underline{\text{C}}_q$ ); 164,88 ( $\text{C}^2$ - $\underline{\text{COOH}}$ )

$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm} = 7,39$  (t, 1 H,  $\text{H}^6$ ); 7,45 (t, 1 H,  $\text{H}^5$ ); 7,84 (d, 1 H,  $\text{H}^7$ ); 7,87 (d, 1 H,  $\text{H}^4$ ); 8,06 (s, 1 H,  $\text{H}^3$ ); 10,36 (s, 1 H,  $\text{C}^2$ - $\underline{\text{COOH}}$ )

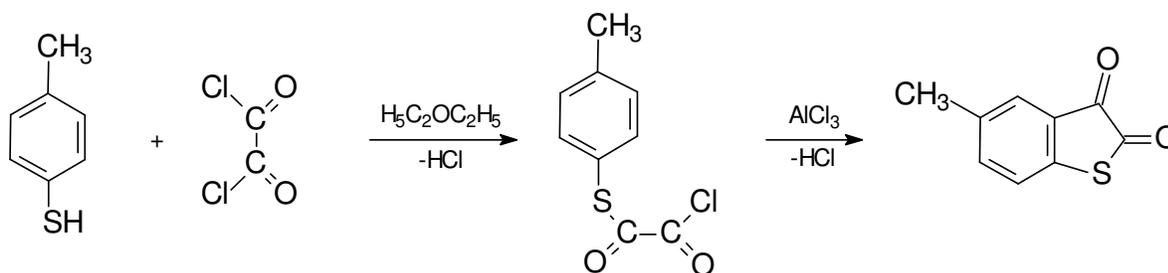
Mass spectrum:

$m/z = 178$  (100 %), 161 (68 %), 133 (21 %), 89 (37 %), 63 (14 %)



**Figure S66** Mass spectrum of benzothiophene-2-carboxylic acid

### 5-Methylbenzothiophene-2,3-quinone



**Figure S67** Synthesis of 5-methylbenzothiophene-2,3-quinone

Reference: [S14, S15]; melting point: 146 °C; purity: 99 % (measured by GC-FID/FPD)

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta/\text{ppm}$  = 20,73 ( $\underline{\text{CH}_3}$ ); 124,43 ( $\underline{\text{CH}}$ ); 125,38 ( $\underline{\text{CH}}$ ); 128,59 ( $\underline{\text{C}_q}$ ); 137,87 ( $\underline{\text{CH}}$ ); 138,66 ( $\underline{\text{C}_q}$ ); 139,16 ( $\underline{\text{C}_q}$ ); 182,01 ( $\underline{\text{CO}}$ ); 186,21 ( $\underline{\text{CO}}$ )

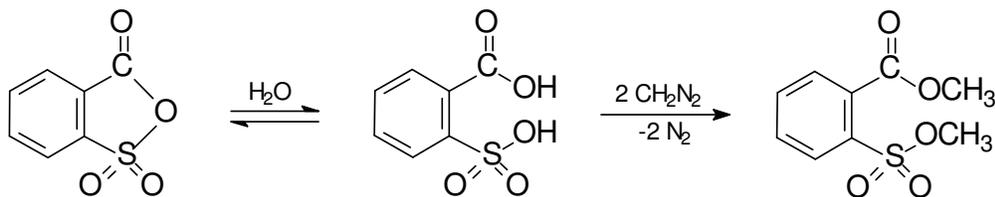
$^1\text{H}$ -NMR ( $\text{CDCl}_3/\text{TMS}$ )

$\delta/\text{ppm}$  = 2,35 (s, 3 H,  $\text{C}^5\text{-CH}_3$ ); 7,25 (d, 1 H,  $\text{H}^7$ ); 7,46 (d, 1 H,  $\text{H}^6$ ); 7,58 (s, 1 H,  $\text{H}^4$ )

Mass spectrum:

$m/z$  = 178 (7 %), 150 (100 %), 121 (70 %), 78 (25 %), 69 (17 %)

## 2-Sulfobenzoic acid dimethyl ester



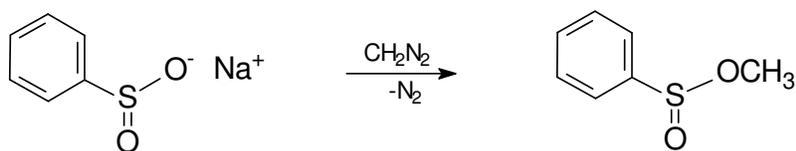
**Figure S68** Synthesis of 2-sulfobenzoic acid dimethyl ester

2-Sulfobenzoic acid cyclic anhydride is available commercially from *SIGMA-ALDRICH*. The compound not isolated since only the mass spectrum is needed for comparison.

Mass spectrum:

$m/z = 230$  (1 %),  $199$  (100 %),  $136$  (28 %),  $135$  (45 %),  $105$  (8 %),  $104$  (8 %),  $92$  (26 %),  $79$  (12 %),  $77$  (49 %),  $76$  (22 %)

## Benzenesulfinic acid methyl ester



**Figure S69** Synthesis of benzenesulfinic acid methyl ester

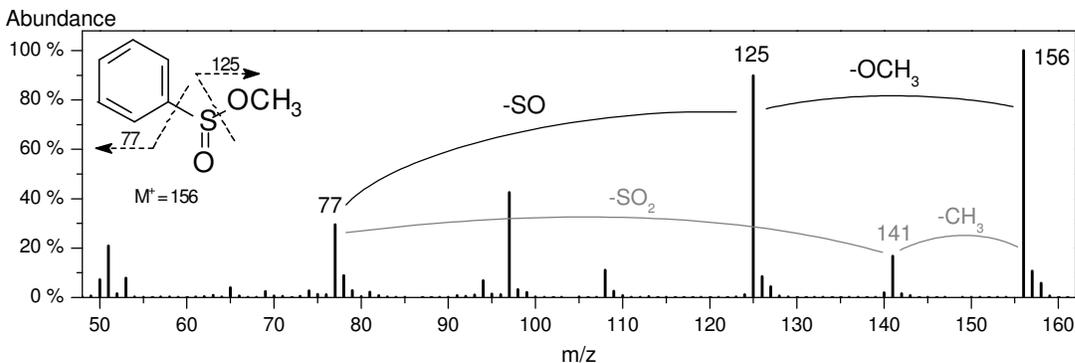
Reason: Does an aromatic sulfinic acid methyl ester show an  $\text{SO}_2$  loss?

Benzenesulfinic acid sodium salt is available commercially from *SIGMA-ALDRICH*.

The compound not isolated since only the mass spectrum is needed for comparison.

Mass spectrum:

$m/z = 156$  (100 %),  $141$  (17 %),  $125$  (90 %),  $108$  (11 %),  $97$  (43 %),  $77$  (29 %)



**Figure S70** Mass spectrum of benzenesulfonic acid methyl ester  
alternative fragmentation with SO<sub>2</sub> loss of lower probability (in gray)

## Non-Synthesized Compounds

Benzothiophene, dibenzothiophene and 4-methyldibenzothiophene are available commercially from *SIGMA-ALDRICH*.

1-Methyldibenzothiophene was synthesized for another work according to [S16].  
Mass spectrum: m/z = 198 (100 %), 197 (66 %), 165 (17 %), 152 (10%)

2,6-Dimethyldibenzothiophene was synthesized for another work according to [S17].  
Mass spectrum: m/z = 212 (100 %), 211 (48 %), 197 (21 %), 178 (9 %), 152 (7 %), 105 (14 %)

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