Preparation and Functionalization of New N- and S-Heterocycles for Material Science Applications

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Für Max

und meine Familie
„Vielleicht geht’s auch nicht ums Happy End, sondern nur um die Geschichte selbst“

-Julia Engelmann-
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A. INTRODUCTION
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1. Overview

Heterocycles and heteroaromatics represent the largest and most varied class of organic compounds. Besides oxygen, the most common heterocycles contain nitrogen and sulfur. Due to their unique properties, heterocyclic compounds found numerous applications in biology\(^1\) and material chemistry.\(^2\) Therefore, it is no surprise that they have attracted much interest in the field of organic chemistry for more than one century. However, the preparation, as well as the functionalization of heterocycles is often challenging and requires harsh conditions.\(^3\) The invention of new derivatives with interesting properties for an application in material science is therefore restricted by conventional ways.

This changed with the discovery of the organometallic chemistry in 1760,\(^4\) which was a revolution in the field of organic chemistry. One of the major pathways for generating organometallic reagents is the directed metalation using alkyl metals or metal amide bases. With this method, a C-H-bond is converted into a carbon-metal bond. In contrast to other preparation methods for organometallics, this synthesis is not limited to the availability of a halide precursor. The first deprotonation reaction of this type was found in 1939 using \(n\)BuLi.\(^5\) After intensive investigation, non-nucleophilic and sterically hindered amide bases, such as LDA and TMPLi (1), were established and seemed to be useful reagents for directed metalations.\(^6\) However, the high reactivity, the strong nucleophilicity and the low functional group tolerance of these bases led to complications, such as side reactions (e.g. Chichibabin addition).\(^7\) Therefore, Hauser and co-workers developed the milder Mg-amide bases \(R_2NMgX\) and \((R_2N)_2Mg.\(^8\) However, the low solubility and low kinetic basicity required a large excess of the magnesium amide. To overcome these drawbacks, Knochel and co-workers developed the “Knochel-Hauser-base” TMPMgCl-LiCl (2).\(^9\) The extra-equivalent of LiCl ensures a monomeric structure\(^10\) of this base and thus a better solubility in THF (1.2 M) leading to a

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higher reactivity. In the same way, the more reactive base TMP\(_2\)Mg\(\cdot\)2LiCl (3)\(^{11}\) was developed for less activated substrates, whereas milder bases, such as TMPZnCl\(\cdot\)LiCl (4)\(^{12}\) and TMP\(_2\)Zn\(\cdot\)2MgCl\(\cdot\)2LiCl (5)\(^{13}\) have been invented for substrates bearing extremely sensitive functional groups.

Using the advantages of the directed metalation with highly soluble TMP-bases for the functionalization of heterocycles, much shorter syntheses of complex molecules can be performed allowing an efficient introduction of a broad range of functional groups and moreover, a regioselective control.\(^{14}\)


2. Quinoxalines

2.1 Directed Metalation of Quinoxalines

Quinoxalines are an important class of $N$-heterocycles, however, a selective functionalization via C-H deprotonation has been scarcely reported. Knochel et al. showed a monofunctionalization of quinoxaline using $\text{TMP}_2\text{Mg}\text{2LiCl}$ (3; 0.55 equiv) in the presence of $\text{ZnCl}_2$ (0.5 equiv). They postulate the formation of an intermediate zinc complex that reacts with $\text{TMP}_2\text{Mg}\text{2LiCl}$ (3) furnishing the zinc derivative after fast transmetalation. Quenching with iodine afforded the monofunctionalized quinoxaline-derivative (Scheme 1).

![Scheme 1](image)

Scheme 1: Postulated mechanism for the preparation of iodinated quinoxaline.

In 1991, Ward tried to achieve a selective metalation of different 2-substituted quinoxalines using the stronger base $\text{TMPLi}$ (1). Treatment of 2-chloroquinoxaline with $\text{TMPLi}$ (1) afforded different results, depending on the electrophile. On one hand, quenching the reaction with DCl furnished a dimer as major product (59%), whereas the trapping of the lithiated species of 2-chloroquinoxaline with acetaldehyde afforded a mixture of the desired product and the dimer. The same mixture of products was obtained, when the substituent on the quinoxaline was changed to methoxy. Interestingly, the addition of $\text{TMPLi}$ (1) to 2-(methylthio)quinoxaline, followed by trapping with $\text{PhCON(OMe)Me}$, afforded the expected product in 42% yield without formation of a dimer (Scheme 2).  

A. INTRODUCTION

Another difunctionalization was achieved by selective metalation of quinoxalines bearing a phosphorodiamidate group as directing group. The addition of \( \text{TMP}_2\text{Mg}_2\text{LiCl} \) (3) at -50 °C led to full magnesiation of the substituted quinoxaline within 1.5 h. After transmetalation to zinc, followed by Negishi cross-couplings, 2,3-difunctionalized quinoxalines were obtained in good yields (Scheme 3).

Quéguiner and co-workers reported the synthesis of trifunctionalized quinoxalines. However, large excess of the base was necessary to achieve metalation and no regioselectivity was observed. Thus, the addition of 4 equivalents of TMPLi (1) to 2-methoxy-3-phenylquinoxaline led to a mixture of 2,3,5- and 2,3,8-substituted derivatives (Scheme 4).

A. INTRODUCTION

2.2 Objectives

The aim of the first part of this work was the development of a selective metalation of the quinoxaline scaffold in the presence of the two electrophilic chlorine substituents in positions 2 and 3. TMP-bases should allow for a stepwise preparation of mono-, di-, tri- and tetrafunctionalized quinoxalines. Furthermore, these functionalized quinoxaline-derivatives should be anellated with dimercaptobenzene or 1,2-benzenediol leading to new tetracyclic heterocycles that should be tested on their optical properties (Scheme 5).

**Scheme 4:** Lithiation of 2,3-difunctionalized quinoxaline leading to a mixture of products.

**Scheme 5:** Desired fully functionalization of 2,3-dichloroquinoxaline followed by anellation reactions.
3. 1,3-Dithiole-2-thione

Dithiolethiones are important S-heterocycles that have attracted much interest for their electrical and optical properties. Due to their different types of sulfur atoms (exocyclic and heterocyclic), these compounds act as multi-functional donors.\textsuperscript{19} The most common representative of this class is 1,3-dithiole-2-thione (DTT) that is furthermore an important precursor for the synthesis of tetrathiafulvalenes (TTF).

3.1 Directed Metalation of 1,3-Dithiole-2-thione

The preparation of functionalized DTT-derivatives can be achieved by lithiation, however, mostly halogenations are described. \textit{Alberola et al.} reported a direct metalation of DTT using LDA (1.0 equiv and 3.0 equiv), followed by reaction with 1,2-dibromotetrachloroethane leading to monobrominated DTT and dibrominated DTT, respectively (Scheme 6).\textsuperscript{20}

\begin{center}
\textbf{Scheme 6}: Preparation of mono- and dibromo-DTT via direct metalation of DTT using LDA.
\end{center}

In contrast, \textit{Suizu} and \textit{Imakubo} had difficulties with the preparation of 4-chloro-5-iodo-DTT using similar reaction conditions. Interestingly, the addition of different amounts of LDA to iodo-DTT followed by treatment with hexachloroethylene afforded a mixture of three products. Due to a disproportionation of the lithiated iodo-DTT into dilithiated DTT and diiodinated DTT, they obtained the desired product, as well as dichloro-DTT and diiodo-DTT (Scheme 7).\textsuperscript{21}

\begin{thebibliography}{9}
\end{thebibliography}
A. INTRODUCTION

Furthermore, undesired side reactions via ring-opening were observed in reactions of DTT with stoichiometric amounts of LDA. Thus, the mono-lithiation of DTT using LDA (1.1 equiv, THF, -78 °C) and subsequent trapping with hexachloroethane (1.1 equiv) furnished dichloro-DTT instead of the desired monochlorinated product. To overcome these side reactions, the dilithiated species of DTT had to be prepared by the addition of an excess of LDA. Quenching dilithiated DTT with hexachloroethane (0.75 equiv) led to the desired monochloro-DTT that can be further lithiated to give the 4-chloro-5-iodo-product after subsequent quenching with ICl (Scheme 8).

In order to prepare more extended systems, Skabara and co-workers tried to synthesize diarylated DTT-derivatives. However, they observed several unexpected 1,4-rearrangements depending on the nature of the arylic residue. Lithiation of DTT with LDA and subsequent reaction with aryl carboxaldehydes furnished the expected diols. The addition of perchloric acid to the bisalcohol bearing phenyl groups led to the formation of a dihydrofuran, whereas 4-methoxyphenyl-substituted alcohols afforded an aldehyde (Scheme 9).²²

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A. INTRODUCTION

Scheme 9: Unexpected 1,4-rearrangements of diols.

3.2 Objectives

As shown above, no selective mono- and difunctionalization of DTT is reported in the literature. Thus, a part of this work was to focus on the development of a convenient sequential bis-functionalization of DTT. To demonstrate the potential of such a methodology, the obtained substituted derivatives should then be converted into their oxygen analogs. Subsequent triethyl phosphite-mediated cross-couplings should furnish new symmetrically and nonsymmetrically tetrafunctionalized TTF-derivatives of interest for material science (Scheme 10).

Scheme 10: Desired bis-functionalization of DTT followed by triethyl phosphite-mediated cross-coupling reactions leading to new tetraarylated tetrathiafulvalenes.

4. Tetrathiafulvalenes

In the field of material chemistry, tetrathiafulvalene (TTF) and its derivatives are the most important representatives of S-heterocycles. TTFs exhibit exceptional π-donor properties due to their ability to be reversibly oxidized to the cation radical, as well as to the dication at
accessible potentials. These properties allow for the preparation of charge-transfer (CT) complexes or even superconducting salts. Since the discovery of the electrical conductive TTF-TCNQ-complex and the related superconducting Fabre-Bechgaard salt, much effort has been made to tune the electronic properties of these materials by modification of the TTF-scaffold (Figure 1).

![Figure 1: Structures of a conductive TTF-TCNQ CT-complex and the superconducting Fabre-Bechgaard salt.](image)

### 4.1 Directed Metalation of Tetrathiafulvalenes

Green reported a general method for the preparation of substituted tetrathiafulvalenes (TTF). The addition of stoichiometric amounts of LDA to TTF led to the lithiated species within 15 min at -70 °C. Quenching with various electrophiles furnished monosubstituted TTF-derivatives (Scheme 11).

![Scheme 11: Preparation of monosubstituted TTF-derivatives by direct metalation of TTF.](image)

However, the addition of excess LDA (2.0 equiv) to TTF, followed by trapping with ethyl chloroformate resulted in a mixture (1:1) of 4,4'- and 4,5'-disubstituted TTF-derivatives that was not separated. In addition, no regioselectivity was achieved by trapping the lithiated species of 4-methyl-TTF with ethyl chloroformate (Scheme 12).

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A. INTRODUCTION

Furthermore, attempts to prepare trifunctionalized TTF-derivatives were less successful as the addition of excess LDA to methylated TTF furnished the trisubstituted derivative in only 30% yield after quenching with ethyl chloroformate. Moreover, a lithiation of the isomeric mixture of 4,4'-dimethyl-TTF and 4,5'-dimethyl TTF was inert towards another lithiation, even at ambient temperature (Scheme 13).

Iyoda et al. reported the successful synthesis of fully functionalized TTF-derivatives by the addition of excess LDA (3.0 equiv) to the dithioether derivative, followed by trapping with halides. Under these conditions, only trace amounts (1-5%) of the trifunctionalized side products were obtained (Scheme 14).²⁷

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The preparation of tetrasubstituted TTFs was also achieved in an one-pot procedure by the addition of 4.4 equiv of LDA to TTF. Quenching of the tetraanionic TTF with various electrophiles, such as disulfides and halides, furnished the corresponding products (Scheme 15).

\[
\text{\text{LDA (4.4 equiv)}} \quad \begin{array}{c}
\text{S-S} \\
\text{E= SMe, SPh, Br, Cl}
\end{array}
\]

Scheme 15: Preparation of tetrafunctionalized TTF-derivatives in an one-pot procedure.

Although functionalizations of the TTF-scaffold are well-studied, no general synthesis has been described allowing for a selective and stepwise substitution of all positions. Moreover, the preparation of TTF-derivatives bearing sensitive functional groups remains difficult due to the harsh reaction conditions.

4.2 Objectives

A part of this work was to focus on a selective metalation of the TTF-skeleton. A stepwise functionalization should provide access to new mono-, di-, tri- and tetrasubstituted derivatives. Furthermore, tetrathiafulvalenes with more extended π–systems should be prepared and tested on their electrochemical properties (Scheme 16).

Scheme 16: Desired stepwise functionalization of the TTF-scaffold.

5. 1,4-Dithiins

A special representative of \( S \)-heterocycles is 1,4-dithiin. In order to avoid destabilization, 1,4-dithiin prefers a non-planar boat conformation with an angle of 132° (Figure 2), whereas accumulation of electron-withdrawing groups, such as azaarenes, forces the dithiin in a planar conformation. Despite the non-planar structure, this heterocycle is described to be antiaromatic due to the negative resonance energy and the non-existence of a diamagnetic ring current, although the strict definition of \( Hückel \)-aromaticity can not be applied.\(^{29}\)

![Figure 2: Non-planar conformation of 1,4-dithiin.](image)

Besides its structural properties, 1,4-dithiin exhibits also interesting electronic properties. The high-lying HOMO of this electron donor causes it to be easily oxidized. The formation of the radical cation can be readily achieved due to one-electron oxidation. Dissolving 1,4-dithiin in sulfuric acid or treatment with AlCl\(_3\) allow for the preparation of a variety of charge-transfer-complexes.\(^{30,31}\)

5.1 Reactions of 1,4-Dithiins

1,4-Dithiin and its derivatives undergo a variety of synthetic transformations. Oxidation of dithiin-derivatives leads to the formation of monosulfoxides that can either be oxidized to the corresponding sulfone or thermally decomposed affording thiophene-derivatives (Scheme 17). Electron-withdrawing substituents, such as nitro groups, facilitate the oxidation of the sulfur next to the nitro group.\(^{29}\)

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**Scheme 17:** Oxidation of a dithiin-derivative leading to a sulfoxide and following transformation.

As mentioned above, dithiins exhibit a low oxidation potential. The reaction of SbCl$_5$ and tetraphenyl-dithiin even furnish the dication as a result of two-electron oxidation (Scheme 18).

**Scheme 18:** Two-electron oxidation of tetraphenyl-dithiin.

Moreover, 1,4-dithiin reacts readily with electrophiles, as well as with nucleophiles. For example, diphenyl dithiin can undergo electrophilic substitutions such as formylation, nitration and bromination. These reactions are postulated to proceed in an addition-elimination process leading to trisubstituted dithiin-derivatives. Nucleophilic attack at the carbon atom can be achieved on dithiin-derivatives bearing electron-withdrawing substituents, such as cyano groups, leading to the formation of five-membered heterocycles (Scheme 19).

**Scheme 19:** Reaction of dithiin-derivatives with electrophiles and nucleophiles.

1,4-Dithiin-fused heterocycles are of high interest for material chemistry due to their electronical properties. Most common are these structures in the field of electroconductive materials and in the field of dyes. The alkylation of 1,2-dibromoethane with 2-thioxo-1,3-dithiole-4,5-bis(thiolate) which can be obtained by electrochemical reduction of carbon disulfide, furnishes a dithiin-fused-DTT. This precursor can be utilized in the preparation of
TTF-derivatives or subjected to further transformations affording 1,4,5,8-tetrathianaphthalene (Scheme 20).²⁹,³²

With regards to dyes, dithiin-fused heteroacenes can be obtained by anellation of dichloroquinoxalines with dimercaptoquinoxalines (Scheme 21).³³

5.2 Objectives

Because of the variety of chemical transformations, the electronical and structural properties, 1,4-dithiin has attracted much interest. Therefore, it is no surprise that much effort has been invested in the preparation of 1,4-dithiin and its derivatives. However, metalations are scarcely reported. Thus, a part of this work was to focus on the functionalization of 1,4-dithiin via directed metalation. The resulting substituted dithiin-derivatives should be further subjected to cyclization reactions leading to new 1,4-dithiin-fused heterocycles that may be of interest for material science (Scheme 22).

³³ Podsiadly, R.; Sokolowska, J. Dyes Pigments 2012, 92, 1300.
B. RESULTS AND DISCUSSION
1. Functionalization of Quinoxalines Using TMP-Bases: Preparation of Tetracyclic Heterocycles with High Photoluminescence Quantum Yields

1.1 Introduction

Quinoxalines are an important class of N-heterocycles, which have found numerous applications as pharmaceutical targets, fluorescent dyes, and as building blocks for new materials. Anellation procedures are known to convert quinoxalines into diazadioxacenes that have interesting optical and electronic properties. Bunz and coworkers developed a successful synthesis of alkynylated diazadioxacenes 8 by coupling an alkynylated 1,2-diol 6 with 2,3-dichloroquinoxaline (7) using a copper-based catalytic procedure (Scheme 23).

However, the alkylation is located at the 1,2-diol unit and its preparation involves multiple steps. As the metalation of the very electrophilic and sensitive 2,3-dichloroquinoxaline (7) is unknown, the selective functionalization of 7 would be of high interest. Furthermore, anellation reactions of functionalized 2,3-dichloroquinoxalines with diols and dithiols, respectively, should lead to new tetracyclic heterocycles with interesting optical and electronic properties due to the extended π-system.

References:

1.2 Preparation of Monofunctionalized 2,3-Dichloroquinoxalines

Therefore, the selective metalation of 2,3-dichloroquinoxaline (7) was examined. Treatment of 7 with the Schlosser bases KOTBu/TMPLi and KOTBu/nBuLi (1.1 equiv, THF, -78 °C, 0.5 h) led to decomposition, whereas the milder Mg-bases, such as TMPMgCl2LiCl (2) or TMP2Mg2LiCl (3)\(^\text{11}\) were ineffective in achieving metalation. No significant magnesiation occurred under various conditions. However, the low temperature treatment of 7 with TMPLi (1; 1.2 equiv, THF, -78 °C, 0.5 h) provided the corresponding 5-lithiated quinoxaline which was quenched with various electrophiles leading to functionalized 2,3-dichloroquinoxalines of type 9 (Scheme 24).

![Scheme 24: Selective lithiation of 2,3-dichloroquinoxaline (7) with TMPLi (1).](image)

The lithiated species was trapped with (BrCl\(_2\))\(_2\) and iodine furnishing the halogenated 2,3-dichloroquinoxaline-derivatives 9a and 9b in 64-73% yield (Table 1, entries 1 and 2). Quenching with an aryl sulfinyl chloride and ethyl cyanoformate afforded compounds 9c and 9d (60-62% yield, entries 3 and 4). After transmetalation to zinc, copper-catalyzed allylation reactions with ethyl 2-(bromomethyl)acrylate,\(^\text{38}\) 3-bromocyclohexene and allylbromide provided the corresponding products 9e-g in 61-75% yield (entries 5-7). Furthermore, after transmetalation to zinc, a copper-mediated acylation with 3-chlorobenzoyl chloride, as well as a Pd-catalyzed Negishi cross-coupling\(^\text{39}\) using ethyl 4-iodobenzoate as electrophile and 6 mol% Pd(PPh\(_3\))\(_4\) as catalyst (THF, 50 °C, 12 h) were performed leading to the expected products 9h and 9i in 70% and 56% yield, respectively (entries 8 and 9).

\(^{38}\) (a) Rambaud, M.; Viellieras, J. *Synthesis* 1984, 406; (b) Viellieras, J.; Rambaud, M. *Synthesis* 1982, 924.

## Table 1: Low temperature metalation of 7 leading to various monofunctionalized quinoxalines of type 9.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(BrCl&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9a: X = Br</td>
<td>73&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9b: X = I</td>
<td>64&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>60&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>EtO₂C-CN</td>
<td></td>
<td>62&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>Br-CO₂Et</td>
<td></td>
<td>68&lt;sup&gt;c,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>61&lt;sup&gt;c,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>Br-</td>
<td></td>
<td>75&lt;sup&gt;c,d&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>Cl-Cl</td>
<td></td>
<td>70&lt;sup&gt;c,e&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>I-CO₂Et</td>
<td></td>
<td>56&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Isolated yield of analytically pure product. <sup>b</sup>MgCl₂ solution (1.3 equiv, 1.0 M in THF) was added. <sup>c</sup>ZnCl₂ solution (1.3 equiv, 1.0 M in THF) was added. <sup>d</sup>CuCN₂LiCl solution (10 mol%, 1.0 M in THF) was added. <sup>e</sup>CuCN₂LiCl solution (13 equiv, 1.0 M in THF) was added. <sup>f</sup>Cross-coupling conditions: ZnCl₂ solution (1.3 equiv, 1.0 M in THF), Pd(PPh₃)₄ (6 mol%), 50 °C, 12 h.
1.3 Preparation of Difunctionalized 2,3-Dichloroquinoxalines

To achieve a regioselective metalation in position 6, different substrates of type 9 bearing a directing group, were submitted to further metalation reactions. As sulfoxides, esters and ketones are known to be efficient ortho-directing groups, compounds 9c, 9d and 9h were tested on its behavior upon metalation in the adjacent position. A magnesiation of the new quinoxaline-derivative 9c was achieved using TMPMgCl·LiCl (2; 1.3 equiv, THF, -70 °C, 0.5 h). Because of pre-complexation/coordination to the sulfoxide residue, the metalation was directed ortho to the sulfoxide, furnishing the desired 6-magnesiated derivate of 9c. The magnesiated intermediate was halogenated giving the iodinated product 10a and the brominated product 10b. After transmetalation to zinc, the 6-magnesiated derivative of 9c was subjected to copper-mediated allylation and acylation yielding products 10c and 10d in good yields (79% and 89%; Scheme 25).

Scheme 25: Access to 5,6-difunctionalized quinoxalines by metalation of 9c using TMPMgCl·LiCl (2).

In contrast, the metalation of the ester 9d showed under similar conditions just 60% conversion of the starting material and only traces of the iodinated product were observed by GC analysis. Moreover, an increase in temperature led to decomposition of the ester compound 9d. The same results were obtained using the milder base TMP₂Zn₂MgCl₂·2LiCl (5; THF, 1.1 equiv, -40 °C, 0.5 h). After the addition of TMPZnCl·LiCl (4; 1.1 equiv, THF, -78 °C) to 9d, no reaction was observed within 0.5 h, whereas longer reactions times led to decomposition. Thus, no successful metalation of 9d was achieved.

---

In case of the ketone 9h, similar results were obtained. The addition of TMPMgCl\textsubscript{2}LiCl (2; 1.1 equiv, THF, -78 °C, 0.5 h) furnished complete decomposition of the starting material. In contrast, no reaction was observed using the milder Zn-bases TMP\textsubscript{2}Zn\textsubscript{2}MgCl\textsubscript{2}2LiCl (5; 1.1 equiv) and TMPZnCl\textsubscript{2}LiCl (4; 1.1 equiv) under various conditions, even when the mixture was heated to 50 °C.

Thus, a directed ortho-metallation could be performed only in the case of a sulfoxide group in the adjacent position.

However, it was found that direct access to difunctionalized quinoxaline-derivatives of type 11 can be achieved by the addition of excess TMPLi (1; 2.4 equiv, THF, -78 °C, 0.5 h) to 7, and subsequent trapping with chloroalkylsilanes\textsuperscript{41} (2.5 equiv). This in situ trapping reaction occurs in the following way: first, the monolithiated intermediate reacts with the silyl electrophile. The compatibility of the silyl chloride with the TMP-base then allows a second metallation of the quinoxaline. Thus, excess TMPLi (1) lithiates the intermediate again in position 8 leading to 5,8-disubstituted quinoxalines. By quenching the reaction with chlorotrimethylsilane, 2,3-dichloro-5,8-bis(trimethylsilyl)-quinoxaline (11a) was prepared in 74% yield. After the addition of ICl (1.0 to 3.0 equiv), the TMS groups were displaced to give the corresponding diiodide 11b and monoiodide 11c, which were found to be useful intermediates and good electrophiles for further transformations (see below). This synthetic route enables a convenient access to the diiodo compound 11b in quantitative yield (Scheme 26).

Scheme 26: Preparation of disilylated quinoxalines 11a and 11d followed by conversion of TMS groups into iodides.

To extend the range of asymmetrically substituted monoiodoquinoxalines, the diiodoquinoxaline 11b was subjected to mono-I/Mg-exchange by the use of stoichiometric amounts of iPrMgClLiCl\textsuperscript{42} (1.1 equiv, THF, -78 °C, 0.5 h). After reaction with the corresponding electrophiles, such as S-phenyl benzenethiosulfonate, 1,2-dibromotetrachloroethane, p-toluenesulfonyl cyanide and an aryl sulfinyl chloride, the expected 5,8-substituted quinoxalines 12a-d were obtained in 51-76% yield (Scheme 27).

---

Since the work of Satoh, sulfoxides are known to undergo exchange reactions with organometallic reagents.\(^{43}\) However, when \(\text{nBuLi (1.1 equiv, THF, -78 °C)}\) was added to the iodo-sulfoxide-quinoxaline-derivative \(\text{12d}\), neither an iodine-magnesium-exchange nor a sulfoxide-magnesium-exchange occurred. In contrast, at higher temperatures (-50 °C), a substitution of the electrophilic chlorine atoms by the butyl residue was observed. The same results were obtained using \(\text{iPrMgCl/LiCl (1.1 equiv, THF, -78 to -50 °C)}\). Similarly, no exchange was achieved using other organometallic reagents, such as \(\text{Bu}_{3}\text{MgLi, nBuMgCl and PhMgCl (1.1 equiv, THF, -50 to -10 °C)}\).

The diiodide \(\text{11b}\) proved to be a key molecule for further transformations, which allowed us to fine-tune the physical properties of these materials. Thus, the functionalized quinoxaline \(\text{11b}\) easily underwent Pd-catalyzed Negishi cross-coupling with \(\text{nBuZnCl (2.2 equiv)}\) leading to the very soluble compound \(\text{13a}\) in 61% yield. Furthermore, \(\text{11b}\) was subjected to Suzuki and Sonogashira cross-coupling reactions leading to the expected products \(\text{13b-d}\). As anticipated, due to the extended π-system, these compounds were excellent candidates for fluorescent dyes (Scheme 28).

---

1.4 Preparation of Trifunctionalized 2,3-Dichloroquinoxalines

To achieve a third site of metalation, two different metalation conditions were developed, depending on the starting material (12c or 12d): the addition of TMPLi (1; 1.5 equiv, THF, -78 °C, 5 min) in the presence of ZnCl₂ solution (1.1 equiv, 1.0 M in THF) to iodoquinoxaline-5-carbonitrile 12c granted access to trisubstituted compounds.⁴⁴ The zincated intermediate was subjected to bromination, as well as copper-catalyzed allylation with 3-bromo-2-methylpropene furnishing compounds 14a and 14b. Alternatively, difunctionalized quinoxaline 12d was magnesiated using TMPMgCl·LiCl (2; 1.5 equiv, THF, 0 °C, 1.5 h). The magnesiated species was quenched with halides affording compounds 14c and 14d in 72-73% yield. In both cases, the derivatization occurred in position 6 due to the directing group in the adjacent position (Scheme 29).

---

B. RESULTS AND DISCUSSION

Scheme 29: Preparation of trifunctionalized quinoxalines 14. [a] ZnCl$_2$ solution (1.1 equiv, 1.0 M in THF), then TMPLi (1; 1.5 equiv), THF, -78 °C, 5 min. [b] TMPMgCl/LiCl (2; 1.5 equiv), THF, 0 °C, 1.5 h.

The preparation of fully functionalized 2,3-dichloroquinoxaline-derivatives could not be achieved, although the trifunctionalized derivatives 14a and 14d were subjected to further metalation. The metalation of these compounds was examined using TMPMgCl/LiCl (2) and TMPZnCl/LiCl (4). Unfortunately, in the case of the stronger Mg-base (1.5 equiv), only decomposition was observed, whereas after the addition of the milder TMPZnCl/LiCl (4; 1.2 equiv), no reaction was observed under various conditions.
B. RESULTS AND DISCUSSION

1.5 Preparation of Tetracyclic Heterocycles

Polycyclic sulfur and oxygen-heterocycles are of special interest for applications in material science. Thus, several anellation reactions were performed to substitute the electrophilic chlorine atoms by oxygen and sulfur. The addition of 1,2-benzenediol, 4,5-dibromobenzene-1,2-diol and benzene-1,2-dithiol (1.3 equiv), in the presence of K$_2$CO$_3$ (5.0 equiv), furnished the expected tetracyclic heteroacene derivatives of type 15 under very mild conditions (DMF, 25 °C, 22-48 h; Scheme 30). This illustrates the utility of the dichloro substituents for various anellations.

Scheme 30: Anellation reactions of functionalized quinoxalines leading to tetracyclic heteroacene derivatives 15.

---

\[ 15a: R^1 = R^2 = H; 94\%
\]
\[ 15b: R^1 = H, R^2 = SOC$_2$H$_2$Me$_2$OMe; 78\%
\]
\[ 15c: R^1 = R^2 = I; 70\%
\]
\[ 15d: R^1 = R^2 = PH; 62\%
\]
\[ 15e: R^1 = R^2 = C\equiv CPh; 84\%
\]

\[ 15f: R^1 = R^2 = H; 81\%
\]
\[ 15g: R^1 = R^2 = nBu; 52\%
\]
\[ 15h: R^1 = R^2 = SiMe$_2$Oct; 73\%
\]
\[ 15i: R^1 = R^2 = H; 54\%
\]
\[ 15j: R^1 = I, R^2 = CN; 81\%
\]
\[ 15k: R^1 = R^2 = I; 87\%
\]
\[ 15l: R^1 = R^2 = Ph; 68\%
\]
\[ 15m: R^1 = R^2 = C\equiv CPh; 92\%
\]

---

\cite{Gingras, M.; Raimundo, J.-M.; Chabre, Y. M. Angew. Chem., Int Ed. 2006, 45, 1686.
1.6 Optical and Electronic Properties of the Tetracyclic Heterocycles

The substituted quinoxalines 13b and 13c exhibit a strong photoluminescence (PL) in the blue and green spectral region, respectively (Table 2 and Figure 3). We found that the optical properties of these molecules can be fine-tuned through careful selection of the substituents and by subsequent extension of the molecular core through annellation.

Figure 3: a) UV-Vis absorption (solid line) and normalized PL spectra (dashed line) of compounds 13b (green) and 13c (red). b) Time-correlated single photon counting (TCSPC) decay of 13c recorded after picosecond excitation at 403 nm. The experimental data was corrected for the instrument response function and fitted to a bi-exponential decay with lifetimes of 6.77 ns (98%) and 0.25 ns (2%). Due to the low extinction coefficient above 400 nm, it was not possible to investigate the decay kinetics of 13b.

The tetracyclic heteroacenes 15 absorb strongly in the UV and blue spectral region with the optical band gap depending on both the chalcogenide within the heterocycle (oxygen or sulfur) and the substituent on the quinoxaline (Figure 4). Dilute solutions of the chromophores show several absorption bands, which exhibit a distinct vibronic fine structure.

We define the optical band gap of these molecules as the absorption maximum of the lowest energy transition (Table 2). Extention of the π-system of 15a by introduction of either phenyl or phenylethynyl groups leads to a red-shift of the absorption onset that, in the latter case, is accompanied by a two-fold increase in the molar extinction coefficient ε (Figure 4b and Table 2). We note that the phenylethynyl substituent of 15e has a much stronger effect on the optical properties than the phenyl group of 15d. The same effect has been observed for substituted porphyrins and has been rationalized to be a result of differences in the overlap between the aromatic systems of the core and substituents. Due to steric constraints a phenyl substituent on the quinoxaline is likely to be tilted out of plane, whereas the phenylethynyl groups are coplanar with the core, allowing for maximum contribution to the aromatic system (Figure 4a).

---

46 These measurements were performed by Dr. F. Auras and are given here for the sake of completeness.
B. RESULTS AND DISCUSSION

Table 2: Optical properties of selected quinoxalines and tetracyclic heterocenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th><em>E</em>$_{\text{g,opt}}$ / eV$^a$</th>
<th>ε / 10$^3$ L mol$^{-1}$ cm$^{-1}$</th>
<th>λ$_{\text{em}}$ / nm$^b$</th>
<th>PLQY / %$^c$</th>
<th>τ / ns$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13b</td>
<td>3.34</td>
<td>9.2</td>
<td>467</td>
<td>60±5</td>
<td>-</td>
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<tr>
<td>13c</td>
<td>2.93</td>
<td>20.7</td>
<td>483</td>
<td>85±5</td>
<td>-</td>
</tr>
<tr>
<td>15a</td>
<td>3.42</td>
<td>11.8±0.5</td>
<td>403</td>
<td>65±5</td>
<td>-</td>
</tr>
<tr>
<td>15d</td>
<td>3.35</td>
<td>15.4±0.5</td>
<td>428</td>
<td>55±5</td>
<td>-</td>
</tr>
<tr>
<td>15e</td>
<td>3.20</td>
<td>34.4±0.5</td>
<td>439</td>
<td>90±5</td>
<td>3.44</td>
</tr>
<tr>
<td>15i</td>
<td>3.25</td>
<td>9.4±0.5</td>
<td>479</td>
<td>6±2</td>
<td>0.82$^e$</td>
</tr>
<tr>
<td>15l</td>
<td>3.24</td>
<td>12.0±0.5</td>
<td>482</td>
<td>3±1</td>
<td>0.25$^e$</td>
</tr>
<tr>
<td>15m</td>
<td>2.91</td>
<td>27.0±0.5</td>
<td>502</td>
<td>8±2</td>
<td>0.93$^e$</td>
</tr>
</tbody>
</table>

$^a$Lowest energy maximum of multi-peak fit. $^b$λ$_{\text{ex}}$ = 365 nm. $^c$Relative measurement, using rhodamine 6G as standard (PLQY = 95%). $^d$λ$_{\text{ex}}$ = 403 nm. $^e$Bi-exponential decay. The value listed in the table is the lifetime with the largest contribution.

The O-heterocyclic tetracycles 15a, 15d and 15e show strong blue photoluminescence with an emission maximum at 403, 428, and 439 nm, respectively. We determined the photoluminescence quantum yield (PLQY) for these chromophores by comparison with a solution of rhodamine 6G (PLQY = 95%). The non-substituted tetracycle 15a and the phenyl-substituted molecule 15d display appreciable PLQYs of 65% and 55%, respectively (Table 2). Introduction of the phenylethynyl substituent in 15e was found to boost the quantum yield to 90%, which renders this molecule a promising candidate as blue fluorescence marker for fluorescence imaging applications.

Similar trends in the absorption and emission properties were observed for the S-heterocyclic tetracycles 15i, 15l and 15m (Figure 4e). Due to the more polarizable sulfur atoms these molecules possess a 0.2-0.3 eV smaller optical band gap and a red-shifted emission compared to their oxygen-containing counterparts. The relative influence of the substituents on the optical band gap, extinction coefficient, emission maximum, and PLQ, however, is comparable to the O-heterocyclic tetracycles. Studies of the fluorescence lifetime by time-correlated single photon counting (TCSPC) measurements reveal significant differences in the decay kinetics between the O- and S-heterocyclic compounds (Figure 4c and 2f). For 15e we observe a mono-exponential decay with a lifetime of 3.44 ns. The decay of the S-heterocyclic compounds on the other hand is bi-exponential with significantly shorter principal lifetimes (Table 2), indicating the presence of an additional relaxation channel. The shorter principal fluorescence lifetimes of 15i, 15l and 15m as well as the trend observed for the different substituents correlate very well with the PL quantum yields of these compounds.
B. RESULTS AND DISCUSSION

Figure 4: a) Crystal structure fragment showing the planar conformation of 15e. b) Optical absorption (solid line) and normalized emission spectra (dashed line) of 25 µM dioxane solutions of selected oxygen-bridged tetracyclic heterocycles. c) Time-correlated single photon counting (TCSPC) decays of 15e, recorded after picosecond excitation at 403 nm. The experimental data was corrected for the instrument response function and fitted to mono-exponential or bi-exponential decay functions, respectively. Due to their low extinction coefficient at the excitation wavelength, the decay kinetics of 15a and 15d could not be investigated. d) Crystal structure fragment of 15m. In contrast to the oxygen-bridged heterocycles the sulfur-containing heteroacenes adopts a bent conformation. e) UV-Vis (solid line) and PL spectra (dashed line) of selected sulfur-bridged heteroacenes. f) Corresponding TCSPC traces of these compounds recorded following picosecond excitation at 403 nm.
2. Selective Metalation of 1,3-Dithiole-2-thiones: An Effective Preparation of New Symmetrically and Nonsymmetrically Tetraarylated Tetrathiafulvalenes

2.1 Introduction

The functionalization of heterocycles is an important synthetic task since many of these ring systems have interesting biological or electronic properties. The directed metalation of heterocycles is one of the most general methods for achieving a broad heterocyclic functionalization. TMP-bases of magnesium and zinc, such as TMPMgCl\(_2\) (2), TMPZnCl\(_2\)-LiCl (4) and TMP\(_2\)Zn2MgCl\(_2\)-2LiCl (5) proved to metalate a range of polyfunctionalized aromatics and heterocycles under mild conditions. The large steric hindrance of the TMP-moiety ensures a monomeric structure for this base and the extra equivalent of LiCl is responsible for the high solubility of these bases in THF (1.2 M). The metalation of sulfur-containing heterocycles can be achieved with lithium bases. However, the presence of additional sensitive functionalities or the nature of the S-heterocycle may lead to side reactions, such as ring fragmentations. This is the case for 1,3-dithiole-2-thione (16; DTT) which produces intermediates of type 17 after metalation. In the next step, the reaction of 17 with an electrophile (E-X) affords substituted heterocycles of type 18. However, the presence of a leaving group in \(\beta\)-position to the carbon-metal bond may lead to ring fragmentation and therefore to the decomposition of intermediate 17 (Scheme 31). This behavior can be expected when the carbon-metal bond is very ionic (Met = Li).
B. RESULTS AND DISCUSSION

Scheme 31: Metalation of 1,3-dithiole-2-thione (16; DTT) leading to the metalated intermediate of type 17 and quenching with an electrophile (E-X).

DTT (16) plays an important role in the field of organic materials as it is a precursor of tetrathiafulvalene (TTF). TTF and its derivatives found numerous applications as charge transfer molecules,\(^\text{52}\) carbon nanotubes,\(^\text{53}\) covalent organic frameworks\(^\text{54}\) and conjugated microporous polymers\(^\text{55}\) due to their electroconductive and photophysical properties. The TTF-scaffold (21) can easily be constructed by a triethyl phosphite-mediated cross-coupling reaction of 1,3-dithiole-2-thione (16; DTT) and 1,3-thiole-2-one (20; Scheme 32).\(^\text{56}\)

Scheme 32: Preparation of TTF (21) via triethyl phosphite-mediated cross-coupling.

The preparation of tailor-made fully substituted TTF-derivatives would be of high interest for material science. Therefore, a convenient sequential bis-functionalization of DTT (16) under smooth conditions would be an interesting synthetical task.


2.2 Preparation of 1,3-Dithiole-2-thione (DTT)

DTT (16) was easily prepared according to a literature procedure.\(^{57}\) In the first step, ethylene trithiocarbonate (22) reacted with dimethyl acetylenedicarboxylate (23) in a cycloaddition-ring-opening reaction leading to dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (24) in 91% yield. The obtained diester (24) was saponified under acidic conditions furnishing the dicarboxylic acid (25) that was converted into the desired DTT (16) by direct decarboxylation using pyridine as solvent (Scheme 33).

![Scheme 33: Preparation of 1,3-dithiole-2-thione (16).]

2.3 Preparation of Monofunctionalized DTT-Derivatives

DTT (16) was subjected to direct metalation using TMP-bases. We found that the metalation of 16 can be achieved with either TMPMgCl\(_2\)LiCl (2; 1.1 equiv, THF, -78 °C, 0.5 h) or TMPMgCl\(_2\)LiCl (2; 1.1 equiv, THF, 0 °C, 0.5 h) in the presence of ZnCl\(_2\) (0.5 equiv) or TMPZnCl\(_2\)LiCl (4; 1.1 equiv, THF, 0°C, 0.5 h). After trapping the metalated species with iodine, the magnesiated DTT-derivative furnished the iodinated product 18a in higher yield (79%; Scheme 34 and Table 3, entry 1) compared to the zincated analogs (72% and 68%, respectively). Therefore, these smooth magnesiation conditions were used for the following reactions.

B. RESULTS AND DISCUSSION

Scheme 34: Direct metalation of 1,3-dithiole-2-thione (16) using different conditions.

Bromination of the magnesiated DTT-derivative with 1,2-dibromotetrachloroethane produced the corresponding halogenated product 18b in 84% isolated yield (Table 3, entry 2). Thiolation with S-methyl methanethiosulfonate furnished the methyl thioether 18c in 75% yield (entry 3). Various carbon electrophiles reacted readily. Thus, the acylation with 3-chlorobenzoyl chloride, after domino-transmetalation with ZnCl$_2$ and CuCN \_2LiCl,\textsuperscript{59} provided ketone 18d in 62% yield (entry 4). Copper-mediated allylation with ethyl (2-bromomethyl)acrylate\textsuperscript{38} led to the allylated DTT 18e in 50% yield (entry 5).

To achieve arylation, the magnesiated DTT-derivative was transmetalated to zinc, followed by a Pd-catalyzed cross-coupling with an aryl iodide. Therefore, different Pd-catalysts (3 mol\%) were examined (Pd(PPh$_3$)$_4$, Pd(PPh$_3$)$_2$Cl$_2$, Pd(OAc)$_2$/SPhos and PEPPSI-iPr) in the coupling with ethyl 4-iodobenzoate. No arylation was observed using Pd(PPh$_3$)$_2$Cl$_2$, Pd(OAc)$_2$/SPhos and PEPPSI-iPr (THF, 25 °C to 50°C). In the case of Pd(PPh$_3$)$_4$, at least traces of the coupling-product were detected by GC analysis. We found that the addition of NMP as polar co-solvent (THF/NMP, 2:1) boost the cross-coupling and the desired product 18f was isolated in 84% yield (entry 6). Further arylations of the electron-rich DTT (16) were achieved with electron-withdrawing, as well as electron-donating groups on the aryl iodides furnishing the expected products 18g-n in high yields (60-94%; entries 7-14).

Table 3: Preparation of monofunctionalized DTT-derivatives of type 18 by magnesiation of DTT (16) with TMPMgCl·LiCl (2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I₂</td>
<td>18a</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>(BrCl₂C)₂</td>
<td>18b</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>MeSO₂SMe</td>
<td>18c</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>Cl₄C₄Cl</td>
<td>18d</td>
<td>62&lt;sup&gt;b,c&lt;/sup&gt;</td>
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<td>5</td>
<td>EtO₂C≡C≡C≡CBr</td>
<td>18e</td>
<td>50&lt;sup&gt;b,c&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>R = CO₂Et</td>
<td>18f: R = CO₂Et</td>
<td>84&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>R = CN</td>
<td>18g: R = CN</td>
<td>94&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>R = Cl</td>
<td>18h: R = Cl</td>
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<td>R = CH₃</td>
<td>18j: R = CH₃</td>
<td>79&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>R = NO₂</td>
<td>18k: R = NO₂</td>
<td>77&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>R = OMe</td>
<td>18l: R = OMe</td>
<td>70&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>R = NO₂</td>
<td>18m: R = NO₂</td>
<td>60&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>14</td>
<td>R = OMe</td>
<td>18n: R = OMe</td>
<td>94&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated Yield of analytically pure product. <sup>b</sup>ZnCl₂ solution was added. <sup>c</sup>CuCN·2LiCl solution was added. <sup>d</sup>Cross-coupling conditions: ZnCl₂ transmetalation, 10 mol% Pd(PPh₃)₄, THF/NMP (2:1).
2.4 Preparation of Difunctionalized DTT-Derivatives

Disubstituted DTT-derivatives of type 19 were obtained by a second magnesiation of various mono-substituted DTTs (18) using similar conditions. Subsequent trapping of the magnesiated 4-bromo-DTT 18b with different electrophiles, such as 1,2-dibromotetrachloroethane, iodine and tert-butyldimethylsilyl trifluoromethanesulfonate furnished the corresponding products 19a-c in 70-94% yield (Table 4, entries 1-3). The dithioether 19d was obtained by the reaction of the magnesiated DTT-derivative 18c with S-methyl methanethiosulfonate (86% yield; entry 4). Iodination of the magnesiated compound 18l led to the expected 4-iodo-5-(4-methoxyphenyl)-DTT 19e in very good yield (94%; entry 5). After transmetalation to zinc, Pd-catalyzed Negishi cross-coupling reactions\textsuperscript{39} using Pd(PPh\textsubscript{3})\textsubscript{4} (10 mol%) as catalyst and an aryl iodide as electrophile were performed (THF/NMP, 2:1) giving the diarylated DTT-derivatives 19f-i in 83-93% yield (entries 6-9).

Table 4: Preparation of disubstituted DTT-derivatives of type 19 by magnesiation of monosubstituted DTT-derivatives of type 18 with TMPMgCl/LiCl (2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18b</td>
<td>(BrCl\textsubscript{2})\textsubscript{2}</td>
<td>19a</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>18b</td>
<td>I\textsubscript{2}</td>
<td>19b</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>18b</td>
<td>tBuMe\textsubscript{2}SiOTf</td>
<td>19c</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>18c</td>
<td>MeSO\textsubscript{2}SMe</td>
<td>19d</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>18l</td>
<td>I\textsubscript{2}</td>
<td>19e</td>
<td>96</td>
</tr>
</tbody>
</table>
2.5 Preparation of Functionalized 1,3-Dithiol-2-one-Derivatives

Various 4,5-disubstituted DTTs of type 19 were converted into the corresponding oxygen analogs of type 20 by treatment with Hg(OAc)$_2$ (3.0 equiv) in a mixture of CHCl$_3$ and AcOH (4:1) (25 °C, 1-2 h).$^{20b}$ Thus, the monobromo-oxygen analog 20a, as well as the diarylated compounds 20b-d were obtained in 75-92% yield (Scheme 35).

![Scheme 35: Preparation of oxygen analogs 20a-d.](image)

2.6 Preparation of Tetraarylated TTF-Derivatives

Both symmetrical and nonsymmetrical TTFs (26) were prepared via a triethyl phosphite-mediated cross-coupling (110 °C, 1.5-3 h).$^{56b}$ In the first case, the functionalized 1,3-dithiole-2-ones 20c and 20d furnished the corresponding tetraarylated TTF-derivatives 26a and 26b (54-63% yield) after treatment with P(OEt)$_3$ (Scheme 36).
Scheme 36: Preparation of symmetrically substituted TTF-derivatives via triethyl phosphite-mediated cross-coupling.

On the other hand, the nonsymmetrically substituted TTF-derivatives 26c and 26d were prepared by cross-coupling of 19i with 20b and 19f with 20d, respectively (53-67% yield; Scheme 37). These new fully functionalized TTF-derivatives are of high interest for material science due to their extended π-system.

Scheme 37: Preparation of nonsymmetrically substituted TTF-derivatives via triethyl phosphite-mediated cross-coupling.
2.7 Donor-Acceptor-TTFs

The preparation of donor-acceptor-TTF-derivatives bearing electron-withdrawing groups on one side and electron-donating groups on the other side is of high interest for organic materials. These compounds could exhibit extraordinary charge transfer properties. As shown in Scheme 37, compound 26c possess both, electron-withdrawing CN-groups, as well as electron-donating CH₃-groups and could therefore be an interesting candidate for material science.

To extend the range of donor-acceptor-molecules, the dithioether 19d was subjected to a triethyl phosphite-mediated cross-coupling reaction with the oxygen analogs 20b-d. However, only traces of the homocoupling-products 26a, 26b and 26h of the oxygen analog were observed. The same result was obtained by reacting the dimethyl-DTT-derivative 19i with the dichloro-oxygen analog 20c leading to compound 26a (Scheme 38).
Furthermore, the stronger electron donor 19j should be prepared. Therefore, the monosubstituted DTT 18l was subjected to a second metalation using TMPMgCl·LiCl (2; 1.1 equiv, THF, -78 °C, 0.5 h), followed by transmetalation to zinc and Pd-catalyzed Negishi cross-coupling with 4-iodoanisole as electrophile. Instead of the desired product, no reaction was observed (Scheme 39).
A possible explanation could be that the DTT-derivative 18I is already very electron-rich so that another strong electron-donating group can not be introduced. In order to remove electron density from the system, the exocyclic sulfur of the iodinated DTT 19e was converted into the oxygen atom by treatment with Hg(OAc)$_2$ (3.0 equiv) furnishing the oxygen analog 20e in 94% yield. Then, the Pd-catalyzed Negishi cross-coupling of this derivative with $p$-anisylzinc iodide using Pd(PPh$_3$)$_4$ (10 mol%) as catalyst in a mixture of THF/NMP (2:1) was analyzed. Unfortunately, no reaction was observed. The same result was obtained, when the iodinated compound 20e was used in the Pd-catalyzed Negishi cross-coupling after iodine-magnesium-exchange with $i$PrMgClLiCl (1.1 equiv, THF, -78°C, 0.5 h) (Scheme 40).
B. RESULTS AND DISCUSSION

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Scheme 40: Attempts to prepare the donor molecule 20f.

2.8 Other TTF Isomers

Another synthetically interesting task would be the preparation of other substituted TTF-isomers as shown in Scheme 41.

shown above:

\[
\begin{array}{c}
\text{new task:} \\
\end{array}
\]

Scheme 41: New synthetic task: The preparation of TTF-isomers.

The dibromo-TTF-derivatives 27a and 27b should give access to these new isomers. Bromine-magnesium-exchange, followed by subsequent trapping of the Mg-species with ethyl cyanoformate should furnish the ester compounds 28a and 28b. Due to the directing effect of
the ester group, a subsequent metalation should proceed in the adjacent position leading to the trifunctionalized TTF-derivatives 29a and 29b. After repeating the same steps, the new TTF-isomers 22i and 22j should be obtained (Scheme 42).

![Scheme 42: Synthetical strategy giving access to new TTF-isomers.](image)

However, the triethyl phosphite-mediated cross-coupling of the monobromo-DTT-derivative 18b with the oxygen analog 20a furnished the isomeric mixture of 27a and 27b in very low yield (18%; Scheme 43).
B. RESULTS AND DISCUSSION

Scheme 43: Preparation of dibromo-TTF-derivatives 27a and 27b via triethyl phosphite-mediated cross-coupling of 18b with 20a.

In contrast, the coupling of the disubstituted DTT-derivative 19c with the oxygen analog 20g afforded the desired isomeric mixture of TTF-derivatives 22k and 22l in 70% yield. Subsequent cleavage of the Si-groups using KF (10 equiv, DMSO/H2O, 25 °C, 2 h) furnished the expected dibromo-isomers 27a and 27b in 80% yield of the isomeric mixture (Scheme 44).

Scheme 44: Preparation of dibromo-TTF-derivatives 27a and 27b via TBDMS-protected DTT-derivatives.

After flash column chromatography using hexane/NEt3 (100:2) as eluent, two different spots were collected. Analysis of these products by single crystal X-ray diffraction showed the trans-isomer in the first spot, whereas the cis-isomer was collected in the second spot (Figure 5).
However, NMR analysis ($^1$H and $^{13}$C) of the actually pure isomers showed different results. As both structures show C$_2$-symmetry, one proton signal and three carbon signals are expected for each isomer. Interestingly, all signals are doubled (1:1 ratio in $^1$H-NMR) leading to the conclusion that no separation of the isomers was achieved (Figure 6). As the single crystal X-ray diffraction does not indicate the degree of purity, it is obvious that these different structures were obtained by coincidence.
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Figure 6: NMR analysis of the trans-isomer: $^1$H-NMR (above) and $^{13}$C-NMR (below).

Thus, all following reactions for the preparation of other symmetrically substituted TTF-derivatives as shown in Scheme 42 were unsuccessful due to the inseparable isomers.

3.1 Introduction

Pioneered by the discovery of Wudl, tetrathiafulvalenes (TTFs) have emerged into an important class of organic materials owing to their unique optical, electronic and magnetic properties. Much effort has been made to functionalize the TTF-scaffold, including C-H arylation and direct metalations. Although the C-H arylation enables a fast access to arylated TTF-derivatives, this methodology has some drawbacks. On one hand, only mono- and tetrasubstituted TTFs can be prepared and furthermore, in the case of tetraarylated TTF-derivatives, all residues are equal (Scheme 45). In contrast, direct metalations via lithiation of TTF allow for an efficient functionalization with robust substituents. However, the preparation of TTFs featuring sensitive functional groups remains difficult due to the high reactivity of the carbon-lithium bond.

![Scheme 45: Preparation of mono- and tetrasubstituted TTF-derivatives via C-H arylation.](image)

Thus, a selective and stepwise functionalization of TTF under gentle reaction conditions leading to symmetrically, as well as nonsymmetrically substituted polyfunctionalized TTFs would be of high interest. Such a synthesis protocol would allow for fine-tuning of optical properties and would therefore be of great importance for the preparation of new organic materials.

---

3.2 Preparation of Tetrathiafulvalene (TTF)

Tetrathiafulvalene was prepared according to the literature.\(^{57}\) In the first step, peracetic acid (4.0 equiv) was added to DTT (16) furnishing the hydrogensulfate salt 29 in 68% yield. Anion exchange by the addition of sodium hexafluorophosphate (1.1 equiv) afforded salt 30 in 83% yield. After deprotonation using NEt\(_3\) (1.1 equiv, MeCN, 25 °C, 0.5 h), TTF (21) was obtained in 94% yield (Scheme 46).

\[
\begin{array}{c}
\text{16} \xrightarrow{\text{CH}_3\text{CO}_2\text{H (4.0 equiv)}} \text{acetone, -50 to 15 °C} \xrightarrow{\text{HSO}_4^- \text{NaPF}_6 (1.1 \text{ equiv})} \text{29: 68%} \\
\text{30} \xrightarrow{\text{NEt}_3 (1.1 \text{ equiv}, \text{MeCN, 25 °C, 0.5 h})} \text{21: 94%}
\end{array}
\]

Scheme 46: Preparation of tetrathiafulvalene (TTF; 21) starting from its precursor DTT (16).

3.3 Preparation of Monofunctionalized TTF-Derivatives

The magnesiation of TTF (21) was conveniently achieved by the addition of TMPMgCl·LiCl (2; 1.1 equiv) at 25 °C within 1 h leading to the magnesiated species 31. This magnesium derivative was treated with various electrophiles (E\(^1\)-X) providing a range of TTF-derivatives of type 32 in 55-92% yield (Scheme 47 and Table 5).

\[
\begin{array}{c}
\text{21} \xrightarrow{\text{TMPMgCl·LiCl (2; 1.1 equiv), THF, 25 °C, 1 h}} \text{31} \\
\text{31} \xrightarrow{\text{E}^1\-X} \text{32}
\end{array}
\]

Scheme 47: Preparation of functionalized TTFs (32) via the magnesiation of TTF (21) with TMPMgCl·LiCl (2).

The halogenation of 31 (iodolysis, bromination and chlorination) proceeded in moderate yields (55-67% yield; Table 5, entries 1-3) due to the limited stability of the heterocyclic halides (32a-c). Methylthiolation of 31 was performed using MeSO\(_2\)SMe affording the thioether 32d in 89% yield (entry 4). An aminomethylation of 31 using the iminium salt Me\(_2\)NCH\(_2\)OCOCF\(_3\)\(^{64}\) provided the amine 32e in 55% yield (entry 5). The acylation of 31 was directly achieved by the addition

of DMF or ethyl cyanoformate leading to the aldehyde 32f and the ester 32g in 60-72% yield (entries 6-7). A copper-catalyzed acylation with pivaloyl chloride provided the ketone 32h (76% yield; entry 8), whereas a Pd-catalyzed Negishi-acylation\(^\text{39}\) furnished the ketone 32i in 83% yield (entry 9). The arylation of 31 was achieved by a transmetalation with zinc chloride followed by a Negishi cross-coupling using 3 mol% Pd(dba)\(_2\) (dba = dibenzylideneacetone) and 6 mol% tfp (tri-2-furylphosphine)\(^\text{65}\) as catalyst and an aryl iodide as electrophile. Interestingly, electron-withdrawing, as well as electron-donating groups were attached to the electron-rich TTF-core producing the corresponding arylated TTF-derivatives 32j-m in 61-92% yield (entries 10-13).

Table 5: Preparation of 4-substituted TTF-derivatives of type 32 by magnesiation of TTF (21) with TMPMgCl LiCl (2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I(_2)</td>
<td>32a: R = I</td>
<td>55(^a)</td>
</tr>
<tr>
<td>2</td>
<td>(BrCl(_2))</td>
<td>32b: R = Br</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>PhSO(_2)Cl</td>
<td>32c: R = Cl</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>MeSO(_2)SMe</td>
<td>32d: R = SMe</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>Me(_2)N=CHOCOCF(_3)</td>
<td>32e: R = CH(_2)NMe(_2)</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>DMF</td>
<td>32f: R = H</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>NC-CO(_2)Et</td>
<td>32g: R = OEt</td>
<td>72</td>
</tr>
<tr>
<td>8</td>
<td>tBuCOCl</td>
<td>32h: R = tBu</td>
<td>76(^b)</td>
</tr>
<tr>
<td>9</td>
<td>3-Cl-C(_6)H(_4)COCl</td>
<td>32i: R = 3-Cl-C(_6)H(_4)</td>
<td>83(^c)</td>
</tr>
<tr>
<td>10</td>
<td>R = 4-Cl</td>
<td>32j: R = 4-Cl</td>
<td>86(^d)</td>
</tr>
<tr>
<td>11</td>
<td>R = 4-CO(_2)Et</td>
<td>32k: R = 4-CO(_2)Et</td>
<td>87(^d)</td>
</tr>
<tr>
<td>12</td>
<td>R = 4-OMe</td>
<td>32l: R = 4-OMe</td>
<td>61(^d)</td>
</tr>
<tr>
<td>13</td>
<td>R = 3-CF(_3)</td>
<td>32m: R = 3-CF(_3)</td>
<td>92(^d)</td>
</tr>
</tbody>
</table>

\(^a\)Isolated yield of analytically pure product. \(^b\)CuCN\(_2\)LiCl solution was added. \(^c\)Pd-catalyzed acylation reaction using 10 mol% Pd(PPh\(_3\))\(_4\). \(^d\)Cross-coupling conditions: ZnCl\(_2\) transmetalation, 3 mol% Pd(dba)\(_2\), 6 mol% tfp.

3.4 Preparation of Difunctionalized TTF-Derivatives

The preparation of symmetrically and nonsymmetrically disubstituted TTF-derivatives of type 33 was achieved by a selective metalation of various monofunctionalized TTF-derivatives. The presence of an electron-withdrawing substituent, such as a chlorine, an acyl or a carboethoxy group on the TTF-core directed the second metalation to the adjacent position. In case of a chloride (32c) or a carboethoxy group (32g), the metalation was best performed with TMPMgClLiCl (2). Thus, the treatment of 4-chloro-TTF (32c) with TMPMgClLiCl (2) at 0 °C (THF, 1.1 equiv, 0.5 h) followed by the copper-catalyzed allylation reaction with ethyl 2-(bromomethyl)acrylate furnished the disubstituted TTF 33a in 85% yield (Table 6, entry 1). After transmetalation with zinc chloride, a Pd-catalyzed Negishi acylation reaction with benzoyl chloride and Negishi cross-coupling reactions with various aryl iodides were achieved leading to 4,5-disubstituted TTF-derivatives 33b-d in 78-92% yield (entries 2-4). Magnesiation of the ester 32g was performed using TMPMgClLiCl (2; 1.1 equiv) at -20 °C (THF, 1.1 equiv, 0.5 h). Subsequent trapping with ethyl cyanoformate led to the diester-TTF 33e in 65% yield (entry 5). The thioethers 33f-33g were obtained in 59-65% yield by quenching the magnesiated TTF-derivative of 32g with PhSO2SPh and MeSO2SMe (entries 6-7). In the case of a benzoyl substituent (33e), a metalation with a magnesium base was too harsh and led to unwanted side reactions. However, a zincation with TMP2Zn2MgCl22LiCl (5; 1.1 equiv, THF, 0 °C, 0.5 h) led to the corresponding zinctated-TTF in quantitative yield. After iodolysis, the corresponding iodide 33h was obtained in 83% yield (entry 8).
Table 6: Preparation of 4,5-disubstituted TTF-derivatives of type 33 by metalation of the monosubstituted TTFs 32c, 32g and 32i with Mg- and Zn-TMP-bases.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32c</td>
<td>Br-CHOEt</td>
<td>33a</td>
<td>85b,c</td>
</tr>
<tr>
<td>2</td>
<td>32c</td>
<td>Cl-Ph</td>
<td>33b</td>
<td>83b,d</td>
</tr>
<tr>
<td>3</td>
<td>32c</td>
<td>R = OMe</td>
<td>33c: R = OMe</td>
<td>78b,e</td>
</tr>
<tr>
<td>4</td>
<td>32c</td>
<td>R = CN</td>
<td>33d: R = CN</td>
<td>92b,e</td>
</tr>
<tr>
<td>5</td>
<td>32g</td>
<td>NC-CO2Et</td>
<td>33e</td>
<td>65f</td>
</tr>
<tr>
<td>6</td>
<td>32g</td>
<td>PhSO2SPh</td>
<td>33f: R = Ph</td>
<td>59f</td>
</tr>
<tr>
<td>7</td>
<td>32g</td>
<td>MeSO2SMe</td>
<td>33g: R = Me</td>
<td>65f</td>
</tr>
<tr>
<td>8</td>
<td>32i</td>
<td>I2</td>
<td>33h</td>
<td>83g</td>
</tr>
</tbody>
</table>

*Isolated yield of analytically pure product. **TMPMgCl/LiCl (1.1 equiv, 0 °C) was used. **CuCN 2LiCl solution was added. **ZnCl2 solution was added. Pd-catalyzed acylation reaction using 10 mol% Pd(PPh3)4. **Cross-coupling conditions: ZnCl2 transmetalation, 3 mol% Pd(dba)2, 6 mol% ttp. **TMPMgCl/LiCl (1.1 equiv, -20 °C) was used. **TMP2Zn2MgCl2 2LiCl (1.1 equiv, 0 °C) was used.

3.5 Preparation of Trifunctionalized TTF-Derivatives

For the preparation of completely nonsymmetrical substituted TTFs, compound 33b was subjected to further metalation using TMP2Zn2MgCl2 2LiCl (5; THF, 1.2 equiv, 25 °C, 0.5 h). After quenching the zinicated intermediate with iodine, a mixture of two isomeric compounds (34a and 34b) was obtained in 51% yield and could not be separated (Scheme 48).
Further trifunctionalized TTF-derivatives were readily prepared starting from the symmetrically substituted 4,5-diethyl ester-TTF 33e using the mild base TMPZnCl·LiCl (4; 1.3 equiv, THF, -30 °C, 0.5 h). Reaction of the zincated intermediate with iodine afforded the halogenated product 34c in 90% yield. A copper-catalyzed allylation with 3-bromocyclohexene furnished the expected product 34d (83% yield). Negishi cross-coupling reactions with various aryl iodides using Pd(dba)$_2$ (3 mol%) and tfp (6 mol%) as catalytic system, produced the tri-substituted TTF-derivatives 34e-g in 66-94% yield (Scheme 49).

**Scheme 49:** Preparation of trisubstituted TTF-derivatives of type 34 using TMPZnCl·LiCl (3).

### 3.6 Preparation of Tetrafunctionalized TTF-Derivatives

Fully functionalized TTFs of type 35 were prepared by the zincation of 34e-g using TMPZnCl·LiCl (4; 1.3 equiv) at 0 °C within 0.5 h. Trapping the zincated-TTF-derivative of 34e and 34f with iodine gave the tetrasubstituted TTFs 35a and 35b in 76-88% yield (Table 7, entries 1 and 2). Furthermore, various Negishi cross-couplings with different aryl iodides were
performed leading to the symmetrically substituted TTF-derivatives 35c-e (63-90% yield; entries 3-5). Copper-catalyzed allylation with ethyl 2-(bromomethyl)acrylate\textsuperscript{38} furnished the expected product 35f in 85% yield (entry 6). The reactions of the zincated intermediates of 34e and 34f in Pd-catalyzed Negishi acylations provided the corresponding tetrasubstituted TTFs 35g and 35h (80-85% yield; entries 7 and 8).

Table 7: Preparation of fully functionalized TTF-derivatives of type 35 using TMPZnCl/LiCl (4).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34e</td>
<td>I\textsubscript{2}</td>
<td>35a: R = CO\textsubscript{2}Et</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>34f</td>
<td>I\textsubscript{2}</td>
<td>35b: R = CN</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>34e</td>
<td>R\textsubscript{2} = CO\textsubscript{2}Et</td>
<td>35c: R\textsubscript{1} = R\textsubscript{2} = CO\textsubscript{2}Et</td>
<td>90\textsuperscript{b}</td>
</tr>
<tr>
<td>4</td>
<td>34f</td>
<td>R\textsubscript{2} = CN</td>
<td>35d: R\textsubscript{1} = R\textsubscript{2} = CN</td>
<td>63\textsuperscript{b}</td>
</tr>
<tr>
<td>5</td>
<td>34g</td>
<td>R\textsubscript{2} = OMe</td>
<td>35e: R\textsubscript{1} = R\textsubscript{2} = OMe</td>
<td>63\textsuperscript{b}</td>
</tr>
<tr>
<td>6</td>
<td>34e</td>
<td>Br, CO\textsubscript{2}Et</td>
<td>85\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>34e</td>
<td>EtO\textsubscript{2}C, Ph</td>
<td>85\textsuperscript{d}</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>34f</td>
<td>EtO\textsubscript{2}C, 3-Cl-Ph</td>
<td>80\textsuperscript{d}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Isolated yield of analytically pure product. \textsuperscript{b}Cross-coupling conditions: 3 mol% Pd(dba)\textsubscript{2}, 6 mol% tfp. \textsuperscript{c}CuCN/2LiCl solution was added. \textsuperscript{d}Pd-catalyzed acylation reaction using 10 mol% Pd(PPh\textsubscript{3})\textsubscript{4}. 
3.7 UV-VIS and DPV Data of Functionalized TTF-Derivatives

All TTF-derivatives feature a strong UV absorption and exhibit a broad absorption band in the visible spectral region (Figure 7). While the VIS absorption is weak for the unsubstituted TTF, it can be significantly enhanced by attaching substituents. In particular, the non-symmetric 1- and 3-fold substituted TTFs possess systematically higher extinction coefficients in the VIS region compared to their symmetrically functionalized counterparts. On the other hand, the larger conjugated π-systems of the 2- and 4-fold substituted molecules, respectively, extend the absorption further into the red.

Figure 7: a) UV-VIS absorption spectra of TTF (21) and compounds 32g and 33e. b) Absorption spectra of the tri- and tetrafunctionalized TTFs 34e-g and 35c-e. c) Magnified view on the absorption in the VIS range of these compounds.

We then studied the effect of the nature and number of substituents on the energy levels of the TTF-derivatives using differential pulse voltammetry (DPV). The highest occupied molecular orbital (HOMO) energies were extracted from scans in oxidation direction (Figure 8) and referenced to the oxidation of ferrocene ($E_{\text{Fc/Fc}^+} = -4.80$ eV vs. vacuum).

---

66 These measurements were performed by Dr. F. Auras and are given here for the sake of completeness.
B. RESULTS AND DISCUSSION

Figure 8: a-i) DPV data of compounds 21, 32g, 33e, 34e-g and 35c-e, respectively (black), multi-Gaussian fits to the data (red) and the single Gaussian components (orange). The oxidation signal of the ferrocene internal reference is marked with an asterisk. The potential of the first oxidation, corresponding to the HOMO energy, is converted to vacuum scale assuming $E_{\text{FC/FC}^+} = -4.8$ eV. k-l) DPV data of the mono-substituted compounds 6c and 32g, respectively (black), multi-Gaussian fits to the data (red) and the single Gaussian components (orange). Since the oxidation signal of the ferrocene internal reference (marked with an asterisk) overlaps strongly with the first oxidation signal of the compounds, we measured the additional DPV scans without ferrocene in the electrolyte (blue data points).

We found that indeed the substitution has a profound effect on the position of the HOMO, spanning a range of more than 200 meV (Figure 9). While a single -CO$_2$Et or -Cl substituent shifts the HOMO upwards (Figure 8k and Figure 8l), the energy levels of all multi-substituted TTFs are significantly lower than for bare TTF. For the series of aryl substituents, the HOMO
can be further fine-tuned by adjusting the electron-accepting end group. For the molecules of type 34 and 35 deeper HOMO levels were observed as the acceptor strength was increased from -OMe to -CO$_2$Et and -CN. This approach for systematic fine-tuning of the energy levels allows for matching the work function of contact layers or electrodes, such as gold, silver or indium tin oxide, which is of key importance for possible applications of these materials in electronic devices.

**Figure 9**: Highest occupied molecular orbital energies of selected substituted TTF-derivatives measured by differential pulse voltammetry.
4. Selective Functionalization of 1,4-Dithiin Using TMP-Bases: Access to New Heterocycles

4.1 Introduction

The preparation and functionalization of new sulfur-heterocycles is an important synthetic task since fully conjugated S-heterocyclic derivatives are of great importance for their electronical properties. In the previous chapters, 1,3-dithiole-2-thione (16; DTT) and the tetrathiafulvalene-scaffold (21; TTF) were functionalized using the kinetically active bases TMPMgCl\textsubscript{2}LiCl (2),\textsuperscript{9} TMPZnCl\textsubscript{2}LiCl (4),\textsuperscript{12} and TMP\textsubscript{2}Zn2MgCl\textsubscript{2} (5).\textsuperscript{13} All these five-membered S-heterocycles have found applications in material material science as shown above. The availibility of more symmetrical functionalized 6-membered S-heterocycles is of high interest for the construction of new organic materials.\textsuperscript{68} However, the functionalization of S-heterocycles is challenging. The addition of a base may lead to side reactions, such as rearrangements. This is the case for 1,4-dithiin and 1,4,5,8-tetrathianaphthalene. The 1,4-dithiin-derivative rearranges in the presence of catalytic amounts of Bu\textsubscript{4}NOH via an open-ring-structure leading to 1,4-dithiafulvalenes.\textsuperscript{69} In addition, tetrathianaphthalene is known to isomerize to TTF in the presence of strong bases, such as KO\textsubscript{t}Bu and LDA (Scheme 50).\textsuperscript{31,70}

Therefore, the selective functionalization of 1,4-dithiin is of high interest. Smooth reaction conditions need to be developed to overcome these problems.


4.2 Preparation of 1,4-Dithiin

1,4-Dithiin (38) was prepared by the reaction of 1,4-dithiane-2,5-diol (37; 1.0 equiv) with thionyl chloride (3.5 equiv, DMF, 25 °C, 2 h).\(^\text{71}\) Co-distillation of the crude product with DMF, followed by extraction afforded 1,4-dithiin (38) in 81% yield (Scheme 51).

\[
\text{SOCI}_2 (3.5 \text{ equiv}) \quad \text{DMF, 25 °C, 2 h} \quad \text{38: 81%}
\]

Scheme 51: Preparation of 1,4-dithiin (38).

4.3 Preparation of Monofunctionalized 1,4-Dithiin-Derivatives

The magnesiation of 1,4-dithiin (38) was conveniently achieved by the addition of TMPMgCl LiCl (2; 1.1 equiv) at -40 °C within 0.5 h leading to the magnesiated derivative 39. This magnesium intermediate was treated with various electrophiles (E\(^1\)-X) providing a range of monofunctionalized dithiin-derivatives of type 40 in 56-97% yield (Scheme 52 and Table 8). No side reactions were observed under these smooth reaction conditions.

\[
\text{THF, -40 °C, 0.5 h} \quad \text{38} \quad \text{TMPMgCl LiCl (2; 1.1 equiv)} \quad \text{39} \quad \text{E}^1\text{-X} \quad \text{40}
\]

Scheme 52: Magnesiation of 1,4-dithiin (38) with TMPMgCl LiCl (2) and subsequent trapping with electrophiles.

Iodination of the magnesiated derivative 39 afforded the expected product 40a in 83% yield (Table 8, entry 1). Similarly, bromination with (BrCl\(_2\))\(_2\) and chlorination with PhSO\(_2\)Cl furnished the halogenated products 40b and 40c in 78% and 56% yield, respectively (entries 2-3). Quenching of the magnesiated intermediate 39 with p-toluenesulfonyl cyanide led to the corresponding dithiin-derivative 40d (60% yield; entry 4). Thiolation of 39 was performed using MeSO\(_2\)SMe and PhSO\(_2\)SPh affording the thiethers 40e and 40f in 75% and 77% yield, respectively (entries 5 and 6). The alcohol 40g was prepared by quenching the reaction with benzaldehyde (97% yield; entry 7). Acylation of 39 was directly achieved by the addition of ethyl cyanoformate leading to the ethyl ester 40h in 89% yield (entry 8), whereas a range of copper-mediated acylation reactions provided the ketones 40i-m (56-89% yield; entries 9-13).

After transmetalation to zinc, a copper-mediated allylation reaction with 3-bromocyclohexene furnished the expected product 40n in 73% yield (entry 14). The arylation of dithiin (38) was performed by a transmetalation with zinc chloride, followed by a Negishi cross-coupling using 3 mol% Pd(dba)$_2$ and 6 mol% tfp as catalytic unit and an aryl iodide as electrophile. Interestingly, electron-withdrawing, as well as electron-donating groups were attached to the dithiin-core furnishing the corresponding arylated derivatives 40o-q in high yields (85-94% yield; entries 15-17).

Table 8: Preparation of substituted 1,4-dithiin-derivatives of type 40 by magnesiation of 1,4-dithiin (39) with TMPMgClLiCl (2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I$_2$</td>
<td>40a: R = I</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>(BrCl$_2$)$_2$</td>
<td>40b: R = Br</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>PhSO$_2$Cl</td>
<td>40c: R = Cl</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>Tos-CN</td>
<td>40d: R = CN</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>MeSO$_2$SMe</td>
<td>40e: R = SMe</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>PhSO$_2$SPh</td>
<td>40f: R = SPh</td>
<td>77</td>
</tr>
<tr>
<td>7</td>
<td>PhCHO</td>
<td>40g</td>
<td>97</td>
</tr>
<tr>
<td>8</td>
<td>NC-CO$_2$Et</td>
<td>40h: R = OEt</td>
<td>89</td>
</tr>
<tr>
<td>9</td>
<td>Cl-CO$_2$Et</td>
<td>40i: R = CO$_2$Et</td>
<td>56$^{b,c}$</td>
</tr>
<tr>
<td>10</td>
<td>tBuCOCl</td>
<td>40j: R = tBu</td>
<td>89$^{b,c}$</td>
</tr>
<tr>
<td>11</td>
<td>3-Cl-C$_6$H$_4$COCl</td>
<td>40k: R = 3-Cl-C$_6$H$_4$</td>
<td>80$^{b,c}$</td>
</tr>
<tr>
<td>12</td>
<td>PhCOCl</td>
<td>40l: R = Ph</td>
<td>78$^{b,c}$</td>
</tr>
<tr>
<td>13</td>
<td>c-C$_3$H$_5$COCl</td>
<td>40m: R = c-C$_3$H$_5$</td>
<td>65$^{b,c}$</td>
</tr>
<tr>
<td>14</td>
<td>3-Br</td>
<td>40n</td>
<td>73$^{b,c}$</td>
</tr>
<tr>
<td>15</td>
<td>R = 2-NH$_2$</td>
<td>40o: R = 2-NH$_2$</td>
<td>94$^d$</td>
</tr>
<tr>
<td>16</td>
<td>R = 3-Me</td>
<td>40p: R = 3-Me</td>
<td>85$^d$</td>
</tr>
<tr>
<td>17</td>
<td>R = 4-CO$_2$Et</td>
<td>40q: R = 4-CO$_2$Et</td>
<td>87$^d$</td>
</tr>
</tbody>
</table>

*aIsolated yield of analytically pure product. *bZnCl$_2$ solution was added. *cCuCN. 2LiCl solution was added. *dCross-coupling conditions: ZnCl$_2$ transmetalation, 3 mol% Pd(dba)$_2$, 6 mol% tfp.
4.4 Preparation of Difunctionalized 1,4-Dithiin-Derivatives

Disubstituted dithiins of type 41 were obtained by a second metalation of various mono-substituted derivatives (40). The presence of electron-withdrawing substituents, such as halides, a cyano group, a carboethoxy or an acyl group on the dithiin-core directed the second metalation to the adjacent position. In case of a halide (40a-c), a cyanide (40d) or an acyl group (40i, k, l), the metalation was best performed with TMPZnCl LiCl (4; 1.1 equiv, THF, -40 °C or 0 °C, 0.5 h). In contrast, a selective metalation of the ethyl ester 40h was achieved using TMPMgCl LiCl (2; 1.1 equiv, THF, -78 °C, 0.5 h).

Thus, the treatment of the dithiin-derivatives 40a, 40c, and 40d with TMPZnCl LiCl (4) followed by iodination afforded the corresponding products 41a-c in 68-86% yield (Table 9, entries 1-3). Subsequent trapping of the magnesiated species of the ester 40h with iodine furnished the expected compound 41d in 62% yield (entry 4). The halogenated ketones 41f and 41g were obtained by the reaction of the zincated dithiin-derivatives of 40k and 40l with iodine (69% and 78% yield; entries 6 and 7). A copper-mediated allylation reaction of zincated 2-bromo-dithiin 40b with allyl bromide furnished the corresponding product 41h in 74% yield (entry 8). The symmetrically substituted diketones 41i and 41k were obtained by Pd-catalyzed Negishi acylation reactions of the zincated intermediates of 40k and 40l with 3-chlorobenzoyl chloride and benzoyl chloride, respectively (52-59% yield; entries 9 and 10).
Table 9: Preparation of disubstituted 1,4-dithiin-derivatives of type 41 by metalation of various monosubstituted 1,4-dithiins of type 40.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Electrophile</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40a</td>
<td>I₂</td>
<td>41a: E¹ = I</td>
<td>68ᵇ</td>
</tr>
<tr>
<td>2</td>
<td>40c</td>
<td>I₂</td>
<td>41b: E¹ = Cl</td>
<td>71ᵇ</td>
</tr>
<tr>
<td>3</td>
<td>40d</td>
<td>I₂</td>
<td>41c: E¹ = CN</td>
<td>86ᵇ</td>
</tr>
<tr>
<td>4</td>
<td>40h</td>
<td>I₂</td>
<td>41d: E¹ = CO₂Et</td>
<td>62ᶜ</td>
</tr>
<tr>
<td>5</td>
<td>40i</td>
<td>I₂</td>
<td>41e: E¹ = COCO₂Et</td>
<td>50ᵇ</td>
</tr>
<tr>
<td>6</td>
<td>40k</td>
<td>I₂</td>
<td>41f: E¹ = 3-Cl-C₆H₄CO</td>
<td>69ᵇ</td>
</tr>
<tr>
<td>7</td>
<td>40l</td>
<td>I₂</td>
<td>41g: E¹ = COPh</td>
<td>78ᵇ</td>
</tr>
<tr>
<td>8</td>
<td>40b</td>
<td>C₃H₅Br</td>
<td>41h</td>
<td>74ᵇ,ᵈ</td>
</tr>
<tr>
<td>9</td>
<td>40k</td>
<td>3-Cl-C₆H₄COCl</td>
<td>41i: R = 3-Cl-C₆H₄</td>
<td>52ᵇ,ᵉ</td>
</tr>
<tr>
<td>10</td>
<td>40l</td>
<td>PhCOCl</td>
<td>41j: R = Ph</td>
<td>59ᵇ,ᵉ</td>
</tr>
</tbody>
</table>

ᵇ Isolated yield of analytically pure product. ｃTMPZnCl₂, LiCl (1.1 equiv, THF, -40 °C or 0 °C, 0.5 h). ｃTMPMgCl₂, LiCl (1.1 equiv, THF, -78 °C, 0.5 h). ｃCuCN 2LiCl solution was added. ｃPd(PPh₃)₄ (10 mol%) was added.

table

4.5 Preparation of 1,4-Dithiin-Fused Quinolines

The arylated dithiin 40o turned out as useful starting material for the preparation of new heterocycles. The addition of an aldehyde (1.3 equiv) to 40o (EtOH, MW, 130 °C, 15 min) in the presence of trifluoroacetic acid (2.0 equiv) furnished dithiin-fused quinolines of type 6.⁷²

Thus, treatment of 40o with furural and 2-thiophenecarboxaldehyde led to the expected products 42a and 42b in 52% and 60% yield, respectively. Furthermore, the reaction of amine 40o with 3-pyridinecarboxaldehyde and benzaldehyde afforded the corresponding heterocycles 42c and 42d (53% and 54% yield; Scheme 53).

B. RESULTS AND DISCUSSION

Scheme 53: Preparation of dithiin-fused quinolines of type 42.

4.6 Iodine-Mediated Electrophilic Cyclizations of Alkynylated 1,4-Dithiin-Derivatives

Disubstituted dithiins bearing an iodine residue were found to be useful substrates for further transformations. Consequently, the dithiin-derivatives 41c and 41d were subjected to Pd-catalyzed Sonogashira reactions. The reaction of 41c with 1-octyne (1.5 equiv) in the presence of 2 mol% CuI and 1 mol% Pd(PPh$_3$)$_2$Cl$_2$ (NEt$_3$, 25 °C, 4 h) furnished the alkynylated cyanide 43a in 91% yield. Under similar conditions, the disubstituted dithiin 41d reacted with different alkynes, such as 1-octyne, phenylacetylene and trimethylsilylacetylene, leading to the expected compounds 43b-d in 77-93% yield (Scheme 54).

Scheme 54: Preparation of alkynylated 1,4-dithiin-derivatives of type 43 via Pd-catalyzed Sonogashira reactions.
The obtained dithiin-derivatives 43b-d easily underwent electrophilic cyclizations under smooth conditions (CH$_2$Cl$_2$, 25 °C, 5-12 h) using iodine (1.2 equiv). According to Baldwin’s rules, 6-exo-dig, as well as 5-exo-dig reactions are favoured allowing for the formation of two different products (Scheme 55).

![Scheme 55: Possible ring formation according to Baldwin’s rules.]

Interestingly, the 6-membered rings 44a and 44b were obtained, when iodine was added to the alkynylated esters 43b and 43c (84-88% yield), whereas the electrophilic cyclization of 43d in the presence of iodine furnished the 5-membered ring 44c (81% yield; Scheme 56). These different results can be explained with the β-silicon effect. In the latter case, a 5-exo-dig-cyclization implicates the positive charge in β-position to the TMS-group and therefore the formation of the 5-membered ring is favoured.

![Scheme 56: Electrophilic cyclizations of alkynylated 1,4-dithiin-derivatives.]

### 4.7 Preparation of a 1,4-Dithiin-Fused Pyridazine

For the preparation of a 1,4-dithiin-fused pyridazine, the symmetrically substituted diketone 41i was treated with hydrazine monohydrate (3.0 equiv) under smooth conditions (THF, 25 °C, 1 h) leading to the new heterocycle 45 in 60% yield (Scheme 57).
B. RESULTS AND DISCUSSION

Scheme 57: Preparation of the 1,4-dithiin-fused pyridazine 45 using hydrazine monohydrate.

4.8 Preparation of 1,4-Dithiin-Fused Pyrazines

The preparation of 1,4-dithiin-fused pyrazines was achieved by anellation. Therefore, 2,3-dichloropyrazine (46) was first converted into 2,3-dimercaptopyrazine (47) using NaHS (5.0 equiv) under harsh conditions (H2O, 120 °C, 5 h). The following anellation step was best performed in the presence of K2CO3 (5.0 equiv) at higher temperatures (DMF, 80 °C, 8 h) leading to the heteroacene 48 in 76% yield (Scheme 58).

Scheme 58: Preparation of 2,3-dimercaptopyrazine (47) followed by anellation with 2,3-dichloropyrazine (46).

For the construction of larger S-arrays owning interesting electronic properties, we developed an iterative synthesis. First, disilylated pyrazine-derivatives of type 50 should be anellated with dimercaptopyrazine 47 furnishing larger representatives of type 51. In another step, the silyl groups should be converted into halides (52), followed by another reaction with dimercaptopyrazine 47 affording heteropentacene 53 (Scheme 59).

---

Thus, the silylation of dichloropyrazine 46 was first examined. Low temperature lithiation was achieved by the slow addition of TMPLi (1; 1.1 equiv) to 46 in the presence of TMSCl (5.0 equiv, THF, -78 °C, 0.5 h) furnishing the mono-TMS-substituted pyrazine-derivative 49 in 76% yield. A disilylation of 46 was performed in an one-pot procedure under the same conditions using excess TMPLi (2.2 equiv, THF, -78 °C, 0.5 h) in the presence of TMSCl (5.0 equiv) or Et$_3$SiCl (5.0 equiv) affording the corresponding products 50a and 50b in 52% and 68% yield, respectively. Even dibromopyrazine 54 was subjected to lithiation with TMPLi (1; 2.2 equiv) in the presence of TMSCl (5.0 equiv, THF, -78 °C, 0.5 h) leading to the di-TMS-substituted pyrazine 50c in an one-pot procedure (Scheme 60).
**B. RESULTS AND DISCUSSION**

The dichloro-di-TMS-substituted pyrazine 50a was then treated with 2,3-dimercaptopyrazine (47; 1.3 equiv) under the same conditions as described above. After 6 h reaction time at 80 °C, full conversion of the starting material was observed, however, the desired product 51a was obtained in low yield (39%) and two side products were isolated (Scheme 61).

**Scheme 61**: Anellation of dichloro-di-TMS-substituted pyrazine 50a with 2,3-dimercaptopyrazine (47).

So we repeated the anellation step with dichloropyrazine 50b bearing the more stable triethylsilyl groups. Reaction of 50b with dimercaptopyrazine (47; 1.3 equiv) in the presence of K₂CO₃ (5.0 equiv) led to the heteroacene 51b (DMF, 80 °C, 6 h) in 51% yield (Scheme 62).

**Scheme 62**: Anellation of bis(triethylsilyl)-substituted pyrazine 50b with 2,3-dimercaptopyrazine (47).

Conversion of the silyl groups of 51b into iodides was achieved by treatment with ICl (6.0 equiv, CH₂Cl₂, 50 °C, 4 h) leading to the dihalide 52a in 67% yield. The corresponding heteroacene 52b was obtained in 60% yield after addition of excess bromine (39 equiv) to 51b (CH₂Cl₂, 25 °C, 20 h). Furthermore, the TMS groups of 50a were transformed into iodides by the reaction with ICl (12.0 equiv) leading to the tetrahalide 52c (Scheme 63).
However, another ring enlargement could not be achieved. Neither the iodinated heterocycle 52a, nor the brominated compound 52b showed any reaction with dimercaptopyrazine under various conditions.
5. Summary

This work focused on the selective and stepwise functionalization of \(N\) - and \(S\)-heterocycles using TMP-bases. Directed metalation of 2,3-dichloroquinoxaline, 1,3-dithiole-2-thione, tetrathiafulvalene and 1,4-dithiin followed by the reaction with various electrophiles led to a range of polysubstituted compounds owning interesting properties for their application as organic materials.

5.1 Functionalization of Quinoxalines Using TMP-Bases: Preparation of Tetracyclic Heterocycles with High Photoluminescence Quantum Yields

A selective functionalization of the quinoxaline scaffold in the presence of two electrophilic chlorine substituents in positions 2 and 3 was performed with TMP-bases, such as TMPLi and TMPMgCl\(_2\) LiCl. Smooth reaction conditions allowed for the preparation of mono- and difunctionalized quinoxaline-derivatives (Scheme 64).

![Scheme 64: Preparation of mono- and difunctionalized 2,3-dichloroquinoxalines.](image)

Direct access to 5,8-difunctionalized quinoxalines was achieved by the addition of excess TMPLi and subsequent trapping with chloroalkylsilanes. Conversion of the silyl groups led to diiodoquinoxaline, an useful reagent for further transformations (Scheme 65).
B. RESULTS AND DISCUSSION

Diiodoquinoxaline was subjected to I/Mg-exchange reactions using \( {^{t}}\text{PrMgCl}_{2} \text{LiCl} \), as well as Pd-catalyzed cross-coupling reactions furnishing various 5,8-difunctionalized quinoxalines (Scheme 66).

Another selective metalation of the corresponding difunctionalized derivatives using TMLPLi in the presence of ZnCl\(_2\) or using TMPMgCl\(_2\) LiCl afforded 5,6,8-trifunctionalized quinoxalines in 55-73% yield (Scheme 67).
B. RESULTS AND DISCUSSION

Scheme 67: Preparation of trifunctionalized quinoxalines.

Furthermore, various anellation reactions with 1,2-benzenediol and benzene-1,2-dithiol were performed leading to a series of novel O- and S-heterocyclic tetracenes owning very high photoluminescence quantum yields (Scheme 68).

Scheme 68: Anellation reactions of functionalized 2,3-dichloroquinoxalines.
5.2 Selective Metalation of 1,3-Dithiole-2-thiones: An Effective Preparation of New Symmetrically and Nonsymmetrically Tetraarylated Tetrathiafulvalenes

A novel synthesis was developed allowing for the preparation of tailor-made fully substituted TTF-derivatives via a selective functionalization of the DTT-precursor. DTT was magnesiated using TMPMgCl/LiCl leading to new mono- and difunctionalized DTT-derivatives under gentle reaction conditions (Scheme 69).

Conversion of the exocyclic sulfur into an oxygen atom by treatment with Hg(OAc)$_2$ furnished the corresponding 1,3-dithiole-2-ones in very good yields (Scheme 70).

Subsequent triethyl phosphite-mediated cross-coupling of the functionalized 1,3-dithiole-2-thione-derivatives with their oxygen analogs led to symmetrically and nonsymmetrically tetraarylated TTF-derivatives (Scheme 71).
B. RESULTS AND DISCUSSION

5.3 Selective Functionalization of Tetrathiafulvalene Using Mg- and Zn-TMP-Bases: Preparation of Mono-, Di-, Tri- and Tetrasubstituted Derivatives

An efficient fully functionalization of TTF was achieved using TMP-bases under smooth reaction conditions.

TTF was magnesiated with TMPMgCl\textsubscript{2}LiCl affording a range of new monosubstituted TTF-derivatives. The selective metalation of various monofunctionalized TTFs allowed for the preparation of symmetrically and nonsymmetrically disubstituted TTF-derivatives (Scheme 72).

The diester-TTF was subjected to further metalation using TMPZnCl\textsubscript{2}LiCl. Trapping of the zincated species with different electrophiles afforded trifunctionalized TTF-derivatives in 66-94% yield. Due to the gentle reaction conditions a wide range of sensitive functional groups was tolerated (Scheme 73).
B. RESULTS AND DISCUSSION

Symmetrically and nonsymmetrically tetrafunctionalized TTFs were prepared by zincation of the corresponding trisubstituted derivatives using TMPZnCl·LiCl, followed by the reaction with various electrophiles (Scheme 74).

This novel synthesis protocol allowed for fine-tuning of optical properties and energy levels and thus provides a strategy for realizing tailor-made molecular semiconductors.

5.4 Selective Functionalization of 1,4-Dithiin Using TMP-Bases: Access to New Heterocycles

A selective functionalization of 1,4-dithiin was performed with TMP-bases allowing the preparation of novel dithiin-fused heterocycles. A sequential bisfunctionalization of 1,4-dithiin was achieved with TMPMgCl·LiCl and TMPZnCl·LiCl leading to new mono- and difunctionalized dithiin-derivatives (Scheme 75).
B. RESULTS AND DISCUSSION

Various dithiin-fused quinolines were prepared by condensation of an aldehyde with a monosubstituted dithiin bearing an arylamine under microwave conditions (Scheme 76).

A range of iodinated disubstituted dithiin-derivatives was subjected to Sonogashira reactions leading to alkynylated dithiins. Subsequent iodine-mediated electrophilic cyclizations gave access to new heterocycles in good yields (Scheme 77).
B. RESULTS AND DISCUSSION

Furthermore, the condensation of the symmetrically substituted diketone with hydrazine monohydrate furnished a dithiin-fused pyridazine (Scheme 78).

The anellation of dichloropyrazines with dimercaptopryazine afforded new heteroacenes. Subsequent conversion of the silyl groups into halides furnished the corresponding halogenated dithiin-fused pyrazines (Scheme 79).
Scheme 79: Preparation of 1,4-dithiin-fused pyrazines followed by conversion of silyl groups into halides.
C. EXPERIMENTAL PART
1. General Information

If not otherwise stated, all reactions were carried out using standard Schlenk-techniques in flame dried glassware under argon. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use.

1.1 Solvents

Solvents were dried according to the following standard procedures via distillation over drying agents and stored under argon atmosphere.

CH$_2$Cl$_2$ was predried over CaCl$_2$ and distilled from CaH$_2$.

DMF was refluxed over CaH$_2$ (14 h) and distilled from CaH$_2$.

DMPU was predried over CaH$_2$ (4 h) and distilled.

Et$_2$O was predried over CaCl$_2$ and dried with the solvent purification system SPS-400-2 from Innovative Technologies Inc.

NEt$_3$ was dried over KOH and distilled.

NMP was refluxed over CaH$_2$ and distilled from CaH$_2$.

THF was continuously refluxed and freshly distilled from Na/benzophenone ketyl under nitrogen and stored over molecular sieve under argon atmosphere.

Solvents for column chromatography were distilled prior to use.

1.2 Reagents

Commercially available reagents were used without further purification unless otherwise stated. Liquid aldehydes, amines and acid chlorides were distilled prior to use. 2,3-dichloroquinoxaline was obtained from Sigma-Aldrich and was purified by column chromatography prior to use.

TMPH was distilled under argon prior to use.
**C. EXPERIMENTAL PART**

**CuCN·2LiCl** solution (1.0 M in THF) was prepared by drying CuCN (7.17 g, 80 mmol) and LiCl (6.77 g, 160 mmol) in a *Schlenk*-flask under high vacuum at 140 °C for 5 h. After cooling, dry THF (80 mL) was added and stirring was continued until all salts were dissolved (24 h).

**MgCl₂·LiCl** (0.5 M in THF) was prepared by placing LiCl (424 mg, 10 mmol) in a *Schlenk*-flask and heating at 400 °C (heatgun) for 15 min under high vacuum. Then, Mg turnings (243 mg, 10 mmol) were added, followed by dry THF (5 mL). Afterwards 1,2-dichloroethane (0.79 mL, 10 mmol) was added in one portion. The reaction was started by gentle warming of the reaction mixture. Once the reaction was started, the mixture was cooled by further addition of THF (15 mL) and stirred until all salts were dissolved.

**ZnCl₂** solution (1.0 M in THF) was prepared by drying ZnCl₂ (13.63 g, 100 mmol) in a *Schlenk*-flask under vacuum at 140 °C for 5 h. After cooling, dry THF (100 mL) was added and stirring was continued until all salts were dissolved (12 h).

**iPrMgCl·LiCl** solution was purchased from Rockwood Lithium GmbH.

**nBuLi** solution in hexane was purchased from Rockwood Lithium.

**TMPMgCl·LiCl** was prepared according to a literature procedure.⁹

**TMP₂Mg·2LiCl** was prepared according to a literature procedure.¹¹

**TMPLi** was prepared by the slow addition of *n*BuLi (4.26 mL, 2.35 M in hexane, 10 mmol) to a solution of TMPH (1.41 g, 1.70 mL, 10 mmol) in THF (10 mL) at -40 °C and stirring the reaction mixture for 30 min at -40 °C.

**TMPZnCl·LiCl** was prepared according to a literature procedure.¹²

**TMP₂Zn·2MgCl₂·2LiCl** was prepared according to a literature procedure.¹²

The content of organometallic reagent was determined by titration:

- **Organozinc** and **organomagnesium** reagents were titrated against I₂ in THF.

- **Organolithium** reagents were titrated with anhydrous 2-propanole using 1,10-phenanthroline as indicator in THF.

**TMPLi** was titrated using *N*-benzyl benzamide as titrating agent and indicator in THF.
C. EXPERIMENTAL PART

TMPMgCl, TMP₂Mg₂LiCl, TMPZnCl₂LiCl and TMP₂Zn₂MgCl₂2LiCl were titrated against benzoic acid using 4-(phenylazo)diphenylamine as indicator in THF.

1.3 Chromatography

Thin layer chromatography (TLC) was performed using aluminium plates coated with SiO₂ (Merck 60, F-254). The spots were visualized by UV-light or staining of the TLC plate with the solution below followed by heating if necessary:

- Iodine absorbed on silica gel.
- KMnO₄ (3.0 g), 5 drops of conc. H₂SO₄ in water (300 mL)

Flash column chromatography was performed using SiO₂ (0.040 – 0.063 mm, 230 – 400 mesh) from Merck.

1.4 Analytical Data

Gas chromatography was performed with machines of type Hewlett-Packard 6890 or 5890 series II, using a column of type HP 5 (Hewlett-Packard, 5% phenylmethylpolysiloxane; length: 15 m, diameter: 0.25 mm; film thickness: 0.25 μm). The detection was accomplished by using a flame ionization detector. The carrier gas was nitrogen. Undecane and heptadecane were used as internal standards.

NMR spectra were recorded on Varian Mercury 200, Bruker AXR 300, VXR 400 S and Bruker AMX 600 instruments. Chemical shifts are reported as δ-values in ppm relative to the solvent peak. For the characterization of the observed signal multiplicities the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sept (septet), m (multiplet), as well as br (broadened).

Infrared spectra (IR) were recorded from 4000-550 cm⁻¹ on a Perkin-Elmer Spectrum BX-59343 instrument. Samples were measured neat (ATR, Smiths Detection DuraSample IR II Diamond ATR). The absorption bands are reported in wavenumbers (cm⁻¹).

Mass spectroscopy: High resolution (HRMS) and low resolution (MS) spectra were recorded on a Finnigan MAT 95Q instrument. Electron impact ionization (EI) was conducted with an electron energy of 70 eV. For the coupled gas chromatography/mass spectrometry, a Hewlett-Packard HP6890/MSD 5973 GC/MS system was used.
Melting points (m.p.) were determined on a Büchi B-540 apparatus and are uncorrected.

UV-Vis spectra were recorded using a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere.

Photoluminescence spectra were recorded with a Horiba Jobin Yvon iHR320 spectrometer equipped with a photomultiplier tube and using a pulsed 365 nm LED (photon flux $4.9 \times 10^{17}$ s$^{-1}$ cm$^{-2}$) as excitation source. Photoluminescence quantum yields were measured in an argon atmosphere and were determined relative to rhodamine 6G. All solutions were diluted to an optical density of 0.050 at the respective excitation wavelength (350 nm for the quinoxaline dyes, 488 nm for rhodamine 6G) to ensure a spatially homogeneous excitation.

PLQY measurements were performed on a Photon Technology International QuantaMaster 40 spectrometerer at an incident photon flux of $1.6 \times 10^{12}$ s$^{-1}$ cm$^{-2}$.

Time-correlated single photon counting (TCSPC) measurements were performed using a PicoQuant FluoTime 300 spectrometer equipped with a 403 nm picosecond diode laser.
2. Functionalization of Quinoxalines Using TMP-Bases: Preparation of Tetracyclic Heterocycles with High Photoluminescence Quantum Yields

2.1 Typical Procedures

Typical Procedure 1 for the metalation of 2,3-dichloroquinoxaline (7) with TMPLi (1) (TP 1):

A dry and argon flushed Schlenk-flask was charged with a solution of 2,3-dichloroquinoxaline (7; 1.0 equiv) in dry THF (0.2 M). TMPLi (1; 1.2 equiv, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF using undecane as internal standard.

Typical Procedure 2 for the magnesiation of 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (9c) with TMPMgCl·LiCl (2) (TP 2):

A dry and argon flushed Schlenk-flask was charged with a solution of 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (9c; 1.0 equiv) in dry THF (0.25 M). TMPMgCl·LiCl (2; 1.3 equiv, 1.12 M in THF) was added dropwise at -70 °C and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with iodine in dry THF.

Typical Procedure 3 for the iodine/magnesium-exchange of 2,3-dichloro-5,8-diiodoquinoxaline (11b) with iPrMgCl·LiCl (TP 3):

A dry and argon flushed Schlenk-flask was charged with a solution of 2,3-dichloro-5,8-diiodoquinoxaline (11b; 1.0 equiv) in dry THF (0.5 M). iPrMgCl·LiCl (1.1 equiv, 1.23 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with sat. aq. NH₄Cl solution.

Typical Procedure 4 for the metalation of 2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (12c) with TMPLi (1) in the presence of ZnCl₂ (TP 4):

A dry and argon flushed Schlenk-flask was charged with a solution of 2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (12c; 1.0 equiv) in dry THF (0.25 M). ZnCl₂ solution (1.1 equiv,
1.0 M in THF) was added and the reaction mixture was cooled to -78 °C. TMPLi (1; 1.5 equiv, 0.63 M in THF) was added dropwise at this temperature and the resulting solution was stirred for 5 min. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF using undecane as internal standard.

**Typical Procedure 5 for the magnesiation of 2,3-dichloro-5-iodo-8-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (12d) with TMPMgCl·LiCl (2) (TP 5):**

A dry and argon flushed Schlenk-flask was charged with a solution of 2,3-dichloro-5-iodo-8-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (12d; 1.0 equiv) in dry THF (0.2 M). TMPMgCl·LiCl (2; 1.5 equiv, 1.12 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 1.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with iodine in dry THF.

**Typical Procedure 6 for anellation reactions (TP 6):**

A suspension of the corresponding 2,3-dichloroquinoxaline (1.0 equiv), K₂CO₃ (5.0 equiv) and 1,2-benzenediol, 4,5-dibromobenzene-1,2-diol or benzene-1,2-dithiol (1.3 equiv), respectively, in DMF (0.1 M) was stirred at 25 °C for the indicated time. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with sat. aq. NH₄Cl solution using undecane as internal standard.

### 2.2 Preparation of Monofunctionalized 2,3-Dichloroquinoxalines

**Synthesis of 5-bromo-2,3-dichloroquinoxaline (9a)**

![5-bromo-2,3-dichloroquinoxaline](image)

According to **TP 1**, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C at and the reaction mixture was stirred for 0.5 h. MgCl₂ solution (2.6 mL, 1.3 mmol, 0.5 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. 1,2-Dibromotetrachloroethane (423 mg, 1.3 mmol) was added and the resulting solution was stirred at -78 °C for 1 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column
C. EXPERIMENTAL PART

chromatography on silica gel (i-hexane/CH₂Cl₂, 5:1) yielding 9a as colorless solid (203 mg, 73%).

m.p.: 134.7 – 136.8 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.10 (d, J = 7.4 Hz, 1H), 8.04 – 7.90 (m, 1H), 7.73 – 7.57 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 146.5, 146.4, 141.3, 138.7, 134.7, 131.4, 127.9, 122.6.


MS (70 eV, EI) m/z (%) = 280 (42), 278 (100), 276 (59) [M⁺], 245 (11), 243 (46), 241 (33), 182 (18), 180 (19), 100 (14), 75 (14).

HRMS for C₈H₃BrCl₂N₂ (275.8857): found: 275.8858.

Synthesis of 2,3-dichloro-5-iodoquinoxaline (9b)

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. MgCl₂ solution (2.6 mL, 1.3 mmol, 0.5 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. Iodine (330 mg, 1.3 mmol) was added and the resulting solution was stirred at -78 °C for 1 h. The reaction mixture was quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 95:5) yielding 9b as yellow solid (208 mg, 64%).

m.p.: 129.8 – 131.7 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.36 (dd, J = 7.6, 1.2 Hz, 1H), 8.01 (dd, J = 8.5, 1.2 Hz, 1H) 7.64 – 7.41 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 146.5, 141.5 (2C), 141.0, 140.6, 132.1, 128.9, 99.6.
C. EXPERIMENTAL PART

$\text{IR (cm}^{-1})$: $\tilde{\nu} = 2948, 2896, 2847, 1586, 1289, 1265, 1200, 1166, 1121, 999, 977, 915, 894, 828, 807, 775, 692, 692, 654$.

$\text{MS (70 eV, EI) m/z (%)} = 326 (62), 325 (12), 324 (100) [M^+]$, 289 (12), 228 (18), 198 (13), 101 (25), 75 (21), 74 (11), 43 (17).

$\text{HRMS for C}_{8}\text{H}_{3}\text{Cl}_{2}\text{IN}_{2} (323.8718): found: 323.8713}$.

**Synthesis of 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (9c)**

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. MgCl$_2$ solution (2.6 mL, 1.3 mmol, 0.5 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared magnesium reagent was added to a precooled (-78 °C) solution of 4-methoxy-3,5-dimethylbenzenesulfinyl chloride (9a; 284 mg, 1.3 mmol) in dry THF (2 mL). The reaction was completed within 1 h at -78 °C and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (ihexane/EtOAc, 2:1) yielding 9c as colorless solid (229 mg, 60%).

**m.p.:** 169.9 – 175.0 °C (decomp.).

$^1\text{H-NMR (300 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 8.50$ (dd, $J = 7.2$, 1.4 Hz, 1H), 8.12 – 7.93 (m, 2H), 7.55 (s, 2H), 3.67 (s, 3H), 2.26 (s, 6H).

$^{13}\text{C-NMR (75 MHz, CDCl}_3\text{)} \delta/\text{ppm} = 159.5$, 146.4, 145.1, 143.7, 140.4, 138.7, 136.3, 132.2, 131.3, 130.0, 126.3, 126.2, 59.6, 16.2.

$\text{IR (cm}^{-1})$: $\tilde{\nu} = 2919, 1694, 1547, 1464, 1449, 1411, 1375, 1267, 1219, 1202, 1177, 1131, 1093, 1069, 1064, 1004, 902, 894, 875, 837, 824, 774, 763, 699, 669$. 

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C. EXPERIMENTAL PART

**MS** (70 eV, EI) m/z (%) = 382 (75), 380 (100) [M⁺], 334 (65), 332 (88), 319 (43), 317 (66), 183 (89), 167 (44), 151 (84).

**HRMS** for C₁₇H₁₄Cl₂N₂O₂S (380.0153): found: 380.0146.

**Synthesis of ethyl 2,3-dichloroquinoxaline-5-carboxylate (9d)**

According to **TP 1**, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. MgCl₂ solution (2.6 mL, 1.3 mmol, 0.5 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min, before ethyl cyanoformate (129 mg, 1.3 mmol) was added. The resulting solution was allowed to warm to 25 °C over 5 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 9:1) yielding 9d as colorless solid (168 mg, 62%).

**m.p.:** 163.3 – 165.8 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 8.27 – 8.05 (m, 2H), 7.91 – 7.76 (m, 1H), 4.52 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 165.4, 146.3, 146.1, 140.4, 138.1, 132.3, 131.6, 130.6, 130.3, 61.9, 14.3.


**MS** (70 eV, EI) m/z (%) = 270 (20) [M⁺], 229 (10), 228 (14), 227 (70), 226 (18), 225 (100), 200 (66), 199 (34), 198 (94), 197 (44), 162 (10), 101 (10), 43 (11).

**HRMS** for C₁₁H₈Cl₂N₂O₂ (269.9963): found: 269.9964.
C. EXPERIMENTAL PART

Synthesis of ethyl 2-((2,3-dichloroquinoxalin-5-yl)methyl)acrylate (9e)

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.3 mL, 1.3 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (0.1 mL, 0.1 mmol, 10 mol%, 1.0 M in THF) was added and the resulting solution was allowed to stir at -40 °C for 15 min, before ethyl 2-(bromomethyl)acrylate (38) (0.30 mL, 251 mg, 1.3 mmol) was added. The reaction mixture was allowed to warm to 25 °C over 12 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (n-hexane/CH₂Cl₂, 3:2) yielding 9e as colorless solid (212 mg, 68%).

m.p.: 43.9 – 47.5 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.96 – 7.85 (m, 1H), 7.77 – 7.62 (m, 2H), 6.30 (s, 1H), 5.60 (s, 1H), 4.30 – 4.09 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 166.7, 145.2, 144.3, 140.9, 139.4, 138.9, 137.8, 131.2, 131.0, 127.4, 126.6, 60.8, 32.5, 14.1.


MS (70 eV, El) m/z (%) = 317 (13), 310 (14) [M⁺], 306 (13), 305 (61), 283 (23), 281 (35), 265 (13), 240 (14), 239 (64), 238 (49), 237 (100), 236 (66), 201 (17), 140 (16).

HRMS for C₁₄H₁₂Cl₂N₂O₂ (310.0276): found: 310.0265.
Synthesis of 2,3-dichloro-5-(cyclohex-2-en-1-yl)quinoxaline (9f)

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.3 mL, 1.3 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (0.1 mL, 0.1 mmol, 10 mol%, 1.0 M in THF) was added and the resulting solution was allowed to stir at -40 °C for 15 min, before 3-bromocyclohexene (0.15 mL, 209 mg, 1.3 mmol) was added. The reaction mixture was allowed to warm to -30 °C over 1 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/EtOAc, 99:1) yielding 9f as colorless solid (170 mg, 61%).

m.p.: 100.7 – 102.7 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.95 – 7.81 (m, 1H), 7.81 – 7.61 (m, 2H), 6.12 – 5.95 (m, 1H), 5.80 – 5.64 (m, 1H), 4.73 – 4.54 (m, 1H), 2.29 – 2.06 (m, 3H), 1.94 – 1.32 (m, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 144.9, 144.1, 140.9, 138.9 (2C), 131.0, 129.6, 129.5, 129.2, 126.0, 35.0, 31.4, 25.1, 20.8.

IR (cm⁻¹): ν = 3022, 2932, 2905, 2868, 2829, 1948, 1649, 1599, 1567, 1538, 1469, 1458, 1440, 1430, 1379, 1294, 1268, 1176, 1153, 1137, 1126, 1079, 1069, 1033, 992, 954, 912, 892, 883, 875, 853, 822, 766, 725, 701, 683, 665, 647, 617, 603, 560, 571.

MS (70 eV, EI) m/z (%) = 280 (41), 278 (68) [M⁺], 251 (29), 249 (43), 245 (30), 243 (100), 239 (22), 237 (33), 225 (24), 223 (33), 67 (36).

HRMS for C₁₄H₁₂N₂Cl₂ (278.0378): found: 278.0382.
Synthesis of 5-allyl-2,3-dichloroquinoxaline (9g)

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.3 mL, 1.3 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (0.1 mL, 0.1 mmol, 10 mol%, 1.0 M in THF) was added and the resulting solution was allowed to stir at -40 °C for 15 min, before allyl bromide (157 mg, 1.3 mmol) was added. The reaction was completed within 12 h at 25 °C and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 99:1) yielding 9g as colorless solid (179 mg, 75%).

m.p.: 74.3 – 76.8 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.90 (dd, J = 8.3, 1.4 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.68 – 7.61 (m, 1H), 6.18 – 5.99 (m, 1H), 5.21 – 5.08 (m, 2H), 3.97 (d, J = 6.6 Hz, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 145.2, 144.3, 140.9, 139.2, 139.0, 136.2, 131.1, 130.6, 126.4, 116.8, 34.7.

IR (cm⁻¹): ν = 2950, 2897, 2847, 1748, 1640, 1599, 1567, 1469, 1425, 1313, 1269, 1238, 1180, 1162, 1062, 1041, 1003, 981, 963, 929, 867, 810, 768, 695, 660.

MS (70 eV, El) m/z (%) = 241 (8), 238 (45) [M⁺], 225 (65), 223 (100), 140 (15), 115 (13), 85 (9), 43 (10).

HRMS for C₁₁H₈Cl₂N₂ (238.0065): found: 238.0059.
Synthesis of (3-chlorophenyl)(2,3-dichloroquinoxalin-5-yl)methanone (9h)

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 1.90 mL, 1.2 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.3 mL, 1.3 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (1.3 mL, 1.3 mmol, 1.0 M in THF) was added and the resulting solution was allowed to stir at -40 °C for 15 min, before 3-chlorobenzoyl chloride (0.17 mL, 228 mg, 1.3 mmol) was added. The reaction mixture was allowed to warm to 25 °C over 12 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 92:8) yielding 9h as colorless solid (236 mg, 70%).

**m.p.:** 127.9 – 132.9 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 8.21 (dd, J = 7.7, 1.9 Hz, 1H), 7.98 – 7.83 (m, 2H), 7.78 (s, 1H), 7.68 – 7.51 (m, 2H), 7.39 (t, J = 7.9 Hz, 1H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 193.6, 146.5, 146.1, 140.2, 138.9, 138.2, 137.5, 134.9, 133.6, 130.6, 130.6, 130.4, 129.8, 129.8, 128.3.

**IR** (cm⁻¹): ν = 3069, 1916, 1720, 1674, 1589, 1567, 1463, 1454, 1426, 1376, 1334, 1308, 1265, 1203, 1171, 1133, 1077, 1061, 1044, 1002, 983, 978, 927, 905, 850, 828, 801, 775, 747, 736, 705, 672, 646, 607, 590, 569.

**MS** (70 eV, EI) m/z (%) = 338 (60), 336 (69) [M⁺], 310 (49), 309 (89), 307 (92), 227 (46), 225 (70), 139 (87), 111 (100), 75 (62).

**HRMS** for C₁₅H₁₂Cl₃N₂O (335.9624): found: 335.9613.
C. EXPERIMENTAL PART

Synthesis of ethyl 4-(2,3-dichloroquinoxalin-5-yl)benzoate (9i)

According to TP 1, 2,3-dichloroquinoxaline (7; 239 mg, 1.2 mmol) was dissolved in dry THF (6 mL). TMPLi (1; 2.29 mL, 1.4 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.6 mL, 1.6 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. Pd(PPh₃)₄ (69 mg, 0.06 mmol) and ethyl 4-iodobenzoate (276 mg, 1.0 mmol) were added and the resulting solution was allowed to stir at 50 °C for 12 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 95:5) yielding 9i as colorless solid (229 mg, 66%).

m.p.: 156.1 – 158.4 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.22 – 8.15 (m, 2H), 8.10 – 8.03 (m, 1H), 7.90 – 7.85 (m, 2H), 7.76 – 7.70 (m, 2H), 4.44 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 166.4, 145.6, 145.1, 141.5, 141.0, 139.2, 138.3, 131.6, 131.0, 130.5, 130.1, 129.4, 128.2, 61.1, 14.4.

IR (cm⁻¹): ν = 2983, 1702, 1608, 1595, 1566, 1538, 1470, 1450, 1404, 1363, 1312, 1269, 1182, 1157, 1182, 1157, 1128, 1104, 1026, 996, 863, 822, 768, 707, 699, 654.

MS (70 eV, EI) m/z (%) = 348 (51), 346 (78) [M⁺], 301 (100), 203 (65), 177 (51), 150 (22), 133 (29), 119 (28), 101 (20), 89 (58), 75 (65), 43 (40).

HRMS for C₁₇H₁₂Cl₂N₂O₂ (346.0276): found: 346.0270.
2.3 Preparation of Difunctionalized 2,3-Dichloroquinoxalines

Synthesis of 2,3-dichloro-6-iodo-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (10a)

According to TP 2, 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (9c; 381 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl-LiCl (3; 1.16 mL, 1.3 mmol, 1.12 M in THF) was added dropwise at -70 °C and the reaction mixture was stirred for 0.5 h. Iodine (355 mg, 1.4 mmol) was added and the resulting solution was stirred at -70 °C for 0.5 h. The reaction mixture was quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 4:1) yielding 10a as yellow solid (269 mg, 53%).

m.p.: 275.5 – 281.3 °C (decomp.).

$^1$H-NMR (400 MHz, CDCl$_3$) δ/ppm = 8.21 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 9.0$ Hz, 1H), 7.60 (s, 2H), 3.68 (s, 3H), 2.27 (s, 6H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) δ/ppm = 159.2, 146.6, 145.4, 143.2, 142.8, 141.1, 137.8, 137.2, 133.2, 131.9, 126.0, 125.7, 59.7, 16.2.

IR (cm$^{-1}$): $\tilde{\nu} = 2924, 1698, 1594, 1456, 1362, 1221, 1169, 1094, 1009, 966, 869, 812.$

HRMS (ESI) for C$_{17}$H$_{14}$Cl$_{3}$IN$_2$O$_2$S (506.9198): found: 506.9196 [M+H$^+$].
Synthesis of 6-bromo-2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)-quinoxaline (10b)

According to TP 2, 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (9c; 381 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl-LiCl (3; 1.16 mL, 1.3 mmol, 1.12 M in THF) was added dropwise at -70 °C and the reaction mixture was stirred for 0.5 h. 1,2-Dibromotetrachloroethane (456 mg, 1.4 mmol) was added and the resulting solution was stirred at -70 °C for 1 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 4:1) yielding 10b as yellow solid (381 mg, 83%).

m.p.: 270.9 – 275.9 °C (decomp.).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 7.99 – 7.94 (m, 1H), 7.94 – 7.89 (m, 1H), 7.59 (s, 2H), 3.72 (s, 3H), 2.30 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃) δ/ppm = 159.1, 146.5, 145.8, 140.3, 140.2, 138.5, 136.9, 136.6, 132.0, 131.9, 127.0, 125.5, 59.7, 16.2.

IR (cm⁻¹): ʋ = 2923, 1706, 1595, 1468, 1376, 1307, 1271, 1216, 1133, 1097, 1006, 967, 915, 819, 783, 735.

HRMS (ESI) for C₁₇H₁₄BrCl₂N₂O₂S (458.9336): found: 458.9337 [M+H⁺].
Synthesis of 2,3-dichloro-6-(cyclohex-2-en-1-yl)-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (10c)

According to TP 2, 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (9c; 381 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (3; 1.16 mL, 1.3 mmol, 1.12 M in THF) was added dropwise at -70 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.4 mL, 1.4 mmol, 1.0 M in THF) was added at -70 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (1.4 mL, 1.4 mmol, 1.0 M in THF) was added and the resulting solution was allowed to stir at -40 °C for 15 min, before 3-bromocyclohexene (0.16 mL, 225 mg, 1.4 mmol) was added. The reaction was completed within 1 h at -40 °C and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 9:1) yielding 10c as yellow solid (381 mg, 83%).

m.p.: 186.5 - 191.6 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 8.00 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.38 (s, 2H), 6.06 – 5.91 (m, 1H), 5.43 (d, J = 9.8 Hz, 1H), 5.08 – 4.89 (m, 1H), 3.69 (s, 3H), 2.53 – 1.55 (m, 12H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 158.9, 153.4, 145.8, 145.2, 139.6, 138.7, 138.3, 137.9, 133.5, 132.2, 131.3, 130.3, 128.8, 125.8, 60.0, 37.0, 33.2, 25.1, 22.1, 16.5.

IR (cm⁻¹): ν = 2930, 1693, 1595, 1475, 1378, 1273, 1219, 1178, 1131, 1095, 1006, 822, 720, 662.

HRMS (ESI) for C₂₃H₂₃Cl₅N₂O₂S (461.0857): found: 461.0857 [M+H⁺].
Synthesis of (3-chlorophenyl)(2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)-quinoxalin-6-yl)methanone (10d)

According to TP 2, 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (9c; 381 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (3; 1.16 mL, 1.3 mmol, 1.12 M in THF) was added dropwise at -70 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.4 mL, 1.4 mmol, 1.0 M in THF) was added at -70 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (1.4 mL, 1.4 mmol, 1.0 M in THF) was added and the resulting solution was allowed to stir at -40 °C for 15 min, before 3-chlorobenzoyl chloride (0.18 mL, 245 mg, 1.4 mmol) was added. The reaction mixture was allowed to warm up to 25 °C over 3 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 6:1) yielding 10d as yellow solid (465 mg, 89%).

m.p.: 189.5 – 192.8 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.14 (d, J = 8.6 Hz, 1H), 7.80 – 7.63 (m, 3H), 7.63 – 7.49 (m, 3H), 7.46 – 7.36 (m, 1H), 3.68 (s, 3H), 2.30 (s, 6H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 193.6, 159.7, 147.4, 146.0, 142.5, 140.5, 140.3, 139.0, 137.5, 136.5, 134.9, 133.2, 132.2, 130.5, 130.1, 129.9, 129.3, 127.4, 127.3, 59.6, 16.3.

IR (cm⁻¹): ν = 2945, 1678, 1572, 1532, 1472, 1412, 1375, 1327, 1274, 1256, 1232, 1219, 1185, 1147, 1129, 1095, 1060, 1011, 911, 896, 886, 879, 840, 795, 775, 752, 735, 720, 688, 673, 662.

MS (70 eV, EI) m/z (%) = 522 (15), 520 (36), 518 (33) [M⁺], 371 (26), 370 (13), 369 (64), 367 (64), 184 (14), 183 (100), 168 (11), 167 (14), 139 (14), 91 (13).

HRMS for C₂₆H₁₇Cl₃N₂O₃S (518.0025): found: 518.0023.
Synthesis of 2,3-dichloro-5,8-bis(trimethylsilyl)quinoxaline (11a)

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 3.80 mL, 2.4 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. Chlorotrimethylsilane (0.32 mL, 271 mg, 2.5 mmol) was added and the resulting solution was stirred at -78 °C for 1 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 11a as colorless oil (254 mg, 74%).

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.89 (s, 2H), 0.44 (s, 18H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 144.6, 143.0, 142.5, 136.6, 140.6, 125.9, 1245, 1221, 1163, 1082, 1027, 940, 917, 829, 759, 748, 692, 679.

IR (cm⁻¹): ν = 3040, 2953, 2898, 1928, 1694, 1551, 1522, 1450, 1428, 1406, 1369, 1309, 1276, 1259, 1245, 1221, 1163, 1082, 1027, 940, 917, 829, 759, 748, 692, 679.

MS (70 eV, El) m/z (%) = 342 (1) [M⁺], 331 (14), 330 (14), 329 (71), 328 (22), 327 (100).

HRMS for C₁₄H₂₀Cl₂N₂Si₂ (342.0542): found: 342.0538.

Synthesis of 2,3-dichloro-5,8-diiodoquinoxaline (11b)

ICl (0.15 mL, 487 mg, 3.0 mmol) was added dropwise to a solution of 2,3-dichloro-5,8-bis(trimethylsilyl)quinoxaline (11a; 343 mg, 1.0 mmol) in CH₂Cl₂ (2 mL) at 0 °C. The reaction mixture was stirred for 10 min and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 9:1) yielding 11b as yellow solid (450 mg, quantitative).
m.p.: 178.0 – 183.5 °C.

\(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 8.05\) (s, 2H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 147.7, 142.0, 140.9, 100.3\).

IR (cm\(^{-1}\)): \(\tilde{\nu} = 1658, 1569, 1519, 1435, 1354, 1262, 1169, 1091, 998, 823, 828, 661, 640, 607, 576, 563, 555\).

MS (70 eV, El) \(m/z\) (%) = 454 (10), 452 (62), 450 (100) [M\(^+\)], 325 (16), 323 (25), 198 (11), 196 (18), 100 (14), 74 (12).

HRMS for C\(_8\)H\(_2\)Cl\(_2\)I\(_2\)N\(_2\) (449.7684): found: 449.7678.

**Synthesis of 2,3-dichloro-5-iodo-8-(trimethylsilyl)quinoxaline (11c)**

ICI (0.05 mL, 162 mg, 1.0 mmol) was added dropwise to a solution of 2,3-dichloro-5,8-bis(trimethylsilyl)quinoxaline (11a; 343 mg, 1.0 mmol) CH\(_2\)Cl\(_2\) (2 mL) at 0 °C. The reaction mixture was stirred for 10 min and was then quenched with sat. aq. Na\(_2\)S\(_2\)O\(_3\) solution (5 mL), extracted with CH\(_2\)Cl\(_2\) (3 x 10 mL) and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (\(i\)hexane) yielding **11c** as yellowish solid (250 mg, 63%).

m.p.: 104.3 – 105.8 °C.

\(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 8.31\) (d, \(J = 7.4\) Hz, 1H), 7.60 (d, \(J = 7.4\) Hz, 1H), 0.43 (s, 9H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 145.8, 144.8, 144.5, 142.7, 141.0, 140.9, 138.0, 101.0, -0.6\).

IR (cm\(^{-1}\)): \(\tilde{\nu} = 2950, 2895, 1913, 1676, 1566, 1530, 1523, 1451, 1421, 1358, 1288, 1256, 1242, 1199, 1164, 1089, 1017, 918, 887, 833, 751, 702, 689, 670, 649, 627, 586, 555\).

MS (70 eV, El) \(m/z\) (%) = 396 (7) [M\(^+\)], 385 (12), 384 (10), 383 (67), 382 (16), 381 (100).

HRMS for C\(_{11}\)H\(_{11}\)Cl\(_2\)IN\(_2\)Si (395.9113): found: 395.9101.
C. EXPERIMENTAL PART

Synthesis of 1,1'-(2,3-dichloroquinoxaline-5,8-diyl)bis(dimethylsilanediyl))bis(octan-1-one) (11d)

According to TP 1, 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPLi (1; 3.80 mL, 2.4 mmol, 0.63 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. Chlorodimethyloctylsilane (0.32 mL, 271 mg, 2.5 mmol) was added and the resulting solution was stirred at -78 °C for 1 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 11d as colorless oil (254 mg, 74%).

¹H-NMR (300 MHz, CDCl₃) δ/ ppm = 7.87 (s, 2H), 1.41 – 1.14 (m, 24H), 1.02 – 0.82 (m, 10H), 0.40 (s, 12H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 145.0, 143.3, 142.4, 137.4, 77.9, 34.0, 32.3, 29.7, 24.4, 23.1, 16.3, 14.5, -1.8.

IR (cm⁻¹): ν = 3041, 2953, 2920, 2851, 1551, 1466, 1427, 1377, 1340, 1275, 1259, 1246, 1220, 1164, 1083, 1082, 1026, 916, 836, 818, 804, 769, 720, 705, 671.

MS (70 eV, EI) m/z (%) = 539 (1) [M⁺], 523 (5), 425 (100), 411 (3), 313 (16), 299 (4), 245 (6), 157(8), 133(11).

HRMS for C₂₉H₄₆Cl₂N₂Si₂ (538.7233): found: 538.7219.

Synthesis of 2,3-dichloro-5-iodo-8-(phenylthio)quinoxaline (12a)

According to TP 3, 2,3-dichloro-5,8-diiodoquinoxaline (11b; 451 mg, 1.0 mmol) was dissolved in dry THF (2 mL). iPrMgCl·LiCl (0.89 mL, 1.1 mmol, 1.23 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. S-Phenyl benzenethiosulfonate (300 mg,
C. EXPERIMENTAL PART

1.2 mmol) was added and the resulting solution was allowed to warm to 25 °C over 4 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 9:1) yielding 12a as yellow solid (219 mg, 51%).

**m.p.:** 142.6 – 146.5 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 8.04 (d, J = 8.2 Hz, 1H), 7.63 (dd, J = 6.3, 2.6 Hz, 2H), 7.55 – 7.33 (m, 3H), 6.76 (d, J = 8.1 Hz, 1H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 147.1, 145.4, 141.7, 141.0, 140.9, 137.3, 135.7, 130.1, 129.9, 129.8, 127.8, 93.8.

**IR** (cm⁻¹): ν = 1560, 1526, 1474, 1440, 1359, 1268, 1259, 1192, 1169, 1099, 1014, 1000, 915, 838, 826, 822, 747, 705, 688, 673.

**MS** (70 eV, El) m/z (%) = 434 (45), 432 (87) [M⁺], 127 (31), 69 (29), 57 (44), 55 (49), 44 (100) 43 (31), 43 (93), 41 (31).

**HRMS** for C₁₄H₇Cl₂IN₂S (431.8752): found: 431.8754.

**Synthesis of 5-bromo-2,3-dichloro-8-iodoquinoxaline (12b)**

According to TP 3, 2,3-dichloro-5,8-diiodoquinoxaline (11b; 451 mg, 1.0 mmol) was dissolved in dry THF (2 mL). iPrMgCl·LiCl (0.89 mL, 1.1 mmol, 1.23 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. 1,2-Dibromotetrachloroethane (391 mg, 1.2 mmol) was added and the resulting solution was allowed to warm to 25 °C over 2 h. The reaction mixture was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 95:5) yielding 12b as yellowish solid (305 mg, 76%).

**m.p.:** 172.4 – 175.9 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 8.21 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H).
C. EXPERIMENTAL PART

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 147.7, 147.6, 141.6, 141.3, 138.7, 135.3, 123.5, 98.8.

IR (cm$^{-1}$): $\tilde{\nu}$ = 1890, 1657, 1577, 1524, 1441, 1358, 1262, 1173, 1109, 1094, 1026, 1003, 931, 900, 889, 858, 828, 769, 666.

MS (70 eV, EI) $m$/z (%) = 406 (42), 404 (100), 402 (58) [M$^+$], 279 (10), 277 (20), 275 (13).

HRMS for C$_8$H$_2$BrCl$_2$IN$_2$ (401.7823): found: 401.7836.

Synthesis of 2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (12c)

According to TP 3, 2,3-dichloro-5,8-diiodoquinoxaline (11b; 451 mg, 1.0 mmol) was dissolved in dry THF (2 mL). $i$PrMgCl·LiCl (0.89 mL, 1.1 mmol, 1.23 M in THF) was added dropwise at $-78$ °C and the reaction mixture was stirred for 0.5 h. P-Toluenesulfonyl cyanide (218 mg, 1.2 mmol) was added and the resulting solution was allowed to warm to 25 °C over 3 h. The reaction mixture was quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 9:1) yielding 12c as yellow solid (227 mg, 65%).

m.p.: 179.8 – 181.9 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 8.47 (d, $J$ = 8.0 Hz, 1H), 7.86 (d, $J$ = 7.8 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 149.3, 148.9, 140.9, 139.5, 136.5, 114.7, 112.6, 107.1.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3063, 2923, 2231, 1912, 1716, 1556, 1542, 1520, 1457, 1428, 1414, 1368, 1271, 1223, 1169, 1107, 1048, 1007, 970, 895, 858, 842, 797, 702, 654.

MS (70 eV, EI) $m$/z (%) = 351 (60), 349 (100) [M$^+$], 314 (17), 224 (11), 222 (19), 126 (13), 100 (11), 75 (11).

HRMS for C$_9$H$_2$Cl$_2$IN$_2$ (348.8670): found: 348.8661.
Synthesis of 2,3-dichloro-5-iodo-8-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (12d)

According to TP 3, 2,3-dichloro-5,8-diiodoquinoxaline (11b; 451 mg, 1.0 mmol) was dissolved in dry THF (2 mL). iPrMgCl·LiCl (0.89 mL, 1.1 mmol, 1.23 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a precooled (-78 °C) solution of 4-methoxy-3,5-dimethylbenzenesulfinyl chloride (262 mg, 1.2 mmol) in dry THF (1 mL). The resulting solution was allowed to stir at -78 °C for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/EtOAc, 5:1) yielding 12d as yellow solid (309 mg, 61%).

**m.p.:** 234.1 – 238.1 °C.

**1H-NMR** (300 MHz, CDCl₃) δ/ppm = 8.55 (d, J = 7.7 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.52 (s, 2H), 3.67 (s, 3H), 2.26 (s, 6H).

**13C-NMR** (75 MHz, CDCl₃) δ/ppm = 159.6, 147.5, 146.3, 144.6, 141.4, 140.8, 138.3, 135.9, 132.3, 127.1, 126.2, 102.3, 59.6, 16.2.

**IR** (cm⁻¹): ν = 3047, 1739, 1571, 1524, 1471, 1434, 1366, 1270, 1261, 1217, 1173, 1096, 1084, 1056, 1009, 994, 907, 893, 869, 796, 764, 735, 700, 671.

**MS** (70 eV, El) m/z (%) = 506 (60) [M⁺], 460 (69), 458 (100), 443 (49), 183 (61), 167 (55), 151 (51).

**HRMS** for C₁₇H₁₃Cl₂IN₂O₂S (505.9119): found: 505.9116.
C. EXPERIMENTAL PART

Synthesis of 5,8-dibutyl-2,3-dichloroquinoxaline (13a)

ZnCl₂ solution (2.2 mL, 2.2 mmol, 1.0 M in THF) was added dropwise to nBuMgCl (1.42 mL, 2.2 mmol, 1.55 M in THF) at -20 °C and the reaction mixture was stirred for 20 min. This freshly prepared nBuZnCl solution was added dropwise to a solution of 2,3-dichloro-5,8-diiodoquinoxaline (11b; 451 mg, 1.0 mmol) and Pd(PPh₃)₄ (69 mg, 0.06 mmol) in THF (2 mL) at 25 °C. The resulting solution was allowed to stir at 50°C for 2 h and was then quenched with sat. aq. NaCl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 13a as colorless solid (190 mg, 61%).

m.p.: 59.8 – 63.7 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.53 (s, 2H), 3.22 – 3.06 (m, 4H), 1.79 – 1.62 (m, 4H), 1.50 – 1.32 (m, 4H), 0.96 (t, J = 7.3 Hz, 6H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 143.5, 139.8, 138.9, 130.1, 32.9, 30.3, 22.6, 14.0.

IR (cm⁻¹): ν = 2948, 2924, 2866, 2851, 1895, 1585, 1531, 1463, 1453, 1373, 1296, 1268, 1258, 1247, 1208, 1173, 1143, 1095, 1054, 930, 900, 840, 782, 771, 727, 714, 657.

MS (70 eV, EI) m/z (%): 310 (12) [M⁺], 283 (24), 281 (39), 270 (12), 268 (20), 267 (13), 255 (71), 254 (15), 253 (100), 241 (12), 239 (23), 237 (13), 228 (13), 227 (18), 226 (28), 225 (25), 213 (24), 211 (30), 43 (17), 41 (22).

HRMS for C₁₆H₂₀Cl₂N₂ (310.1004): found: 310.0996.
Synthesis of 2,3-dichloro-5,8-diphenylquinoxaline (13b)

A solution of diiodoquinoxaline 11b (448 mg, 1.0 mmol), phenylboronic acid (254 mg, 2.1 mmol), K$_2$CO$_3$ (420 mg, 3.0 mmol) and Pd(PPh$_3$)$_4$ (50 mg, 0.04 mmol) in degassed THF (10 mL) and H$_2$O (3 mL) was refluxed for 48 h. The reaction mixture was cooled 25 °C, sat. aq. NaCl (10 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (2 x 20 mL). The organic fractions were dried over anhydrous MgSO$_4$, and the solvents were removed in vacuo. Flash column chromatography on silica gel (i hexane/EtoAc) yielded 13b as colourless solid (144 mg, 44%).

**m.p.:** 149.2 – 150.6 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 7.93 (s, 2H), 7.75 – 7.69 (m, 4H), 7.59 – 7.45 (m, 6H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 144.6, 139.2, 138.8, 137.2, 131.3, 130.5, 128.2, 128.1.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3056, 1564, 1533, 1501, 1473, 1460, 1432, 1365, 1317, 1259, 1168, 1159, 1125, 1088, 1004, 996, 953, 853, 749, 692, 656.

MS (70 eV, EI) $m/z$ (%) = 354 (10), 352 (59), 351 (62), 350 (100) [M$^+$], 313 (10), 279 (13), 273 (31), 175 (11), 44 (10).

HRMS for C$_{20}$H$_{12}$Cl$_2$N$_2$ (350.0378): found: 350.0374.

Synthesis of 2,3-dichloro-5,8-bis(phenylethynyl)quinoxaline (13c)

A solution of diiodoquinoxaline 11b (1.35 g, 3.0 mmol), phenylacetylene (622 mg, 6.1 mmol), Pd(PPh$_3$)$_4$ (50 mg, 0.04 mmol) and Cul (50 mg, 0.26 mmol) in degassed NEt$_3$ (20 mL) and toluene (30 mL) was stirred at 25 °C for 12 h. The reaction mixture was quenched with sat. aq.
NH₄Cl (100 mL) and extracted with Et₂O (2 x 100 mL). The organic layer was dried over anhydrous MgSO₄, and after filtration, the solvents were removed in vacuo. Purification by crystallisation from a mixture of CH₂Cl₂ and Et₂O yielded 13c as pale yellow crystals (792 mg, 66%).

m.p.: 176.1 – 179.2 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.97 (s, 2H), 7.71 – 7.66 (m, 4H), 7.44 – 7.39 (m, 6H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 146.5, 140.9, 134.0, 132.0, 129.1, 128.4, 122.9, 122.7, 98.5, 85.3.

IR (cm⁻¹): ν = 3056, 2209, 1556, 1534, 1492, 1270, 1260, 1170, 1123, 1102, 1058, 999, 938, 915, 843, 720, 684.

MS (70 eV, El) m/z (%) = 402 (15), 400 (71), 398 (100) [M⁺], 363 (13), 328 (11), 299 (10), 199 (10), 150 (5), 43 (5).

HRMS for C₂₄H₁₂Cl₂N₂ (398.0378): found: 398.0367.

Synthesis of 2,3-dichloro-5,8-bis((trimethylsilyl)ethynyl)quinoxaline (13d)

A solution of diiodoquinoxaline 11b (4.0 g, 8.9 mmol), trimethylsilylacetylene (1.75 g, 17.8 mmol), Pd(PPh₃)₄ (70 mg, 0.06 mmol) and Cul (100 mg, 0.5 mmol) in degassed NEt₃ (20 mL) and benzene (40 mL) was stirred at 25 °C for 12 h. The reaction mixture was quenched with sat. aq. NH₄Cl (100 mL) and extracted with Et₂O (2 x 100 mL). The organic fraction was dried over anhydrous MgSO₄, and after filtration, the solvents were removed in vacuo. Purification by flash column chromatography on silica gel (ihexane/EtOAc 99:1) yielded 13d as pale solid (1.77 g, 80%).

m.p.: 156.4 – 159.7 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.86 (s, 2H), 0.34 (s, 18H).
C. EXPERIMENTAL PART

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 146.6, 140.8, 134.6, 122.9, 104.8, 99.8, -0.2.

IR (cm$^{-1}$): ν = 3075, 2953, 2918, 2850, 1591, 1477, 1467, 1455, 1410, 1371, 1314, 1279, 1242, 1238, 1209, 1172, 1099, 973, 869, 834, 808, 768, 719.

MS (70 eV, EI) m/z (%) = 392 (9), 390 (10) [M$^{+}$], 377 (17), 275 (26), 77 (100), 62 (12), 49 (11), 44 (14), 43 (76).

HRMS for C$_{18}$H$_{20}$Cl$_2$N$_2$Si$_2$ (390.0542); found: 390.0517.

2.4 Preparation of Trifunctionalized 2,3-Dichloroquinoxalines

**Synthesis of 6-bromo-2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (14a)**

According to TP 4, 2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (12c; 451 mg, 1.0 mmol) was dissolved in dry THF (4 mL). ZnCl$_2$ solution (1.1 mL, 1.1 mmol, 1.0 M in THF) was added and the reaction mixture was cooled to -78 °C, before TMPLi (1; 2.38 mL, 1.5 mmol, 0.63 M in THF) was added dropwise. The resulting solution was stirred at -78 °C for 5 min and then bromine (0.08 mL, 256 mg, 1.6 mmol) was added dropwise. The reaction was completed within 1 h at -78 °C and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 9:1) yielding 14a as yellow solid (292 mg, 68%).

m.p.: 208.2 – 211.8 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 8.64 (s, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 149.9, 148.8, 144.3, 140.1, 139.8, 130.8, 115.2, 113.7, 107.3.

IR (cm$^{-1}$): ν = 2923, 2229, 1724, 1550, 1529, 1422, 1365, 1274, 1265, 1237, 1206, 1196, 1143, 1060, 969, 926, 896, 881, 728, 692.

MS (70 eV, EI) m/z (%) = 431 (38), 430 (10), 429 (100), 427 (51) [M$^{+}$], 99 (10).
HRMS for C₉HBrCl₂N₃ (426.7776): found: 426.7772.

**Synthesis of 2,3-dichloro-8-iodo-6-(2-methylallyl)quinoxaline-5-carbonitrile (14b)**

According to TP 4, 2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (12c; 451 mg, 1.0 mmol) was dissolved in dry THF (4 mL). ZnCl₂ solution (1.1 mL, 1.1 mmol, 1.0 M in THF) was added and the reaction mixture was cooled to -78 °C, before TMPLi (1; 2.38 mL, 1.5 mmol, 0.63 M in THF) was added dropwise. The resulting solution was stirred at -78 °C for 5 min. CuCN·2LiCl solution (0.1 mL, 0.1 mmol, 10 mol%, 1.0 M in THF) was added and the reaction mixture was allowed to stir at -30 °C for 15 min, before 3-bromo-2-methylpropene (216 mg, 1.6 mmol) was added. The reaction was completed within 1 h at -30 °C and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH₂Cl₂, 2:1) yielding 14b as yellow solid (224 mg, 55%).

m.p.: 143.6 – 148.3 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.34 (s, 1H), 5.01 (s, 1H), 4.80 (s, 1H), 3.77 (s, 2H), 1.77 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 149.9, 149.0, 148.0, 142.6, 141.4, 139.7, 139.6, 115.0, 114.0, 112.2, 106.2, 42.8, 22.3.

IR (cm⁻¹): ν = 3079, 2970, 2936, 2358, 2233, 2153, 1806, 1647, 1575, 1537, 1441, 1431, 1376, 1293, 1271, 1206, 1172, 1149, 1073, 1027, 1005, 963, 919, 900, 893, 826, 797, 724, 699.

MS (70 eV, El) m/z (%) = 403 (13) [M⁺], 280 (14), 179 (11), 278 (73), 277 (18), 276 (100), 127 (24), 41 (26).

HRMS for C₁₃H₈Cl₂N₃ (402.9140): found: 402.9127.
Synthesis of 2,3-dichloro-6,8-diiodo-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)-quinoxaline (14c)

According to TP 5, 2,3-dichloro-5-iodo-8-((4-methoxy-3,5-dimethylphenyl)sulfinyl)-quinoxaline (12d; 507 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPMgCl·LiCl (2; 1.34 mL, 1.5 mmol, 1.12 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 1.5 h, before iodine (406 mg, 1.6 mmol) was added. The reaction was completed within 1 h at 0 °C and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 4:1) yielding 14c as yellow solid (456 mg, 72%).

m.p.: 200.0 – 203.7 °C.

¹H-NMR (400 MHz, benzene-d₆) δ/ppm = 8.39 (s, 1H), 7.88 (s, 2H), 3.21 (s, 3H), 2.13 (s, 6H).

¹³C-NMR (101 MHz, benzene-d₆) δ/ppm = 159.9, 151.9, 147.2, 145.9, 144.8, 141.9, 139.6, 137.4, 132.4, 126.7, 105.6, 99.8, 59.6, 16.6.

IR (cm⁻¹): ν = 3047, 2923, 2853, 1689, 1571, 1546, 1536, 1509, 1474, 1428, 1410, 1391, 1376, 1359, 1311, 1267, 1218, 1183, 1119, 1094, 1071, 1060, 913, 875, 734, 700, 667.

MS (70 eV, EI) m/z (%) = 632 (18) [M⁺], 598 (13), 566 (23), 254 (12), 183 (53), 151 (21), 141 (100), 127 (74), 97 (60), 43 (67), 41 (60).

Synthesis of 6-bromo-2,3-dichloro-8-iodo-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)-quinoxaline (14d)

According to TP 5, 2,3-dichloro-5-iodo-8-((4-methoxy-3,5-dimethylphenyl)sulfinyl)-quinoxaline (12d; 507 mg, 1.0 mmol) was dissolved in dry THF (5 mL). TMPMgCl-LiCl (2; 1.34 mL, 1.5 mmol, 1.12 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 1.5 h, before 1,2-dibromotetrachloroethane (521 mg, 1.6 mmol) was added. The reaction completed within 1 h at 0 °C and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 5:1) yielding 14d as yellow solid (428 mg, 73%).

m.p.: 113.8 – 116.0 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.56 (s, 1H), 7.56 (s, 2H), 3.71 (s, 3H), 2.30 (s, 6H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 159.2, 147.4, 146.8, 145.7, 140.8, 137.6, 136.8, 132.0, 126.9, 125.5, 104.8, 59.7, 16.3.

IR (cm⁻¹): ν = 2922, 1692, 1552, 1514, 1471, 1428, 1412, 1359, 1268, 1216, 1175, 1122, 1094, 1069, 1012, 874, 759, 723, 667.

MS (70 eV, EI) m/z (%) = 588 (22), 586 (44), 584 (25) [M⁺], 538 (42), 536 (23), 167 (32), 151 (100), 91 (27).

HRMS for C₁₇H₁₂BrCl₂N₂O₂S (583.8225): found: 583.8217.
2.5 Preparation of Tetracyclic Heterocycles

Synthesis of benzo[5,6][1,4]dioxino[2,3-b]quinoxaline (15a)

According to TP 6, a suspension of 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol), K₂CO₃ (691 mg, 5.0 mmol) and 1,2-benzenediol (143 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 22 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 1:1) yielding 15a as colorless solid (221 mg, 94%).

m.p.: 264.8 – 268.2 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.89 – 7.71 (m, 2H), 7.66 – 7.47 (m, 2H), 7.22 – 6.95 (m, 4H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 144.7, 140.4, 139.1, 128.9, 127.3, 125.2, 117.2.


MS (70 eV, El) m/z (%) = 237 (15), 236 (97) [M⁺], 118 (10), 92 (19), 69 (11), 64 (20), 44 (100), 43 (28).

HRMS for C₁₄H₈N₂O₂ (236.0586): found: 236.0590.
Synthesis of 7-((4-methoxy-3,5-dimethylphenyl)sulfinyl)benzo[5,6][1,4]dioxino[2,3-b]quinoxaline (15b)

According to TP 6, a suspension of 2,3-dichloro-5-((4-methoxy-3,5-dimethylphenyl)sulfinyl)-quinoxaline (9c; 381 mg, 1.0 mmol), K$_2$CO$_3$ (691 mg, 5.0 mmol) and 1,2-benzenediol (143 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 48 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (CH$_2$Cl$_2$/MeOH, 97:3) yielding 15b as colorless solid (326 mg, 78%).

m.p.: 234.0 – 236.0 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 8.26 (dd, $J = 7.3$, 1.3 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.52 (s, 2H), 7.21 – 7.03 (m, 4H), 3.66 (s, 3H), 2.26 (s, 6H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 159.3, 145.2, 144.4, 142.1, 140.1, 140.1, 139.4, 139.0, 135.2, 132.1, 129.3, 128.9, 126.1, 125.6, 125.5, 124.2, 117.2, 117.2, 59.6, 16.2.

IR (cm$^{-1}$): $\tilde{\nu} = 2935, 1614, 1521, 1498, 1457, 1433, 1363, 1352, 1338, 1295, 1271, 1232, 1217, 1164, 1153, 1141, 1105, 1094, 1062, 1046, 1007, 966, 942, 931, 917, 870, 856, 814, 805, 766, 756, 730, 720, 668.

MS (70 eV, EI) $m/z$ (%) = 419 (28), 418 (100) [M$^+$], 402 (39), 387 (33), 370 (43), 355 (54), 167 (27), 151 (65).

HRMS for C$_{23}$H$_{18}$N$_2$O$_4$S (418.0987): found: 418.0979.
Synthesis of 7,10-diiodobenzo[5,6][1,4]dioxino[2,3-b]quinoxaline (15c)

According to TP 6, a suspension of 2,3-dichloro-5,8-diiodoquinoxaline (11b; 453 mg, 1.0 mmol), K$_2$CO$_3$ (691 mg, 5.0 mmol) and 1,2-benzenediol (143 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 3:2) yielding 15c as colorless solid (344 mg, 70%).

m.p.: 299.4 – 301.4 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 7.84 (s, 2H), 7.23 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 146.3, 140.1, 139.8, 139.5, 125.7, 117.4, 98.9.

IR (cm$^{-1}$): $\tilde{\nu}$ = 1880, 1634, 1611, 1560, 1548, 1539, 1494, 1472, 1463, 1424, 1361, 1316, 1299, 1286, 1280, 1268, 1214, 1150, 1102, 1028, 954, 944, 871, 821, 818, 756, 720, 703.

MS (70 eV, El) m/z (%) = 489 (25), 488 (100) [M$^+$], 244 (13), 235 (11), 234 (78).

HRMS for C$_{14}$H$_6$I$_2$N$_2$O$_2$ (487.8519): found: 487.8510.

Synthesis of 7,10-diphenylbenzo[5,6][1,4]dioxino[2,3-b]quinoxaline (15d)

According to TP 6, a suspension of 2,3-dichloro-5,8-diphenylquinoxaline (6j; 351 mg, 1.0 mmol), K$_2$CO$_3$ (691 mg, 5.0 mmol) and 1,2-benzenediol (143 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by crystallisation from CH$_2$Cl$_2$ yielding 15d as colorless solid (241 mg, 62%).
C. EXPERIMENTAL PART

m.p.: > 300 °C.

$^1$H-NMR (400 MHz, 80 °C, DMSO-$d_6$) $\delta$/ppm = 7.72 (s, 2H), 7.68 – 7.64 (m, 4H), 7.54 – 7.49 (m, 4H), 7.47 – 7.41 (m, 2H), 7.21 – 7.17 (m, 2H), 7.15 – 7.10 (m, 2H).

$^{13}$C-NMR: The low solubility and rapid precipitation of this compound frustrated attempts at collecting a $^{13}$C spectrum.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3064, 1610, 1493, 1468, 1457, 1420, 1406, 1329, 1319, 1265, 1210, 1181, 1104, 1073, 1030, 961, 858, 846, 762, 758, 724, 699, 659.

MS (70 eV, EI) $m/z$ (%) = 389 (31), 388 (100) [M$^+$$]$], 387 (90), 330 (5), 311 (11), 194 (7), 165 (4).

HRMS for $C_{26}H_{16}N_2O_2$ (388.1212): found: 388.1208.

Synthesis of 7,10-bis(phenylethynyl)benzo[5,6][1,4]dioxino[2,3-b]quinoxaline (15e)

According to TP 6, a suspension of 2,3-dichloro-5,8-bis(phenylethynyl)quinoxaline (13b; 399 mg, 1.0 mmol), $K_2CO_3$ (691 mg, 5.0 mmol) and 1,2-benzenediol (143 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by crystallisation from CH$_2$Cl$_2$ yielding 15e as pale yellow solid (367 mg, 84%).

m.p.: 279.0 – 281.4 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 7.79 (s, 2H), 7.68 (d, $J$ = 7.4 Hz, 4H), 7.43 – 7.37 (m, 6H), 7.18 (dd, $J$ = 5.9, 3.6 Hz, 2H), 7.11 (dd, $J$ = 5.9, 3.6 Hz, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 145.3, 140.4, 139.6, 132.3, 131.9, 128.7, 128.3, 125.4, 123.0, 121.9, 117.3, 97.1, 85.9.
C. EXPERIMENTAL PART

IR (cm\(^{-1}\)): \(\nu = 2897, 1495, 1441, 1423, 1341, 1315, 1271, 1217, 1164, 1108, 1068, 1026, 931, 915, 899, 889, 852, 844, 768, 758, 750, 684, 667\).

MS (70 eV, EI) \(m/z (\%) = 437 (35), 436 (100) [M^+]\), 327 (7), 218 (13), 189 (5), 43 (3).

HRMS for C\(_{30}\)H\(_{16}\)N\(_2\)O\(_2\) (436.1212): found: 436.1211.

Synthesis of 2,3-dibromobenzo[5,6][1,4]dioxino[2,3-b]quinoxaline (15f)

According to TP 6, a suspension of 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol), K\(_2\)CO\(_3\) (691 mg, 5.0 mmol) and 4,5-dibromobenzene-1,2-diol (348 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 \(^\circ\)C for 39 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH\(_2\)Cl\(_2\), 1:1) yielding 15f as colorless solid (318 mg, 81%).

\(m.p.: 274.5 - 276.2 \, ^{\circ}C\).

\(^1\)H-NMR (600 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 7.84 \, (\text{dd}, J = 6.2, 3.4 \, \text{Hz}, 2\, \text{H}), 7.64 \, (\text{dd}, J = 6.3, 3.3 \, \text{Hz}, 2\, \text{H}), 7.40 \, (s, 2\, \text{H})\).

\(^{13}\)C-NMR (151 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 143.5, 140.0, 139.1, 129.5, 127.5, 121.6, 119.8\).

IR (cm\(^{-1}\)): \(\nu = 3063, 1594, 1531, 1475, 1460, 1426, 1379, 1369, 1341, 1332, 1283, 1251, 1221, 1185, 1170, 1139, 1117, 1098, 1015, 981, 957, 950, 934, 890, 880, 869, 791, 772, 763, 682\).

MS (70 eV, EI) \(m/z (\%) = 396 (49), 395 (16), 394 (100), 392 (49) [M^+]\), 316 (19), 314 (21), 143 (10), 141 (10).

Synthesis of 2,3-dibromo-7,10-dibutylbenzo[5,6][1,4]dioxino[2,3-b]quinoxaline (15g)

According to **TP 6**, a suspension of 5,8-dibutyl-2,3-dichloroquinoxaline (13a; 311 mg, 1.0 mmol), K₂CO₃ (691 mg, 5.0 mmol) and 4,5-dibromobenzene-1,2-diol (348 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 6:1) yielding **15g** as colorless solid (264 mg, 52%).

**m.p.**: 195.3 – 198.4 °C.

**¹H-NMR** (600 MHz, CDCl₃) δ/ppm = 7.38 (d, J = 9.3 Hz, 4H), 3.05 (t, J = 7.8 Hz, 4H), 1.69 (quin, J = 7.6 Hz, 4H), 1.42 (q, J = 7.5 Hz, 4H), 0.96 (t, J = 7.3 Hz, 6H).

**¹³C-NMR** (151 MHz, CDCl₃) δ/ppm = 142.0, 140.3, 138.1, 138.0, 128.6, 121.5, 119.4, 32.8, 30.5, 22.6, 14.1.

**IR** (cm⁻¹): ν = 2954, 2923, 2851, 1597, 1477, 1460, 1415, 1324, 1280, 1223, 1192, 1178, 1095, 964, 918, 904, 874, 864, 844, 837, 812, 767, 747, 726, 676.

**MS** (70 eV, El) m/z (%): 506 (37), 504 (21) [M⁺], 479 (28), 477 (56), 475 (34), 464 (46), 451 (45), 449 (100), 447 (56), 435 (30), 421 (49), 407 (45), 41 (20).

**HRMS** for C₂₂H₂₂Br₂N₂O₂ (504.0048): found: 504.0039.

Synthesis of 1,1’-((2,3-dibromobenzo[5,6][1,4]dioxino[2,3-b]quinoxaline-7,10-diyl)bis(dimethylsilanediyl))bis(octan-1-one) (15h)

According to **TP 6**, a suspension of 1,1’-((2,3-dichloroquinoxaline-5,8-diyl)bis(dimethylsilanediyl))bis(octan-1-one) (11d; 568 mg, 1.0 mmol), K₂CO₃ (691 mg, 5.0 mmol) and 4,5-
dibromobenzene-1,2-diol (348 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/CH₂Cl₂, 6:1) yielding 15h as colorless oil (557 mg, 73%).

**1H-NMR** (300 MHz, CDCl₃) δ/ppm = 7.71 (s, 2H), 7.43 (s, 2H), 1.36 – 1.19 (m, 24H), 0.98 – 0.90 (m, 4H), 0.87 (t, 7.0 Hz, 6H), 0.40 (s, 12H).

**13C-NMR** (75 MHz, CDCl₃) δ/ppm = 143.5, 141.8, 140.9, 140.7, 135.4, 121.8, 119.3, 33.8, 32.2, 29.5, 29.5, 24.2, 22.9, 16.1, 14.3, -1.9.

**IR** (cm⁻¹): ν = 3074, 2953, 2918, 2850, 1591, 1477, 1455, 1464, 1415, 1370, 1314, 1278, 1268, 1237, 1226, 1209, 1172, 1099, 973, 915, 869, 834, 808, 768, 719.

**MS** (70 eV, EI) m/z (%) = 732 (1) [M⁺], 623 (55), 621 (100), 619 (46), 541 (15), 253 (14), 113 (4), 55 (7), 44 (14), 43 (28).

**HRMS** for C₃₄H₅₀Br₂N₂O₂Si₂ (732.1778): found: 732.1766.

**Synthesis of benzo[5,6][1,4]dithiino[2,3-b]quinoxaline (15i)**

According to TP 6, a suspension of 2,3-dichloroquinoxaline (7; 199 mg, 1.0 mmol), K₂CO₃ (691 mg, 5.0 mmol) and benzene-1,2-dithiol (185 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 22 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/CH₂Cl₂, 3:2) yielding 15i as yellow solid (144 mg, 54%).

**m.p.:** 165.8 – 170.2 °C.

**1H-NMR** (300 MHz, CDCl₃) δ/ppm = 8.04 – 7.83 (m, 2H), 7.78 – 7.59 (m, 2H), 7.58 – 7.41 (m, 2H), 7.36 – 7.17 (m, 2H).

**13C-NMR** (75 MHz, CDCl₃) δ/ppm = 152.3 (2C), 140.7 (2C), 131.5 (2C), 130.1 (2C), 128.8 (2C), 128.3 (4C).
C. EXPERIMENTAL PART

**IR (cm⁻¹):** ν = 2923, 2852, 1739, 1563, 1475, 1466, 1453, 1419, 1334, 1257, 1182, 1132, 1112, 1049, 1010, 935, 859, 787, 758, 736, 708, 660.

**MS (70 eV, El) m/z (%) = 268 (20) [M⁺], 69 (14), 57 (14), 55 (12), 44 (100), 43 (21), 41 (12).**

**HRMS** for C₁₄H₉N₂S₂ (268.0129): found: 268.0129.

**Synthesis of 10-iodobenzo[5,6][1,4]dithiino[2,3-b]quinoxaline-7-carbonitrile (15j)**

According to TP 6, a suspension of 2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (12c; 350 mg, 1.0 mmol), K₂CO₃ (691 mg, 5.0 mmol) and benzene-1,2-dithiol (185 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 1:1) yielding 15j as orange solid (340 mg, 81%).

**m.p.:** 273.8 – 280.2 °C.

**¹H-NMR (600 MHz, CDCl₃) δ/ppm = 8.29 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.37 – 7.31 (m, 2H).**

**¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 156.8, 156.3, 140.8, 140.1, 139.4, 135.2, 130.0, 128.8, 128.8, 128.7, 128.7, 115.4, 112.4, 108.0.**

**IR (cm⁻¹):** ν = 3050, 2226, 1908, 1567, 1545, 1505, 1453, 1423, 1354, 1259, 1173, 1110, 1063, 973, 889, 837, 798, 740, 711, 701, 658.

**MS (70 eV, El) m/z (%) = 421 (11), 420 (19), 419 (100) [M⁺], 292 (31).**

**HRMS** for C₁₅H₁₆N₃S₂ (418.9048): found: 418.9043.
Synthesis of 7,10-diiodobenzo[5,6][1,4]dithiino[2,3-b]quinoxaline (15k)

According to \textbf{TP 6}, a suspension of 2,3-dichloro-5,8-diiodoquinoxaline (11b; 451 mg, 1.0 mmol), K$_2$CO$_3$ (691 mg, 5.0 mmol) and benzene-1,2-dithiol (185 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated \textit{in vacuo}. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 5:1) yielding 15k as yellow solid (453 mg, 87%).

\textbf{m.p.:} 248.6 – 253.0 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 7.94 (s, 2H), 7.47 (dd, $J = 5.8, 3.3$ Hz, 2H), 7.32 (dd, $J = 5.8, 3.3$ Hz, 2H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 155.1, 141.0, 140.8, 130.7, 128.7, 128.6, 101.5.

\textbf{IR (cm$^{-1}$):} $\tilde{v} =$ 2923, 1873, 1706, 1645, 1566, 1501, 1453, 1422, 1413, 1346, 1273, 1266, 1258, 1252, 1171, 1121, 1114, 1085, 1051, 1018, 948, 898, 875, 823, 765, 758, 708, 700, 659.

\textbf{MS (70 eV, El) $m/z$ (%) =} 522 (11), 521 (18), 520 (100) [M$^+$], 488 (11), 450 (12), 393 (16), 266 (41), 234 (12), 140 (25), 108 (11).

\textbf{HRMS} for C$_{14}$H$_6$I$_2$N$_2$S$_2$ (519.8062): found: 519.8061.

Synthesis of 7,10-diphenylenbenzo[5,6][1,4]dithiino[2,3-b]quinoxaline (15l)

According to \textbf{TP 6}, a suspension of 2,3-dichloro-5,8-diphenylquinoxaline (13b; 351 mg, 1.0 mmol), K$_2$CO$_3$ (691 mg, 5.0 mmol) and benzene-1,2-dithiol (185 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the
solvents were evaporated in vacuo. The crude product was purified by crystallisation from CH$_2$Cl$_2$ yielding 15m as yellow solid (286 mg, 68%).

**m.p.:** 219.4 – 222.5 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.80 (s, 2H), 7.77 – 7.69 (m, 4H), 7.60 – 7.38 (m, 8H), 7.31 – 7.23 (m, 2H).

$^{13}$C-NMR: The low solubility and rapid precipitation of this compound frustrated attempts at collecting a $^{13}$C spectrum.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3049, 3032, 2920, 1725, 1598, 1575, 1563, 1511, 1499, 1454, 1424, 1273, 1253, 1246, 1167, 1128, 1118, 1084, 1072, 1049, 1011, 956, 899, 839, 836, 759, 755, 686

**MS** (70 eV, El) m/z (%): 423 (13), 422 (43), 421 (86), 420 (100) [M$^+$], 419 (62), 388 (16), 387 (41), 386 (19), 343 (15), 279 (7), 193 (13), 71 (21).

**HRMS** for C$_{26}$H$_{16}$N$_2$S$_2$ (420.0755): found: 420.0751.

**Synthesis of 7,10-bis(phenylethynyl)benzo[5,6][1,4]dithino[2,3-b]quinoxaline (15m)**

According to TP 6, a suspension of 2,3-dichloro-5,8-bis(phenylethynyl)quinoxaline (13c; 399 mg, 1.0 mmol), K$_2$CO$_3$ (691 mg, 5.0 mmol) and benzene-1,2-dithiol (185 mg, 1.3 mmol) in DMF (10 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by crystallisation from CH$_2$Cl$_2$ yielding 15m as yellow solid (431 mg, 92%).

**m.p.:** 207.0 – 210.3 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.86 (s, 2H), 7.73 – 7.68 (m, 4H), 7.48 (dd, $J = 5.6$, 3.3 Hz, 2H), 7.45 – 7.38 (m, 6H), 7.30 (dd, $J = 5.6$, 3.3 Hz, 2H).
C. EXPERIMENTAL PART

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 153.6, 140.9, 133.1, 132.0, 131.3, 128.8, 128.7, 128.4, 128.4, 122.9, 122.8, 97.8, 85.9.

IR (cm$^{-1}$): $\tilde{\nu} = 3054, 2919, 2215, 1595, 1566, 1554, 1511, 1489, 1463, 1453, 1439, 1423, 1360, 1331, 1253, 1166, 1118, 1071, 1024, 936, 915, 844, 757, 751, 745, 687.$

MS (70 eV, EI) $m/z$ (%) = 469 (36), 468 (100) [M$^+$], 467 (18), 436 (4), 234 (10), 43 (13).

HRMS for C$_{30}$H$_{16}$N$_2$S$_2$ (468.0755): found: 468.0753.
3. Selective Metalation of 1,3-Dithiole-2-tiones: An Effective Preparation of New Symmetrically and Nonsymmetrically Tetraarylated Tetrathiafulvalenes

3.1 Typical Procedures

Typical Procedure 1 for the magnesiation of DTT (16) with TMPMgCl·LiCl (2) (TP 1):

A dry and argon flushed Schlenk-flask was charged with a solution of DTT (16; 1.0 equiv) in dry THF (0.5 M). TMPMgCl·LiCl (2; 1.1 equiv, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF using undecane as internal standard.

Typical Procedure 2 for the magnesiation of 4-functionalized DTT-derivatives with TMPMgCl·LiCl (2) (TP 2):

A dry and argon flushed Schlenk-flask was charged with a solution the corresponding 4-functionalized DTT-derivative (1.0 equiv) in dry THF (0.10 - 0.50 M). TMPMgCl·LiCl (2; 1.1 equiv, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with iodine in dry THF.

Typical Procedure 3 for the preparation of 1,3-dithiol-2-one-derivatives (TP 3):

According to the literature,20b the corresponding DTT-derivative (1.0 equiv) was dissolved in CHCl₃ (0.05 M) and conc. AcOH (0.16 M). Hg(OAc)₂ (3.0 equiv) was added portion wise at 25 °C and the reaction mixture was stirred at this temperature for the indicated time. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq. NH₄Cl solution.

Typical Procedure 4 for the preparation of TTF-derivatives (TP 4):

According to the literature,20b the corresponding thiketone (1.0 equiv) was dissolved in freshly distilled P(OEt)₃ (0.1 M). The corresponding ketone (1.2 equiv) was added at 25 °C and the reaction mixture was stirred at 110 °C for the indicated time. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq. NH₄Cl solution.
3.2 Preparation of Starting Material

Synthesis of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (24)

According to the literature, dimethyl acetylenedicarboxylate (23; 21.3 g, 18.4 mL, 150 mmol) was added to a solution of ethylene trithiocarbonate (22; 20.4 g, 150 mmol) in toluene (150 mL) at 25 °C. The reaction mixture was refluxed for 48 h and was then allowed to cool to 25 °C. After removing the solvent *in vacuo*, the crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 7:1) yielding 24 as yellow solid (34.2 g, 91%).

\[ ^1H-NMR \, (200\, MHz, \, CDCl_3) \delta/\text{ppm} = 3.91 (s, 6H). \]

Synthesis of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylic acid (25)

According to the literature, concentrated hydrochloric acid (45 mL) and water (60 mL) were added to a solution of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (24; 9.76 g, 39 mmol) in conc. acetic acid (20 mL) at 25 °C. The reaction mixture was refluxed for 2 h and was then allowed to cool to 25 °C. After the addition of water (200 mL), the aqueous layer was extracted with EtOAc (4 x 100 mL). The combined organic layers were dried over anhydrous MgSO₄ and after filtration, the solvents were evaporated *in vacuo*. The crude product 25 was obtained as orange solid (8.58 g, 99%) and was used without further purification.

Synthesis of 1,3-dithiole-2-thione (16; DTT)

According to the literature, a solution of 2-thioxo-1,3-dithiole-4,5-dicarboxylic acid (25; 8.45 g, 38.0 mmol) in pyridine (55 mL) was refluxed for 3 h and was then allowed to cool to 25 °C. After removing the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 2:1) yielding 16 as yellow solid (4.44 g, 87%).

\[ ^1H-NMR \, (300\, MHz, \, CDCl_3) \delta/\text{ppm} = 7.11 (s, 2H). \]
3.3 Preparation of Monofunctionalized DTT-Derivatives

Synthesis of 4-iodo-1,3-dithiole-2-thione (18a)

According to TP 1, DTT (16; 1.07 g, 8.0 mmol) was dissolved in dry THF (16 mL). TMPMgCl-LiCl (2; 7.93 mL, 8.8 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of iodine (2.44 g, 9.6 mmol) in dry THF (20 mL) at -78 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. Na₂S₂O₃ solution (50 mL), extracted with Et₂O (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/Et₂O, 95:5) yielding 18a as brownish solid (1.65 g, 79%).

m.p.: 105.7 – 108.8 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 7.21 (s, 1H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 215.1, 133.8, 69.9.

IR (cm⁻¹): ν = 3066, 2922, 2852, 2358, 2064, 1746, 1519, 1485, 1463, 1378, 1184, 1045, 1015, 919, 885, 758, 645, 566, 555.

MS (70 eV, El) m/z (%): 260 (62) [M⁺], 184 (13), 135 (11), 133 (100), 127 (22), 89 (26), 88 (11), 76 (45).

HRMS for C₃H₇S₃ (259.8285): found: 259.8275.
C. EXPERIMENTAL PART

Synthesis of 4-bromo-1,3-dithiole-2-thione (18b)

According to TP 1, DTT (16; 67.1 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPMgCl·LiCl (2; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of 1,2-dibromotetrachloroethane (195 mg, 0.6 mmol) in dry THF (1 mL) at -78 °C. The reaction mixture was allowed to warm up to 25 °C within 12 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/Et₂O, 95:5) yielding 18b as yellow solid (90 mg, 84%).

m.p.: 61.8 – 63.5 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.01 (s, 1H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 211.8, 127.4, 106.2.

IR (cm⁻¹): ν = 3071, 1503, 1182, 1047, 1012, 904, 881, 806, 765, 650.

MS (70 eV, El) m/z (%) = 214 (66), 212 (63) [M⁺], 57 (86), 57 (100), 55 (58), 45 (50).

HRMS for C₃HBrS₃ (211.8424): found: 211.8429.

Synthesis of 4-(methylthio)-1,3-dithiole-2-thione (18c)

According to TP 1, DTT (16; 1.07 g, 8.0 mmol) was dissolved in dry THF (16 mL). TMPMgCl·LiCl (2; 7.93 mL, 8.8 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of S-methyl methanethiosulfonate (1.21 g, 0.99 mL, 9.6 mmol) in dry THF (16 mL) at -78 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with Et₂O (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product
was purified by flash column chromatography on silica gel (hexane/Et₂O, 95:5) yielding 18c as brownish solid (1.08 g, 75%).

m.p.: 73.3 – 75.1 °C.

^1^H-NMR (300 MHz, CDCl₃) δ/ppm = 6.91 (s, 1H), 2.51 (s, 3H).

^13^C-NMR (75 MHz, CDCl₃) δ/ppm = 213.5, 138.5, 127.2, 19.8.

IR (cm⁻¹): ν = 3058, 2976, 2909, 1772, 1483, 1469, 1416, 1310, 1191, 1056, 1044, 1028, 985, 964, 938, 906, 889, 816, 737, 713, 660.

MS (70 eV, EI) m/z (%) = 182 (13), 180 (100) [M⁺], 104 (27), 103 (44), 89 (42), 76 (23), 57 (10), 45 (26).

HRMS for C₄H₄S₄ (179.9196): found: 179.9193.

Synthesis of (3-chlorophenyl)(2-thioxo-1,3-dithiol-4-yl)methanone (18d)

According to TP 1, DTT (16; 67.1 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPMgCl·LiCl (2; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir at -40 °C for 15 min, before 3-chlorobenzoyl chloride (105 mg, 0.08 mL, 0.6 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/Et₂O, 9:1) yielding 18d as brown oil (84 mg, 62%).

^1^H-NMR (300 MHz, CDCl₃) δ/ppm = 7.80 – 7.72 (m, 2H), 7.71 – 7.59 (m, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.11 (s, 1H).

^13^C-NMR (75 MHz, CDCl₃) δ/ppm = 210.6, 182.5, 145.3, 139.6, 137.2, 135.3, 133.4, 130.3, 128.8, 126.9.
C. EXPERIMENTAL PART


MS (70 eV, EI) m/z (%) = 274 (26), 272 (58) [M⁺], 196 (21), 141 (30), 139 (100), 111 (53), 75.

HRMS for C₁₀H₅OClS₃ (271.9191): found: 271.9190.

Synthesis of ethyl 2-((2-thioxo-1,3-dithiol-4-yl)methyl)acrylate (18e)

According to TP 1, DTT (16; 134 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir at -40 °C for 15 min, before ethyl 2-(bromomethyl)acrylate⁵⁸ (214 mg, 0.17 mL, 1.2 mmol) was added. The reaction mixture was stirred at -40 °C for 4 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH₂Cl₂, 1:1) yielding 18e as yellow oil (124 mg, 50%).

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 6.76 (s, 1H), 6.36 (s, 1H), 5.75 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.60 (s, 2H), 1.32 (t, J = 7.2 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 213.5, 165.6, 144.2, 136.5, 128.1, 124.3, 61.4, 33.5, 14.1.

IR (cm⁻¹): v = 3404, 3092, 3046, 2978, 2929, 2358, 2114, 1915, 1706, 1630, 1548, 1463, 1443, 1423, 1405, 1367, 1329, 1297, 1278, 1249, 1184, 1138, 1101, 1051, 1022, 953, 931, 877, 858, 814, 773, 720, 661.

MS (70 eV, EI) m/z (%) = 246 (100) [M⁺], 172 (23), 170 (23), 142 (41), 141 (40), 127 (19), 97 (15, 97 (76), 85 (22), 85 (12), 83 (17), 71 (31), 71 (14), 70 (13), 69 (24), 57 (50), 56 (14), 55 (31), 53 (19), 45 (15), 45 (37), 44 (33), 43 (33), 43 (15), 40 (28).

HRMS for C₉H₁₀O₂S₃ (245.9843): found: 245.9844.
**Synthesis of ethyl 4-(2-thioxo-1,3-dithiol-4-yl)benzoate (18f)**

According to TP 1, DTT (16; 134 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl$_2$ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of ethyl 4-iodobenzoate (221 mg, 0.13 mL, 0.8 mmol) and Pd(PPh$_3$)$_4$ (116 mg, 0.10 mmol) in dry NMP (1 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 1 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH$_2$Cl$_2$, 1:1) yielding 18f as yellow solid (191 mg, 84%).

**m.p.:** 135.9 – 138.0 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 8.10 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 8.3$ Hz, 2H), 7.28 – 7.22 (m, 1H), 4.41 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 211.6, 165.5, 144.8, 134.8, 131.3, 130.6, 126.3, 123.7, 61.4, 14.3.

**IR (cm$^{-1}$):** ν = 3058, 3037, 3007, 2982, 2928, 2362, 2340, 1919, 1709, 1602, 1570, 1528, 1454, 1407, 1366, 1316, 1299, 1272, 1233, 1216, 1182, 1172, 1103, 1062, 1053, 1025, 1016, 935, 890, 867, 846, 833, 790, 780, 754, 702, 688, 652, 627.

**MS (70 eV, El) m/z (%) = 283 (13), 282 (100) [M$^+$], 237 (10), 178 (18), 161 (56), 89 (20).**

**HRMS for C$_{12}$H$_{10}$O$_2$S$_3$ (281.9843):** found: 281.9836.
C. EXPERIMENTAL PART

Synthesis of 4-(2-thioxo-1,3-dithiol-4-yl)benzonitrile (18g)

According to TP 1, DTT (16; 1.34 g, 10.0 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (2; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodobenzonitrile (1.83 g, 8.0 mmol) and Pd(PPh₃)₄ (1.15 g, 1.0 mmol) in dry NMP (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 18 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 1:2) yielding 18g as yellow solid (1.77 g, 94%).

m.p.: 195.8 – 198.8 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.74 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.28 (s, 1H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 210.9, 143.4, 134.9, 133.2, 127.0, 124.8, 117.9, 113.2.

IR (cm⁻¹): ν = 3037, 3008, 2360, 2228, 1897, 1604, 1568, 1530, 1495, 1434, 1412, 1323, 1288, 1219, 1190, 1128, 1063, 1020, 948, 933, 896, 835, 818, 783, 764, 713, 691, 674, 637, 584, 556.

MS (70 eV, El) m/z (%) = 237 (16), 236 (18) [M+H⁺], 160 (12), 159 (100), 146 (11), 115 (12), 76 (22).

HRMS for C₁₀H₆NS₃ (235.9662): found: 235.9644.
Synthesis of 4-(4-chlorophenyl)-1,3-dithiole-2-thione (18h)

According to **TP 1**, DTT (16; 269 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl-LiCl (2; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-chloro-4-iodobenzene (382 mg, 1.6 mmol) and Pd(PPh₃)₄ (231 mg, 0.2 mmol) in dry NMP (2 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 3 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (iHexane/CH₂Cl₂, 2:1) yielding 18h as yellow solid (263 mg, 67%).

**m.p.**: 91.4 – 97.9 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 7.46 – 7.30 (m, 4H), 7.11 (s, 1H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 211.7, 144.7, 135.7, 129.6, 129.5, 127.7, 122.3.

**IR** (cm⁻¹): ν = 3052, 3022, 2998, 2429, 2358, 1885, 1766, 1633, 1593, 1570, 1531, 1486, 1402, 1308, 1271, 1220, 1186, 1118, 1098, 1079, 1069, 1034, 1011, 953, 930, 889, 837, 818, 761, 754, 722, 698, 661, 625.

**MS** (70 eV, El) m/z (%) = 245 (49), 245 (14), 244 (100) [M⁺], 170 (40), 155 (13), 136 (16), 89 (31), 75 (10).

**HRMS** for C₉H₅ClS₃ (243.9242): found: 243.9239.

**Synthesis of 4-(4-(trifluoromethyl)phenyl)-1,3-dithiole-2-thione (18i)**

According to **TP 1**, DTT (16; 269 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl-LiCl (2; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -78 °C and the
reaction mixture was stirred for 0.5 h. ZnCl₂ solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-4-(trifluoromethyl)benzene (435 mg, 1.6 mmol) and Pd(PPh₃)₄ (231 mg, 0.2 mmol) in dry NMP (2 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 14 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 2:1) yielding 18i as yellow solid (287 mg, 66%).

**m.p.:** 121.5 – 123.0 °C.

**¹H-NMR** (400 MHz, CDCl₃) δ/ppm = 7.71 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.24 (s, 1H).

**¹³C-NMR** (101 MHz, CDCl₃) δ/ppm = 211.4, 144.1, 134.2, 131.5 (q, J = 32.8 Hz), 126.8, 126.4 (q, J = 3.9 Hz), 123.9, 123.6 (q, J = 272.4 Hz).

**IR** (cm⁻¹): ν = 3041, 3015, 2929, 2360, 2331, 2094, 1914, 1785, 1760, 1667, 1613, 1578, 1537, 1408, 1321, 1238, 1217, 1171, 1124, 1112, 1070, 1053, 1031, 1014, 965, 952, 935, 890, 885, 832, 783, 770, 692, 650, 628, 594.

**MS** (70 eV, EI) m/z (%) = 280 (10), 279 (13), 278 (100) [M⁺], 152 (15).

**HRMS** for C₁₀H₅F₃S₃ (277.9505): found: 277.9497.

**Synthesis of 4-(p-tolyl)-1,3-dithiole-2-thione (18j)**

According to **TP 1**, DTT (16: 269 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl∙LiCl (2; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodotoluene (349 mg, 1.6 mmol) and Pd(PPh₃)₄ (231 mg, 0.2 mmol) in dry NMP (2 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 3 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo.
C. EXPERIMENTAL PART

vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 2:1) yielding 18j as yellow solid (284 mg, 79%).

m.p.: 91.4 – 97.9 °C.

\(^1\)H-NMR (300 MHz, CDCl₃) δ/ppm = 7.36 – 7.28 (m, 2H), 7.28 – 7.19 (m, 2H), 7.06 (s, 1H), 2.40 (s, 3H).

\(^13\)C-NMR (75 MHz, CDCl₃) δ/ppm = 212.4, 146.5, 140.0, 128.3, 126.3, 121.0, 21.3.

IR (cm⁻¹): \(\tilde{\nu} = 3043, 3020, 2953, 2853, 2087, 1888, 1607, 1574, 1536, 1500, 1408, 1374, 1315, 1222, 1209, 1198, 1124, 1060, 1033, 960, 929, 889, 839, 816, 809, 784, 762, 752, 698, 673, 635, 610, 581, 564.

MS (70 eV, EI) m/z (%) = 225 (14), 224 (100) [M⁺], 178 (10), 149 (17), 148 (51), 147 (37), 115 (11), 91 (13), 69 (12), 43 (10).

HRMS for C₁₀H₈S₃ (223.9788): found: 223.9766.

Synthesis of 4-(4-nitrophenyl)-1,3-dithiole-2-thione (18k)

\[
\text{O}_2\text{N} \quad \text{S} \quad \text{S} \quad \text{S}
\]

According to TP 1, DTT (16; 1.34 g, 10.0 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (2; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-4-nitrobenzene (1.99 g, 8.0 mmol) and Pd(PPh₃)₄ (1.15 g, 1.0 mmol) in dry NMP (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 14 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 1:1) yielding 18k as brownish solid (1.57 g, 77%).

m.p.: 209.0 – 210.6 °C.

\(^1\)H-NMR (600 MHz, CDCl₃) δ/ppm = 8.32 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.33 (s, 1H).
C. EXPERIMENTAL PART

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 210.7, 148.0, 142.9, 136.6, 127.2, 125.4, 124.8.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3118, 3079, 3062, 3034, 2955, 2923, 2854, 2446, 2357, 2118, 1915, 1809, 1634, 1593, 1529, 1520, 1503, 1480, 1467, 1432, 1406, 1379, 1366, 1340, 1320, 1238, 1226, 1211, 1187, 1159, 1108, 1080, 1062, 1027, 998, 952, 935, 888, 846, 829, 800, 792, 782, 742, 714, 707, 700, 688, 658, 638, 622.

MS (70 eV, EI) m/z (%) = 257 (15), 256 (13), 255 (100) [M$^+$], 149 (24), 133 (19), 121 (12), 89 (53), 63 (15).

HRMS for C$_9$H$_5$O$_2$NS$_3$ (254.9482): found: 254.9479.

Synthesis of 4-(4-methoxyphenyl)-1,3-dithiole-2-thione (18I)

According to TP 1, DTT (16; 1.34 g, 10.0 mmol) was dissolved in dry THF (20 mL). TMPMgCl$\cdot$LiCl (2; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl$_2$ solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodoanisole (1.87 g, 8.0 mmol) and Pd(PPh$_3$)$_4$ (1.15 g, 1.0 mmol) in dry NMP (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 14 h and was then quenched with sat. aq. NH$_4$Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH$_2$Cl$_2$, 2:1) yielding 18I as yellow solid (1.34 g, 70%).

m.p.: 104.2 – 106.9 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 7.35 (d, $J$ = 8.7 Hz, 2H), 7.00 – 6.90 (m, 3H), 3.85 (s, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 212.3, 160.7, 146.2, 127.9, 123.7, 120.0, 114.7, 55.4.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3026, 3000, 2956, 2924, 2853, 2834, 2552, 2437, 2361, 2339, 2086, 2043, 1887, 1784, 1626, 1602, 1576, 1534, 1498, 1455, 1439, 1418, 1364, 1316, 1294, 1260, 1214, 1180, 1126, 1114, 1077, 1051, 1026, 956, 935, 912, 896, 838, 826, 809, 787, 770, 710, 670, 629, 574.
C. EXPERIMENTAL PART

**MS** (70 eV, El) $m/z$ (%) = 242 (13), 241 (12), 240 (100) [M$^+$], 164 (40), 149 (70), 121 (18).

**HRMS** for C$_{10}$H$_8$OS$_3$ (239.9737): found: 239.9724.

**Synthesis of 4-(3-nitrophenyl)-1,3-dithiole-2-thione (18m)**

![Image of the compound](image)

According to TP 1, DTT (16; 134 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPClLiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl$_2$ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-3-nitrobenzene (199 mg, 0.8 mmol) and Pd(PPh$_3$)$_4$ (116 mg, 0.10 mmol) in dry NMP (1 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 3 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH$_2$Cl$_2$, 3:2) yielding 18m as yellow solid (122 mg, 60%).

m.p.: 183.4 – 186.3 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 8.35 – 8.30 (m, 1H), 8.28 (d, $J$ = 8.2 Hz, 1H), 7.73 (d, $J$ = 8.0 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.30 (s, 1H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 210.8, 148.8, 142.7, 132.5, 132.1, 130.6, 124.5, 124.1, 121.2.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3082, 3051, 3028, 2847, 2360, 2335, 2087, 1982, 1925, 1815, 1747, 1757, 1539, 1515, 1470, 1369, 1346, 1312, 1288, 1201, 1098, 1081, 934, 908, 880, 870, 829, 814, 785, 735, 719, 680, 656, 621, 571.

**MS** (70 eV, El) $m/z$ (%) = 257 (11), 255 (100) [M$^+$], 225 (19), 166 (11), 149 (12), 89 (31), 76 (12), 43 (23).

**HRMS** for C$_9$H$_5$O$_2$NS$_3$ (254.9482): found: 254.9472.
Synthesis of 4-(3-methoxyphenyl)-1,3-dithiole-2-thione (18n)

According to TP 1, DTT (16; 134 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 3-iodoanisole (187 mg, 0.8 mmol) and Pd(PPh₃)₄ (116 mg, 0.10 mmol) in dry NMP (1 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 18 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/CH₂Cl₂, 3:1) yielding 18n as yellow solid (181 mg, 94%).

m.p.: 94.3 – 97.8 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ ppm = 7.34 (t, J = 7.9 Hz, 1H), 7.14 – 7.07 (m, 1H), 7.04 – 6.89 (m, 3H), 3.85 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ ppm = 212.1, 160.1, 146.0, 132.1, 130.4, 122.1, 118.9, 115.0, 112.3, 55.4.

IR (cm⁻¹): ν = 3067, 3039, 2991, 2959, 2928, 2828, 2360, 2331, 2088, 1937, 1732, 1600, 1575, 1531, 1489, 1462, 1450, 1423, 1326, 1290, 1272, 1261, 1223, 1199, 1165, 1092, 1054, 1034, 960, 888, 853, 788, 774, 757, 686, 677, 622, 610, 563.

MS (70 eV, El) m/z (%) = 242 (14), 241 (14), 240 (100) [M⁺], 164 (52), 135 (10), 134 (16), 121 (21), 77 (11).

HRMS for C₁₀H₈OS₃ (239.9737): found: 239.9735.
3.4 Preparation of Difunctionalized DTT-Derivatives

Synthesis of 4,5-dibromo-1,3-dithiole-2-thione (19a)

According to TP 2, 4-bromo-1,3-dithiole-2-thione (18b; 1.66 g, 7.80 mmol) was dissolved in dry THF (31 mL). TMPMgCl·LiCl (2; 7.73 mL, 8.58 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of 1,2-dibromotetrachloroethane (3.04 g, 9.36 mmol) in dry THF (15 mL) at -78 °C. The reaction mixture was allowed to warm up to 25 °C within 12 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with Et₂O (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane) yielding 19a as yellow solid (2.07 g, 91%).

m.p.: 96.3 – 97.7 °C.

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 208.7, 107.2.

IR (cm⁻¹): ν = 2952, 2921, 2852, 2102, 1928, 1501, 1463, 1455, 1377, 1137, 1077, 978, 876, 867, 825, 746, 730.

MS (70 eV, El) m/z (%) = 294 (63), 292 (100), 290 (45) [M⁺], 218 (19), 216 (46), 214 (19), 213 (28), 211 (22), 169 (11), 167 (10), 137 (58), 135 (58), 125 (29), 123 (26), 88 (26), 82 (17), 80 (18), 79 (11), 76 (22), 60 (11), 57 (12), 56 (13), 44 (20), 44 (15), 43 (12).

HRMS for C₃Br₂S₃ (289.7529): found: 289.7518.

Synthesis of 4-bromo-5-iodo-1,3-dithiole-2-thione (19b)

According to TP 2, 4-bromo-1,3-dithiole-2-thione (18b; 107 mg, 0.50 mmol) was dissolved in dry THF (1 mL). TMPMgCl·LiCl (2; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of iodine (152 mg, 0.60 mmol) in dry THF (1 mL) at -78 °C.
The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 19b as yellow solid (186 mg, 70%).

**m.p.:** 126.0 – 129.5 °C.

**$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 213.1, 112.8, 76.1.

**IR (cm$^{-1}$):** $\tilde{\nu}$ = 2920, 2359, 2238, 2089, 1504, 1483, 1456, 1071, 1047, 1018, 969, 956, 898, 878, 842, 742, 714.

**MS (70 eV, EI) $m/z$ (%) = 342 (12), 340 (100), 338 (90) [M$^+$], 264 (16), 262 (15), 213 (58).

**HRMS** for C$_3$BrI$_3$S$_3$ (337.7390): found: 337.7383.

**Synthesis of 4-bromo-5-(tert-butyldimethylsilyl)-1,3-dithiole-2-thione (19c)**

According to TP 2, 4-bromo-1,3-dithiole-2-thione (18b; 1.06 g, 5.0 mmol) was dissolved in dry THF (10 mL). TMPMgCl-LiCl (2; 4.95 mL, 5.50 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of tert-butyldimethylsilyl trifluoromethanesulfonate (1.59 g, 6.0 mmol) in dry THF (10 mL) at -78 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. NH$_4$Cl solution (50 mL), extracted with Et$_2$O (3 x 100 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 19c as yellow solid (1.55 g, 94%).

**m.p.:** 50.1 – 51.1 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$/ppm = 1.01 (s, 9H), 0.41 (s, 6H).

**$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$/ppm = 215.4, 143.7, 110.6, 26.6, 18.5, -4.1.
C. EXPERIMENTAL PART

IR (cm⁻¹): ʋ = 2955, 2944, 2924, 2893, 2879, 2853, 2706, 2126, 1658, 1481, 1467, 1460, 1440, 1407, 1391, 1362, 1258, 1248, 1182, 1074, 1031, 1005, 955, 904, 886, 835, 818, 804, 774, 752, 720, 690, 674, 612, 604, 572.

MS (70 eV, EI) m/z (%) = 328 (86), 326 (74) [M⁺], 272 (100), 270 (91), 195 (55), 193 (53), 149 (45), 115 (45), 73 (46), 71 (64), 57 (58).

HRMS for C₉H₁₅BrS₃Si (325.9289): found: 325.9272.

Synthesis of 4,5-bis(methylthio)-1,3-dithiole-2-thione (19d)

According to TP 2, 4-(methylthio)-1,3-dithiole-2-thione (18c; 1.04 g, 5.8 mmol) was dissolved in dry THF (23 mL). TMPMgCl∙LiCl (2; 5.75 mL, 6.39 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of S-methyl methanethiosulfonate (879 mg, 0.72 mL, 6.98 mmol) in dry THF (14 mL) at -78 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with Et₂O (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/Et₂O, 95:5) yielding 19d as green-brownish solid (1.13 g, 86%).

m.p.: 87.5 – 95.6 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 2.50 (s, 6H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 210.8, 135.9, 19.2.


MS (70 eV, EI) m/z (%) = 228 (29), 226 (100) [M⁺], 207 (20), 150 (28), 135 (51), 103 (33), 91 (55), 88 (52), 76 (43), 73 (16), 61 (19), 48 (15), 47 (17), 45 (35), 44 (10), 43 (26).

HRMS for C₅H₆S₅ (225.9073): found: 225.9049.
Synthesis of 4-iodo-5-(4-methoxyphenyl)-1,3-dithiole-2-thione (19e)

According to TP 2, 4-(4-methoxyphenyl)-1,3-dithiole-2-thione (18l; 240 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of iodine (305 mg, 1.2 mmol) in dry THF (1 mL) at -78 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH$_2$Cl$_2$, 2:1) yielding 19e as yellow solid (353 mg, 96%).

m.p.: 168.8 – 173.8 °C (decomp.).

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.42 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 3.87 (s, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 214.6, 160.9, 146.4, 130.5, 123.5, 114.4, 68.5, 55.4.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3004, 2963, 2922, 2853, 2835, 1888, 1644, 1605, 1570, 1531, 1491, 1459, 1451, 1438, 1301, 1255, 1174, 1114, 1058, 1050, 1028, 955, 902, 856, 829, 812, 792, 742, 635, 610, 570.

MS (70 eV, El) m/z (%) = 368 (8), 367 (8), 366 (53) [M$^+$], 164 (11), 163 (100), 119 (9), 94 (9), 93 (8), 76 (5).

HRMS for C$_{10}$H$_7$OIS$_3$ (365.8704): found: 365.8702.
Synthesis of 4,4’-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzonitrile (19f)

According to TP 2, 4-(2-thioxo-1,3-dithiol-4-yl)benzonitrile (18g; 1.18 g, 5.0 mmol) was dissolved in dry THF (50 mL). TMPMgCl-LiCl (2; 4.95 mL, 5.5 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (6.0 mL, 6.0 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodobenzonitrile (916 mg, 4.0 mmol) and Pd(PPh₃)₄ (578 mg, 0.5 mmol) in dry NMP (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 1:2) yielding 19f as yellow solid (1.12 g, 83%).

m.p.: 184.3 – 189.2 °C (decomp.).

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.63 (d, J = 8.3 Hz, 4H), 7.31 (d, J = 8.3 Hz, 4H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 208.3, 138.5, 134.1, 133.0, 129.8, 117.5, 113.7.

IR (cm⁻¹): ν = 3052, 2923, 2853, 2360, 2226, 1916, 1791, 1602, 1573, 1490, 1471, 1434, 1405, 1311, 1266, 1174, 1118, 1108, 1095, 1052, 1037, 1024, 968, 952, 908, 880, 846, 838, 810, 751, 740, 712, 690, 654, 610, 592, 584.

MS (70 eV, El) m/z (%) = 351 (19), 338 (14), 337 (18), 336 (79) [M⁺], 324 (12), 320 (100), 266 (20), 246 (26).

HRMS for C₁₇H₈N₂S₃ (335.9850): found: 335.9845.
Synthesis of 4,5-bis(4-chlorophenyl)-1,3-dithiole-2-thione (19g)

According to TP 2, 4-(4-chlorophenyl)-1,3-dithiole-2-thione (18h; 1.50 g, 6.13 mmol) was dissolved in dry THF (60 mL). TMPMgCl-LiCl (2; 6.07 mL, 6.74 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (7.36 mL, 7.36 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-chloro-4-iodobenzene (1.17 g, 4.90 mmol) and Pd(PPh₃)₄ (708 mg, 0.6 mmol) in dry NMP (30 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 3:1) yielding 19g as yellow solid (1.62 g, 93%).

m.p.: 154.9 – 158.0 °C.

¹H-NMR (400 MHz, CDCl₃) δ/δppm = 7.34 – 7.27 (m, 4H), 7.18 – 7.11 (m, 4H).

¹³C-NMR (101 MHz, CDCl₃) δ/δppm = 209.7, 138.3, 135.7, 130.4, 129.4, 128.5.

IR (cm⁻¹): ν = 3051, 2922, 2854, 2120, 1900, 1588, 1548, 1488, 1479, 1434, 1398, 1265, 1180, 1121, 1106, 1090, 1066, 1052, 1014, 992, 955, 943, 902, 875, 834, 826, 817, 798, 742, 712, 689, 638.

MS (70 eV, EI) m/z (%): 358 (18), 357 (13), 356 (61), 355 (20), 354 (79) [M⁺], 281 (10), 278 (100), 246 (21), 208 (29), 201 (12), 199 (37), 176 (17), 163 (12), 155 (12), 139 (13).

HRMS for C₁₅H₈Cl₂S₃ (353.9165): found: 353.9161.
C. EXPERIMENTAL PART

Synthesis of 4,5-bis(4-(trifluoromethyl)phenyl)-1,3-dithiole-2-thione (19h)

According to TP 2, 4-(4-(trifluoromethyl)phenyl)-1,3-dithiole-2-thione (18i; 1.39 g, 4.99 mmol) was dissolved in dry THF (40 mL). TMPMgCl-LiCl (2; 4.95 mL, 5.49 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (5.98 mL, 5.98 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-4-(trifluoromethyl)benzene (1.09 g, 3.99 mmol) and Pd(PPh₃)₄ (576 mg, 0.5 mmol) in dry NMP (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 14 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 3:1) yielding 19h as yellow solid (1.50 g, 89%).

m.p.: 162.0 – 166.0 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 7.60 (d, J = 8.2 Hz, 4H), 7.34 (d, J = 8.0 Hz, 4H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 209.2, 138.6, 133.4, 131.6 (q, J = 33.1 Hz), 129.6, 126.3 (q, J = 3.9 Hz), 123.5 (q, J = 272.8 Hz).

¹⁹F-NMR (376 MHz, CDCl₃) δ/ppm = -63.0.


MS (70 eV, El) m/z (%) = 424 (16), 423 (22), 422 (100) [M⁺], 345 (16), 345 (100), 313 (13), 233 (35), 189 (13), 76 (16).

HRMS for C₁₇H₈F₆S₃ (421.9692): found: 421.9687.
C. EXPERIMENTAL PART

Synthesis of 4,5-di-p-tolyl-1,3-dithiole-2-thione (19i)

![Structural formula](image)

According to TP 2, 4-(p-tolyl)-1,3-dithiole-2-thione (18j; 1.09 g, 4.88 mmol) was dissolved in dry THF (40 mL). TMPMgCl-LiCl (2; 4.84 mL, 5.37 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (5.86 mL, 5.86 mmol, 1.0 M in THF) was added at -78 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodotoluene (851 mg, 3.90 mmol) and Pd(PPh₃)₄ (564 mg, 0.49 mmol) in dry NMP (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 2:1) yielding 19i as yellow solid (1.09 g, 89%).

**m.p.:** 155.3 – 157.8 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 7.10 (s, 8H), 2.34 (s, 6H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 211.0, 139.4, 139.1, 129.6, 129.0, 127.5, 21.3.

**IR** (cm⁻¹): ν = 3023, 2916, 2849, 2364, 2087, 1906, 1803, 1605, 1568, 1555, 1510, 1496, 1443, 1409, 1379, 1318, 1212, 1193, 1186, 1116, 1108, 1064, 1047, 1024, 964, 942, 904, 880, 834, 818, 799, 760, 714, 648, 638, 610.

**MS** (70 eV, El) m/z (%) = 316 (15), 315 (20), 314 (99) [M⁺], 239 (18), 238 (100), 237 (18), 221 (10), 179 (15), 178 (14).

**HRMS** for C₁₇H₁₄S₃ (314.0258): found: 314.0254.
3.5 Preparation of Functionalized 1,3-Dithiol-2-one-Derivatives

**Synthesis of 4-bromo-1,3-dithiol-2-one (20a)**

According to TP 3, Hg(OAc)$_2$ (1.91 g, 6.0 mmol) was added portion wise to a solution of 4-bromo-1,3-dithiole-2-thione (18b; 426 mg, 2.0 mmol) in CHCl$_3$ (40 mL) and conc. AcOH (12.5 mL) at 25 °C. The reaction mixture was stirred at this temperature for 1.5 h and the precipitate was then filtered through celite. The resulting solution was washed with sat. aq. Na$_2$CO$_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/Et$_2$O, 95:5) yielding 20a as colorless solid (337 mg, 86%).

**m.p.:** 60.0 – 64.9 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 6.83 (s, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 191.4, 117.0, 99.5.

**IR (cm$^{-1}$):** $\tilde{\nu}$ = 3234, 3074, 3018, 2954, 2928, 2882, 2857, 2716, 1819, 1719, 1643, 1592, 1552, 1520, 1492, 1468, 1409, 1392, 1363, 1253, 1206, 1083, 1006, 956, 916, 875, 836, 820, 804, 775, 710, 692, 675, 638, 612, 574, 561.

**MS** (70 eV, EI) m/z (%) = 198 (4), 196 (4) [M$^+$], 170 (5), 168 (5), 111 (4), 97 (5), 89 (10), 88 (6), 84 (6), 83 (5), 73 (7), 71 (6), 70 (16), 69 (7), 61 (19), 57 (8), 55 (7), 45 (17), 45 (4), 43 (5), 43 (100), 42 (6), 41 (5).

**HRMS** for C$_3$HOBrS$_2$ (195.8652): found: 195.8647.
Synthesis of 4,4’-(2-oxo-1,3-dithiole-4,5-diyl)dibenzonitrile (20b)

According to TP 3, Hg(OAc)$_2$ (1.91 g, 6.0 mmol) was added portion wise to a solution of 4,4’-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzonitrile (19f; 673 mg, 2.0 mmol) in CHCl$_3$ (40 mL) and conc. AcOH (12.5 mL) at 25 °C. The reaction mixture was stirred at this temperature for 2 h and the precipitate was then filtered through celite. The resulting solution was washed with sat. aq. Na$_2$CO$_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 1:2) yielding 20b as yellow solid (480 mg, 75%).

m.p.: 210.2 – 213.8 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.60 (d, $J$ = 8.3 Hz, 4H), 7.31 (d, $J$ = 8.6 Hz, 4H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 188.0, 135.5, 132.8, 130.1, 128.8, 117.7, 113.2.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3091, 3062, 2924, 2223, 1924, 1904, 1789, 1732, 1688, 1656, 1632, 1604, 1502, 1494, 1408, 1314, 1269, 1202, 1181, 1118, 1022, 1000, 972, 952, 889, 840, 830, 804, 762, 730, 712, 653, 609, 592, 582, 571.

MS (70 eV, El) m/z (%) = 322 (11), 321 (24), 320 (100) [M$^+$], 293 (17), 292 (74), 291 (13), 260 (31), 229 (12), 228 (66), 215 (15), 207 (10), 147 (10), 146 (94), 102 (17).

HRMS for C$_{17}$H$_8$ON$_2$S$_2$ (320.0078): found: 320.0072.
Synthesis of 4,5-bis(4-chlorophenyl)-1,3-dithiol-2-one (20c)

According to TP 3, Hg(OAc)$_2$ (1.91 g, 6.0 mmol) was added portion wise to a solution of 4,5-bis(4-chlorophenyl)-1,3-dithiole-2-thione (19g; 711 mg, 2.0 mmol) in CHCl$_3$ (40 mL) and conc. AcOH (12.5 mL) at 25 °C. The reaction mixture was stirred at this temperature for 1 h and the precipitate was then filtered through celite. The resulting solution was washed with sat. aq. Na$_2$CO$_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 2:1) yielding 20c as yellowish solid (624 mg, 92%).

m.p.: 141.2 – 145.7 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$/ppm = 7.31 – 7.23 (m, 4H), 7.19 – 7.09 (m, 4H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$/ppm = 189.5, 135.1, 130.7, 129.8, 129.2, 128.0.

IR (cm$^{-1}$): $\nu$ = 3026, 2358, 1903, 1806, 1781, 1726, 1708, 1686, 1648, 1620, 1587, 1482, 1468, 1446, 1400, 1350, 1278, 1262, 1177, 1145, 1124, 1108, 1090, 1012, 960, 946, 919, 894, 877, 827, 789, 714, 686, 640, 602, 564.

MS (70 eV, El) $m/z$ (%) = 340 (64), 338 (83) [M$^+$], 310 (23), 278 (20), 248 (62), 246 (100), 241 (23), 176 (35), 157 (44), 111 (21).

HRMS for C$_{15}$H$_8$OCl$_2$S$_2$ (337.9394): found: 337.9388.
C. EXPERIMENTAL PART

Synthesis of 4,5-bis(4-(trifluoromethyl)phenyl)-1,3-dithiol-2-one (20d)

According to TP 3, Hg(OAc)$_2$ (1.91 g, 6.0 mmol) was added portion wise to a solution of 4,5-bis(4-(trifluoromethyl)phenyl)-1,3-dithiole-2-thione (19h; 845 mg, 2.0 mmol) in CHCl$_3$ (40 mL) and conc. AcOH (12.5 mL) at 25 °C. The reaction mixture was stirred at this temperature for 1 h and the precipitate was then filtered through celite. The resulting solution was washed with sat. aq. Na$_2$CO$_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 2:1) yielding 20d as yellowish solid (736 mg, 91%).

m.p.: 122.7 – 125.0 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ/ppm = 7.57 (d, J = 8.2 Hz, 4H), 7.34 (d, J = 8.2 Hz, 4H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) δ/ppm = 188.9, 134.8, 131.2 (q, J = 32.8 Hz), 129.9, 128.6, 126.0 (q, J = 3.5 Hz), 123.5 (q, J = 272.4 Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$) δ/ppm = -63.0.

IR (cm$^{-1}$): $\tilde{\nu}$ = 2360, 2339, 1920, 1784, 1732, 1691, 1660, 1641, 1615, 1411, 1320, 1168, 1123, 1112, 1065, 1017, 955, 922, 889, 885, 838, 795, 768, 732, 673, 652, 632, 614, 596, 558.

MS (70 eV, El) m/z (%) = 407 (15), 406 (68) [M$^+$], 387 (10), 378 (31), 346 (19), 314 (45), 190 (11), 189 (100), 145 (13), 139 (12).

HRMS for C$_{17}$H$_8$OF$_6$S$_2$ (405.9921): found: 405.9917.
Synthesis of 4-iodo-5-(4-methoxyphenyl)-1,3-dithiol-2-one (20e)

According to TP 3, Hg(OAc)$_2$ (956 mg, 3.0 mmol) was added portion wise to a solution of 4-iodo-5-(4-methoxyphenyl)-1,3-dithiole-2-thione (19e; 368 mg, 1.0 mmol) in CHCl$_3$ (20 mL) and conc. AcOH (6.25 mL) at 25 °C. The reaction mixture was stirred at this temperature for 2 h and the precipitate was then filtered through celite. The resulting solution was washed with sat. aq. Na$_2$CO$_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 2:1) yielding 20e as colorless solid (329 mg, 94%).

m.p.: 154.0 – 156.3 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.44 – 7.37 (m, 4H), 7.00 – 6.93 (m, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 194.1, 160.6, 135.1, 130.6, 125.1, 114.2, 61.9, 55.4.

IR (cm$^{-1}$): $\nu$ = 3022, 2981, 2947, 2844, 1756, 1725, 1692, 1651, 1603, 1572, 1542, 1497, 1463, 1453, 1438, 1414, 1307, 1294, 1248, 1172, 1107, 1045, 1020, 1012, 973, 919, 906, 879, 846, 820, 805, 786, 731, 711, 638, 578, 568.

MS (70 eV, El) m/z (%) = 352 (10), 351 (11), 350 (80) [M$^+$], 163 (35), 151 (100), 108 (20).

HRMS for C$_{10}$H$_7$O$_2$I$_2$S$_2$ (349.8932): found: 349.8934.

Synthesis of 4-bromo-5-({tert-butyldimethylsilyl})-1,3-dithiol-2-one (20g)

According to TP 3, Hg(OAc)$_2$ (956 mg, 3.0 mmol) was added portion wise to a solution of 4-bromo-5-({tert-butyldimethylsilyl})-1,3-dithiole-2-thione (19c; 327 mg, 1.0 mmol) in CHCl$_3$ (20 mL) and conc. AcOH (6.25 mL) at 25 °C. The reaction mixture was stirred at this temperature for 1.5 h and the precipitate was then filtered through celite. The resulting solution was washed with sat. aq. Na$_2$CO$_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and after filtration, the solvents were evaporated in vacuo. The crude
product was purified by flash column chromatography on silica gel (i hexane) yielding 20g as colorless solid (299 mg, 96%).

m.p.: 27.8 – 29.2 °C.

\(^1H\)-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta/p\text{pm} = 1.01\) (s, 9H), 0.40 (s, 6H).

\(^{13}C\)-NMR (101 MHz, CDCl\textsubscript{3}) \(\delta/p\text{pm} = 194.2, 131.5, 104.0, 26.7, 18.6, -3.6\).

IR (cm\textsuperscript{-1}): \(\nu = 3304, 2950, 2927, 2891, 2856, 1758, 1716, 1656, 1586, 1492, 1470, 1461, 1443, 1410, 1400, 1362, 1253, 1006, 956, 880, 835, 820, 775, 709, 690, 674, 578\).

MS (70 eV, EI) \(m/z\) (%): 312 (37), 310 (34) [M\textsuperscript{+}], 256 (99), 255 (34), 254 (93), 227 (81), 225 (73), 139 (100), 137 (97), 73 (67), 71 (11), 59 (10), 57 (32), 43 (14), 41 (17).

HRMS for \(C_{9}H_{15}OSi_{2}\) (309.9517): found: 309.9512.

3.6 Preparation of Tetraarylated TTF-Derivatives

Synthesis of 4,4',5,5'-tetakis(4-chlorophenyl)-TTF (26a)

According to TP 4, 4,5-bis(4-chlorophenyl)-1,3-dithiol-2-one (20c; 170 mg, 0.5 mmol) was dissolved in freshly distilled P(OEt)\textsubscript{3} (5 mL) and the reaction mixture was stirred at 110 °C for 3 h. After cooling to 25 °C, the crude product was purified by flash column chromatography on silica gel (i hexane/CH\textsubscript{2}Cl\textsubscript{2}, 9:1) yielding 26a as red solid (87 mg, 54%).

m.p.: 260.3 – 262.1 °C.

\(^1H\)-NMR (600 MHz, CDCl\textsubscript{3}) \(\delta/p\text{pm} = 7.24\) (d, \(J = 8.2\) Hz, 8H), 7.14 (d, \(J = 8.5\) Hz, 8H).

\(^{13}C\)-NMR (151 MHz, CDCl\textsubscript{3}) \(\delta/p\text{pm} = 134.6, 130.7, 130.3, 129.1, 128.5, 108.4\).

IR (cm\textsuperscript{-1}): \(\nu = 1894, 1575, 1554, 1488, 1481, 1397, 1298, 1273, 1177, 1106, 1089, 1013, 974, 961, 940, 876, 838, 826, 816, 797, 778, 713, 689\).
C. EXPERIMENTAL PART

**MS** (70 eV, EI) m/z (%) = 650 (19), 649 (21), 648 (60), 647 (34), 646 (100), 645 (23), 644 (62) [M⁺], 493 (11), 491 (24), 489 (22), 324 (11), 323 (15), 322 (10), 278 (14), 248 (53), 247 (13), 246 (83), 176 (31).

**HRMS** for C₃₀H₁₆Cl₄S₄ (643.8889): found: 643.8885.

**Synthesis of 4,4',5,5'-tetrakis(4-(trifluoromethyl)phenyl)-2,2'-bi(1,3-dithiolyldene) (26b)**

According to TP 4, 4,5-bis(4-(trifluoromethyl)phenyl)-1,3-dithiol-2-one (20d; 235 mg, 0.6 mmol) was dissolved in freshly distilled P(OEt)₃ (5 mL) and the reaction mixture was stirred at 110 °C for 3 h. After cooling to 25 °C, the crude product was purified twice by flash column chromatography on silica gel (hexane/EtOAc, 98:2) yielding 26b as red solid (127 mg, 63%).

**m.p.:** 229.5 – 233.1 °C.

**¹H-NMR** (600 MHz, CDCl₃) δ/ppm = 7.57 – 7.49 (m, 8H), 7.38 – 7.29 (m, 8H).

**¹³C-NMR** (151 MHz, CDCl₃) δ/ppm = 135.6, 130.8 (q, J = 32.8 Hz), 129.4, 126.1, 125.9 (q, J = 3.6 Hz), 123.6 (q, J = 272.4 Hz), 108.7.

**¹⁹F-NMR** (376 MHz, CDCl₃) δ/ppm = -62.9.

**IR** (cm⁻¹): ν = 2952, 2923, 1693, 1614, 1583, 1565, 1505, 1462, 1408, 1376, 1366, 1320, 1164, 1121, 1106, 1066, 1016, 955, 880, 842, 810, 780, 767, 731, 673, 656.

**MS** (70 eV, EI) m/z (%) = 781 (11), 780 (24) [M⁺], 535 (10), 454 (13), 391 (10), 378 (22), 344 (100), 314 (11), 313 (53), 294 (10), 233 (10), 189 (55).

**HRMS** for C₃₄H₁₆F₁₂S₄ (779.9943): found: 779.9945.
Synthesis of 4,4′-(4′,5′-di-p-tolyl-TTF-4,5-diyl)dibzonitrile (26c)

According to TP 4, 4,5-di-p-tolyl-1,3-dithiole-2-thione (19i; 314 mg, 1.0 mmol) was dissolved in freshly distilled P(OEt)$_3$ (10 mL). 4,4′-(2-Oxo-1,3-dithiole-4,5-diyl)dibzonitrile (20b; 384 mg, 1.2 mmol) was added at 25 °C and the reaction mixture was stirred at 110 °C for 2 h. After cooling to 25 °C, the crude product was purified twice by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 1:1) yielding 26c as brown solid (393 mg, 67%).

m.p.: 263.1 – 265.1 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$/ppm = 7.52 (d, $J = 8.4$ Hz, 4H), 7.28 – 7.22 (m, 4H), 7.11 – 7.05 (m, 4H), 7.05 – 6.97 (m, 4H), 2.28 (s, 6H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$/ppm = 138.5, 136.7, 132.6, 130.0, 129.7, 129.5, 129.3, 128.9, 128.4, 118.0, 112.5, 104.2, 21.3. (One signal not observed; possible coincidental isochronicity).

IR (cm$^{-1}$): $\varpi$ = 3022, 2917, 2225, 1900, 1601, 1573, 1509, 1500, 1445, 1406, 1308, 1267, 1177, 1112, 1039, 1020, 982, 881, 849, 838, 813, 802, 778, 759, 728, 716, 644, 602, 582, 573.

MS (70 eV, El) $m/z$ (%) = 588 (28), 587 (41), 586 (100) [M$^+$], 451 (16), 440 (11), 420 (19), 419 (65), 397 (19), 293 (12), 260 (24), 238 (19), 229 (13), 228 (65), 215 (11), 206 (51), 205 (17), 191 (10), 189 (12), 146 (27), 135 (15), 44 (10).

HRMS for C$_{34}$H$_{22}$N$_2$S$_4$ (586.0666): found: 586.0664.
Synthesis of 4,4’-(4',5'-bis(4-(trifluoromethyl)phenyl)-TTF-4,5-diyl)dibenzonitrile (26d)

According to TP 4, 4,4’-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzonitrile (19f; 122 mg, 0.36 mmol) was dissolved in freshly distilled P(OEt)\textsubscript{3} (4 mL). 4,5-Bis(4-(trifluoromethyl)phenyl)-1,3-dithiol-2-one (20d; 177 mg, 0.44 mmol) was added at 25 °C and the reaction mixture was stirred at 110 °C for 1.5 h. After cooling to 25 °C, the crude product was purified twice by flash column chromatography on silica gel (i-hexane/CH\textsubscript{2}Cl\textsubscript{2}, 1:1) yielding 26d as dark red solid (132 mg, 53%).

m.p.: 241.2 – 246.6 °C.

\textsuperscript{1}H-NMR (600 MHz, CDCl\textsubscript{3}) \(\delta/\text{ppm} = 7.61 – 7.51 (m, 8H), 7.37 – 7.26 (m, 8H)\).

\textsuperscript{13}C-NMR (151 MHz, CDCl\textsubscript{3}) \(\delta/\text{ppm} = 136.3, 135.4, 132.7, 130.9 (q, J = 32.8 \text{ Hz}), 129.9, 129.7, 129.4, 125.9 (q, J = 3.6 \text{ Hz}), 123.6 (q, J = 272.4 \text{ Hz}), 117.9, 112.8, 110.0, 107.4.\) (One signal not observed; possible coincidental isochronicity).

\textsuperscript{19}F-NMR (376 MHz, CDCl\textsubscript{3}) \(\delta/\text{ppm} = -62.9\).

IR (cm\textsuperscript{-1}): \(\nu = 2227, 1613, 1602, 1573, 1563, 1501, 1407, 1321, 1266, 1163, 1125, 1111, 1067, 1015, 977, 955, 879, 846, 813, 781, 769, 759, 732, 715, 673, 655\).

MS (70 eV, El) \(m/z(\%) = 696 (27), 695 (38), 694 (100) [M^+]\), 505 (11), 347 (17), 314 (39), 228 (32).

HRMS for C\textsubscript{34}H\textsubscript{18}N\textsubscript{2}F\textsubscript{6}S\textsubscript{4} (694.0101): found: 694.0095.

Synthesis of dibromo-TTF-bis(tert-butyldimethylsilane) (22k, I)

According to TP 4, 4-bromo-5-(tert-butyldimethylsilyl)-1,3-dithiole-2-thione (19c; 2.07 g, 6.32 mmol) was dissolved in freshly distilled P(OEt)\textsubscript{3} (60 mL). 4-Bromo-5-(tert-butyldimethylsilyl)-1,3-dithiole-2-one (20f; 2.36 g, 7.58 mmol) was added at 25 °C and the reaction mixture was
stirred at 110 °C for 2.5 h. After cooling to 25 °C, the crude product was purified twice by flash column chromatography on silica gel (i-hexane) yielding the isomeric mixture of 22k and 22l as orange solid (2.73 g, 70%).

**MS** (70 eV, El) m/z (%) = 594 (17), 593 (21), 592 (64), 591 (30), 590 (100), 589 (15), 588 (42) [M*], 340 (31), 338 (27), 161 (12), 139 (24), 137 (23), 115 (10), 88 (10), 83 (10), 73 (56), 57 (12), 41 (10).

**HRMS** for C_{18}H_{30}Br_{2}Si_{2}S_{4} (587.9136): found: 587.9127.

**Synthesis of (Z)-4,4′-dibromo-TTF (27a) and (E)-4,4′-dibromo-TTF (27b)**

The isomeric mixture of dibromo-TTF-bis(tert-butyldimethylsilane) (22k, l; 304 mg, 0.51 mmol) was dissolved in H_{2}O (0.5 mL) and DMSO (10 mL). Potassium fluoride (299 mg, 5.15 mmol) was added at 25 °C and the reaction mixture was stirred for 2 h. The reaction mixture was quenched with sat. aq. NH_{4}Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_{2}SO_{4}. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/NEt_{3}, 100:2) yielding the Z-isomer 27a (87 mg, 47%) and the E-isomer 27b (61 mg, 33%) as red solid.

**Z-isomer (27a):**

m.p.: 101.0 – 106.0 °C.

**^1H-NMR** (400 MHz, CDCI_{3}) δ/ppm = 6.30 (s, 2H), 6.29 (s, 2H).

**^13C-NMR** (101 MHz, CDCI_{3}) δ/ppm = 117.9, 117.8, 112.1, 112.1, 100.6, 100.5.

**IR** (cm⁻¹): ν = 1474, 1185, 894, 785, 7643, 734.

**MS** (70 eV, El) m/z (%) = 364 (16), 362 (26), 360 (12) [M*], 226 (16), 224 (15), 183 (14), 181 (17), 101 (19), 88 (26), 86 (11), 84 (15), 76 (15), 70 (13), 69 (18), 61 (17), 57 (12), 45 (14), 43 (100).

**HRMS** for C_{8}H_{2}Br_{2}S_{4} (359.7406): found: 359.7403.
E-isomer (27b):

m.p.: 136.3 – 141.9 °C.

\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 6.29 (\text{s, 2H}), 6.29 (\text{s, 2H}).

\(^{13}\text{C-NMR}\) (101 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 117.9, 117.8, 112.1, 112.1, 100.6, 100.5.

IR (cm\(^{-1}\)): \(\nu = 3074, 1535, 1472, 1189, 896, 796, 763, 732.

MS (70 eV, El) \(m/z\) (%): 366 (11), 364 (65), 362 (100), 360 (47) [M\(^+\)], 283 (39), 281 (33), 239 (21), 237 (20), 226 (65), 224 (59), 183 (55), 182 (35), 181 (58), 180 (28), 101 (57), 100 (10), 88 (76), 84 (11), 76 (40), 69 (49), 61 (12), 57 (36), 45 (25), 43 (65).


4.1 Typical Procedures

Typical Procedure 1 for the magnesiation of TTF (21) with TMPMgCl-LiCl (2) (TP 1):

A dry and argon flushed Schlenk-flask was charged with a solution of TTF (21; 1.0 equiv) in dry THF (0.5 M). TMPMgCl-LiCl (2; 1.1 equiv, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred at this temperature for 1 h. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF using undecane as internal standard.

Typical Procedure 2 for the magnesiation of 4-chloro-TTF (32c) with TMPMgCl-LiCl (2) (TP 2):

A dry and argon flushed Schlenk-flask was charged with a solution of 4-chloro-TTF (32c; 1.0 equiv) in dry THF (0.25 M). TMPMgCl-LiCl (2; 1.1 equiv, 1.11 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with iodine in dry THF.

Typical Procedure 3 for the magnesiation of ethyl TTF-4-carboxylate (32g) with TMPMgCl-LiCl (2) (TP 3):

A dry and argon flushed Schlenk-flask was charged with a solution of ethyl TTF-4-carboxylate (32g; 1.0 equiv) in dry THF (0.5 M). TMPMgCl-LiCl (2; 1.1 equiv, 1.11 M in THF) was added dropwise at -20 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with iodine in dry THF.

Typical Procedure 4 for the zincation of TTF-4-yl-(3-chlorophenyl)methanone (32i) with TMP$_2$Zn·2MgCl$_2$·2LiCl (5) (TP 4):

A dry and argon flushed Schlenk-flask was charged with a solution of TTF-4-yl-(3-chlorophenyl)methanone (32i; 1.0 equiv) in dry THF (0.15 M). TMP$_2$Zn·2MgCl$_2$·2LiCl (5;
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1.1 equiv, 0.65 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with iodine in dry THF.

**Typical Procedure 5 for the zincation of diethyl TTF-4,5-dicarboxylate (33e) with TMPZnCl·LiCl (4) (TP 5):**

A dry and argon flushed Schlenk-flask was charged with a solution of diethyl TTF-4,5-dicarboxylate (33e; 1.0 equiv) in dry THF (0.25 M). TMPZnCl·LiCl (4; 1.3 equiv, 1.25 M in THF) was added dropwise at -30 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with iodine in dry THF.

**Typical Procedure 6 for the zincation of 34e-g with TMPZnCl·LiCl (4) (TP 6):**

A dry and argon flushed Schlenk-flask was charged with a solution of the corresponding substrate (1.0 equiv) in dry THF (0.1 M). TMPZnCl·LiCl (4; 1.3 equiv, 1.25 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by TLC of reaction aliquots quenched with iodine in dry THF.

### 4.2 Preparation of Starting Material

**Synthesis of 1,3-dithiol-2-ylum hydrogen sulfate (29)**

According to the literature, a precooled solution (-50 °C) of peracetic acid (9.22 g, 121 mmol, 21 mL, 39% in acetic acid) in acetone (50 mL) was added dropwise to a solution of DTT (16; 4.07 g, 30 mmol) in acetone (80 mL) at -50 °C with a rate that the temperature did not rise above -40 °C. After the addition, the cooling bath was removed and the reaction mixture was allowed to warm up to 15 °C over 20 minutes (exothermic reaction). The reaction mixture was cooled again to -50 °C, the cooling bath was removed another time and the reaction mixture was allowed to warm up to 5 °C over 20 minutes. The resulting precipitate was filtered, washed with cold acetone (50 mL) and dried under high vacuum. The title compound (29) was obtained as yellowish solid (4.13 g, 68%) and was used without further purification.
Synthesis of 1,3-dithiol-2-ylum hexafluorophosphate (30)

\[
\begin{array}{c}
\text{S} \\
\text{H} \\
\text{PF}_6
\end{array}
\]

According to the literature,\(^{57}\) a solution of 1,3-dithiol-2-ylum hydrogen sulfate (29; 8.81 g, 44 mmol) in H\(_2\)O (40 mL) was added dropwise to a solution of sodium hexafluorophosphate (8.06 g, 48 mmol) in H\(_2\)O (20 mL) at 25 °C. After the addition, the reaction flask was stored in the fridge for 4 h. The resulting precipitate was filtered, washed with cold H\(_2\)O (50 mL) and dried under high vacuum. The title compound (30) was obtained as colorless solid (9.06 g, 83%) and was used without further purification.

Synthesis of tetrathiafulvalene (TTF) (21)

\[
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{S} \\
\text{S}
\end{array}
\]

According to the literature,\(^{57}\) freshly distilled NEt\(_3\) (3.97 g, 5.5 mL, 39 mmol) was added to a solution of 1,3-dithiol-2-ylum hexafluorophosphate (30; 8.86 g, 36 mmol) in dry acetonitrile (165 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 0.5 h. H\(_2\)O (600 mL) was added and the resulting precipitate was filtered, washed with H\(_2\)O (50 mL) and dried under high vacuum. TTF (21) was obtained as yellow solid (3.58 g, 98%).

\(^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 6.32\) (s, 4H).

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 119.1, 110.1\).

\textbf{MS} (70 eV, EI) \(m/z\) (%) = 206 (11), 204 (55) [M\(^+\)], 159 (17), 146 (16), 103 (10), 102 (70), 88 (38), 78 (10), 76 (100), 58 (61), 57 (30), 45 (85), 44 (27).

\textbf{HRMS} for C\(_6\)H\(_4\)S\(_4\) (203.9195): found: 203.9195.
4.3 Preparation of Monofunctionalized TTF-Derivatives

**Synthesis of 4-iodo-TTF (32a)**

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl⋅LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. The freshly prepared magnesium reagent was added to a solution of iodine (305 mg, 1.2 mmol) in dry THF (2 mL) at -60 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 98:2) yielding 32a as yellow solid (182 mg, 55%).

**m.p.:** 61.8 – 63.5 °C.

**1H-NMR** (600 MHz, CDCl₃) δ/ppm = 6.42 (s, 1H), 6.34 (s, 2H).

**13C-NMR** (151 MHz, CDCl₃) δ/ppm = 124.3, 119.0, 119.0, 112.8, 111.0, 63.7.

**IR** (cm⁻¹): \( \gamma = 3063, 2355, 2115, 1842, 1594, 1548, 1522, 1488, 1293, 1252, 1192, 1086, 868, 794, 770, 746, 735. \)

**MS** (70 eV, El) m/z (%) = 332 (21), 331 (10), 330 (100) [M⁺], 205 (13), 203 (47), 146 (91), 103 (44), 102 (15), 101 (14), 88 (23), 76 (20), 70 (12), 69 (10), 57 (14), 45 (12).

**HRMS** for C₆H₃I₅S₄ (329.8162): found: 329.8154.

**Synthesis of 4-bromo-TTF (32b)**

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl⋅LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. The freshly prepared magnesium reagent was added to a solution of 1,2-dibromotetrachloroethane (391 mg, 1.2 mmol) in dry THF (4 mL) at -50 °C. The
reaction mixture was allowed to warm up to 0 °C within 3 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane) yielding 32b as yellow solid (189 mg, 67%).

m.p.: 52.8 – 53.5 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 6.34 (br. s, 2H), 6.27 (br. s, 1H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 127.6, 119.0, 118.0, 114.0, 100.4. (One quaternary carbon not observed).

IR (cm⁻¹): ν = 3061, 1598, 1557, 1532, 1514, 1486, 1290, 1254, 1199, 1177, 1088, 898, 864, 849, 796, 772, 758, 736.

MS (70 eV, EI) m/z (%) = 284 (81), 282 (69) [M⁺], 201 (47), 146 (87), 103 (100), 102 (69), 88 (57), 76 (71), 57 (41), 46 (41).

HRMS for C₆H₅BrS₄ (281.8301): found: 281.8292.

Synthesis of 4-chloro-TTF (32c)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl∙LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. The freshly prepared magnesium reagent was added to a solution of benzenesulfonyl chloride (212 mg, 1.2 mmol) in dry THF (4 mL) at -60 °C. The reaction mixture was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 99:1) yielding 32c as orange solid (155 mg, 65%).

m.p.: 66.5 – 68.3 °C.

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 6.33 (br. s, 2H), 6.15 (s, 1H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 118.9 (2C), 117.6, 115.1, 114.5. (One quaternary carbon not observed).
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IR (cm\(^{-1}\)): \(\tilde{\nu} = 3064, 2922, 1732, 1564, 1516, 1470, 1252, 1188, 1169, 1075, 945, 867, 811, 796, 775, 737\).

**MS** (70 eV, El) \(m/z\) (%) = 240 (43), 238 (100) \([M^+\]), 203 (12), 193 (22), 146 (18), 136 (15), 103 (19), 102 (43), 88 (21), 76 (34), 69 (11), 45 (11).

**HRMS** for C\(_6\)H\(_3\)ClS\(_4\) (237.8806): found: 237.8797.

**Synthesis of 4-(methylthio)-TTF (32d)**

According to **TP 1**, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl\(\cdot\)LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. The freshly prepared magnesium reagent was added to a solution of \(S\)-methyl methanethiosulfonate (151 mg, 1.2 mmol) in dry THF (4 mL) at -20 °C. The reaction mixture was stirred at this temperature for 4 h and was then quenched with sat. aq. NH\(_4\)Cl solution (5 mL), extracted with Et\(_2\)O (3 x 10 mL) and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH\(_2\)Cl\(_2\), 9:1) yielding 32d as yellow oil (222 mg, 89%).

\(^1\)H-NMR (600 MHz, CDCl\(_3\)) \(\delta/\)ppm = 6.32 (br. s, 2H), 6.29 (br. s, 1H), 2.41 (s, 3H).

\(^{13}\)C-NMR (151 MHz, CDCl\(_3\)) \(\delta/\)ppm = 128.8, 119.7, 119.0, 118.9, 113.0, 109.6, 19.4.

IR (cm\(^{-1}\)): \(\tilde{\nu} = 3860, 3684, 3064, 2987, 2916, 2851, 2182, 1682, 1596, 1575, 1555, 1524, 1466, 1456, 1426, 1416, 1380, 1312, 1253, 1182, 1090, 973, 956, 928, 852, 793, 773, 732.

**MS** (70 eV, El) \(m/z\) (%) = 296 (70), 250 (100) \([M^+\]), 235 (41), 192 (45), 146 (65), 102 (70) 101 (31), 88 (42), 76 (44), 72 (78), 45 (39).

**HRMS** for C\(_7\)H\(_6\)S\(_5\) (249.9073): found: 249.9072.
C. EXPERIMENTAL PART

Synthesis of 1-(TTF-4-yl)-$N,N'$-dimethylmethanamine (32e)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. Trifluoroacetic anhydride (231 mg, 1.1 mmol) was added to a solution of $N,N,N',N'$-tetramethylmethanediamine (112 mg, 1.1 mmol) in dry CH$_2$Cl$_2$ (1 mL) at 0 °C. This reaction mixture was stirred at 0 °C for 0.5 h and then at 25 °C for 10 min. The resulting $N$-methyl-$N$-methylenemethanaminium trifluoromethane-sulfonate was added to the freshly prepared magnesium reagent at -30 °C. The reaction mixture was stirred at this temperature for 2 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (EtOAc) yielding 32e as yellow solid (144 mg, 55%).

**m.p.:** 70.7 – 72.4 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 6.30 (br. s, 2H), 6.10 (s, 1H), 3.21 (s, 2H), 2.27 (s, 6H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 136.4, 119.2, 118.8, 114.2, 110.2, 110.1, 59.5, 45.0.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3062, 3013, 2969, 2937, 2848, 2823, 2798, 2780, 1732, 1574, 1542, 1519, 1496, 1464, 1450, 1437, 1404, 1352, 1260, 1212, 1122, 1088, 1040, 1024, 996, 972, 852, 793, 776, 730.

**MS** (70 eV, EI) $m/z$ (%) = 263 (17), 262 (11), 261 (92) [$M^+$], 206 (11), 204 (55), 154 (11), 146 (29), 58 (100).

**HRMS** for C$_9$H$_{11}$NS$_4$ (260.9774): found: 260.9761.

Synthesis of TTF-4-carbaldehyde (32f)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. The freshly prepared magnesium reagent was added to a...
solution of dry DMF (88 mg, 1.2 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 2:1) yielding 32f as dark red solid (139 mg, 60%).

m.p.: 111.2 – 113.0 °C (decomp.).

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 9.48 (s, 1H), 7.43 (s, 1H), 6.39 – 6.30 (m, 2H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 179.6, 141.5, 139.9, 119.3, 118.7, 115.9, 105.5.

IR (cm⁻¹): ν = 3068, 2921, 1712, 1644, 1550, 1532, 1367, 1252, 1228, 1143, 1074, 865, 829, 796, 776, 736, 696.

MS (70 eV, El) m/z (%) = 234 (20), 233 (12), 232 (100) [M⁺], 159 (13), 146 (56), 103 (12), 102 (54), 88 (21), 76 (39), 69 (12), 58 (11).

HRMS for C₇H₄OS₄ (231.9145): found: 231.9142.

Synthesis of ethyl TTF-4-carboxylate (32g)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl∙LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. The freshly prepared magnesium reagent was added to a solution of ethyl cyanoformate (119 mg, 1.2 mmol) in dry THF (2 mL) at -78 °C. The reaction mixture was allowed to warm up to 25 °C within 3.5 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 3:1) yielding 32g as red solid (199 mg, 72%).

m.p.: 83.8 – 85.7 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 7.28 (br. s, 1H), 6.19 (br. s, 2H), 4.28 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H).
C. EXPERIMENTAL PART

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$/ppm = 159.4, 131.8, 128.7, 119.2, 118.7, 113.5, 107.8, 61.9, 14.2.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3069, 3057, 2976, 2924, 2901, 1693, 1567, 1537, 1472, 1438, 1392, 1366, 1286, 1198, 1154, 1112, 1004, 865, 841, 814, 793, 780, 730, 720, 689, 666.

MS (70 eV, EI) m/z (%) = 278 (13), 276 (92) [M$^+$]. 250 (15), 248 (100), 203 (16), 146 (58), 102 (21), 88 (14), 76 (15).

HRMS for C$_9$H$_8$O$_2$S$_4$ (275.9407): found: 275.9387.

Synthesis of 1-(TTF-4-yl)-2,2-dimethylpropan-1-one (32h)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl∙LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. ZnCl$_2$ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 25 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of pivaloyl chloride (157 mg, 1.3 mmol) and CuCN-2LiCl (0.20 mL, 0.20 mmol, 1.0 M in THF) in dry THF (2 mL) at -20 °C. The reaction mixture was allowed to warm up to 25 °C within 12 h and was then quenched with aq. NH$_4$Cl/NH$_3$ solution (8:1, 5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel ($\phi$hexane/CH$_2$Cl$_2$, 3:1) yielding 32h as dark red solid (219 mg, 76%).

m.p.: 155.9 – 157.4 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 7.33 (br. s, 1H), 6.31 (br. s, 2H), 1.31 (s, 9H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 196.0, 138.2, 130.4, 119.4, 118.6, 43.8, 27.8. (Quaternary carbons not observed).

IR (cm$^{-1}$): $\tilde{\nu}$ = 3079, 2970, 1636, 1552, 1530, 1515, 1472, 1396, 1367, 1271, 1252, 1206, 1141, 1023, 880, 831, 797, 775, 729, 689.

MS (70 eV, EI) m/z (%) = 290 (18), 289 (15), 288 (100) [M$^+$]. 204 (15), 203 (15), 146 (46), 103 (17), 102 (13), 57 (27), 41 (15).
C. EXPERIMENTAL PART

HRMS for C_{11}H_{12}OS_{4} (287.9771): found: 287.9769.

Synthesis of TTF-4-yl(3-chlorophenyl)methanone (32i)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. ZnCl_{2} solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 25 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 3-chlorobenzoyl chloride (210 mg, 1.2 mmol) and Pd(PPh_{3})_{4} (116 mg, 0.10 mmol) in dry THF (4 mL) at 25 °C. The reaction mixture was stirred for 1 h and was then quenched with sat. aq. NH_{4}Cl solution (5 mL), extracted with Et_{2}O (3 x 10 mL) and dried over anhydrous Na_{2}SO_{4}. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH_{2}Cl_{2}, 2:1) yielding 32i as purple solid (285 mg, 65%).

m.p.: 142.6 – 143.6 °C.

^{1}H-NMR (600 MHz, CDCl_{3}) δ/ppm = 7.67 (s, 1H), 7.60 – 7.51 (m, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.20 (s, 1H), 6.41 – 6.28 (m, 2H).

^{13}C-NMR (151 MHz, CDCl_{3}) δ/ppm = 183.7, 139.6, 138.5, 136.6, 134.9, 132.4, 130.0, 128.5, 126.6, 119.4, 118.7, 115.4, 105.9.

IR (cm^{-1}): ν = 3096, 3060, 2922, 1608, 1590, 1564, 1529, 1513, 1472, 1414, 1299, 1258, 1198, 1165, 1124, 1090, 1076, 914, 894, 880, 854, 832, 796, 780, 729, 706, 677.

MS (70 eV, El) m/z (%) = 344 (47), 343 (18), 342 (100) [M^{+}], 148 (13), 146 (89), 139 (26), 111 (26), 103 (14), 102 (24), 76 (12), 75 (13).

HRMS for C_{13}H_{7}OCIS_{4} (341.9068): found: 341.9061.
Synthesis of 4-(4-chlorophenyl)-TTF (32j)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl∙LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 25 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-chloro-4-iodobenzene (191 mg, 0.8 mmol), Pd(dba)₂ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 12 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 3:1) yielding 32j as orange solid (271 mg, 86%).

m.p.: 105.5 – 107.0 °C.

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 7.33 (s, 4H), 6.50 (s, 1H), 6.36 – 6.31 (m, 2H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 134.8, 134.1, 130.9, 129.0, 127.4, 119.1, 119.0, 114.2, 112.2, 108.5.

IR (cm⁻¹): ν = 3064, 2922, 1885, 1592, 1572, 1538, 1486, 1396, 1302, 1252, 1208, 1184, 1114, 1094, 1087, 1011, 951, 924, 820, 797, 779, 758, 738, 716, 696.

MS (70 eV, El) m/z (%) = 316 (45), 315 (14), 314 (100) [M⁺], 271 (11), 269 (23), 178 (19), 157 (10), 146 (14), 138 (10), 136 (31), 102 (84), 76 (22).

HRMS for C₁₂H₇ClS₄ (313.9119): found: 313.9112.

Synthesis of ethyl 4-(TTF-4-yl)benzoate (32k)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl∙LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the
reaction mixture was stirred for 1 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 25 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of ethyl 4-iodobenzoate (221 mg, 0.8 mmol), Pd(dba)₂ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 2:1) yielding 32k as red solid (307 mg, 87%).

m.p.: 126.8 – 128.3 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.02 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 6.66 (br. s, 1H), 6.33 (br. s, 2H), 4.39 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 165.9, 137.3, 137.1, 136.2, 135.1, 130.1, 125.9, 119.0, 116.2, 61.1, 14.3. (Quaternary carbons not observed).

IR (cm⁻¹): ν = 3066, 2985, 2899, 1919, 1710, 1604, 1570, 1536, 1503, 1479, 1460, 1442, 1407, 1367, 1314, 1276, 1242, 1228, 1212, 1183, 1112, 1095, 1024, 965, 924, 877, 848, 830, 802, 779, 748, 688.

MS (70 eV, EI) m/z (%) = 354 (20), 353 (20), 352 (100) [M⁺], 324 (34), 279 (22), 102 (24).

HRMS for C₁₅H₁₂O₂S₄ (351.9720): found: 351.9717.

Synthesis of 4-(4-methoxyphenyl)-TTF (32l)

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 25 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodoanisole (187 mg, 0.8 mmol), Pd(dba)₂ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 12 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo.
The crude product was purified by flash column chromatography on silica gel (Hexane/CH₂Cl₂, 3:1) yielding 32l as yellow solid (189 mg, 61%).

**m.p.:** 159.9 – 161.5 °C.

**¹H-NMR** (600 MHz, CDCl₃) δ/ppm = 7.35 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 6.32 (br. s, 3H), 3.83 (s, 3H).

**¹³C-NMR** (151 MHz, CDCl₃) δ/ppm = 159.7, 135.8, 127.6, 119.0, 114.2 (2C), 111.3, 55.4. (Quaternary carbons not observed).

**IR** (cm⁻¹): ν = 3068, 2996, 2923, 2853, 1602, 1572, 1536, 1517, 1502, 1464, 1450, 1436, 1415, 1310, 1253, 1234, 1206, 1183, 1110, 1080, 1028, 920, 825, 792, 785, 774, 757, 730, 711, 670.

**MS** (70 eV, EI) m/z (%) = 312 (19), 311 (18), 310 (100) [M⁺], 265 (18), 178 (12), 132 (16), 102 (40), 89 (10), 57 (12).

**HRMS** for C₁₃H₁₀OS₄ (309.9614): found: 309.9611.

**Synthesis of 4-(3-(trifluoromethyl)phenyl)-TTF (32m)**

According to TP 1, TTF (21; 204 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 25 °C and the reaction mixture was stirred for 1 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 25 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-3-(trifluoromethyl)benzene (218 mg, 0.8 mmol), Pd(dba)₂ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (Hexane/CH₂Cl₂, 10:1) yielding 32m as red solid (321 mg, 92%).

**m.p.:** 73.2 – 75.1 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 7.70 – 7.62 (m, 1H), 7.62 – 7.43 (m, 3H), 6.64 (s, 1H), 6.34 (br. s, 2H).


C. EXPERIMENTAL PART

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 134.5, 133.2, 131.4\) (q, \(J = 32.5\) Hz), 129.4 (br, 2C), 124.9 (q, \(J = 3.7\) Hz), 123.8 (q, \(J = 273\) Hz), 122.9 (q, \(J = 3.9\) Hz), 119.1, 119.0, 115.6, 112.9, 112.8.

IR (cm\(^{-1}\)): \(\tilde{\nu} = 3065, 1889, 1712, 1608, 1537, 1482, 1440, 1326, 1290, 1225, 1212, 1162, 1106, 1090, 1074, 1060, 997, 959, 908, 890, 838, 808, 794, 779, 767, 756, 734, 690, 682, 654.

MS (70 eV, Ei) \(m/z\) (%) = 350 (16), 349 (14), 348 (100) [M\(^+\)], 303 (16), 170 (18), 102 (20).

HRMS for C\(_{13}\)H\(_7\)F\(_3\)S\(_4\) (347.9383): found: 347.9362.

4.4 Preparation of Difunctionalized TTF-Derivatives

**Synthesis of ethyl 2-((5-chloro-TTF-4-yl)methyl)acrylate (33a)**

![Chemical Structure](image)

According to **TP 2**, 4-chloro-TTF (32c; 239 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl\(-\)LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. ZnCl\(_2\) solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 0 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of ethyl 2-(bromomethyl)acrylate\(^{38}\) (154 mg, 0.8 mmol) and CuCN\(-\)2LiCl (0.20 mL, 0.20 mmol, 1.0 M in THF) in dry THF (2 mL) at -40 °C. The reaction mixture was stirred at 25 °C for 48 h and was then quenched with aq. NH\(_4\)Cl/NH\(_3\) solution (8:1, 5 mL), extracted with CH\(_2\)Cl\(_2\) (3 x 10 mL) and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (i\(\)hexane/CH\(_2\)Cl\(_2\), 3:1) yielding **33a** as orange solid (298 mg, 85%).

**m.p.:** 44.5 – 46.3 °C.

\(^1\text{H-NMR}\) (600 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 6.32\) (s, 3H), 5.73 (s, 1H), 4.25 (q, \(J = 7.1\) Hz, 2H), 3.45 (br. s, 2H), 1.33 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\text{C-NMR}\) (151 MHz, CDCl\(_3\)) \(\delta/\text{ppm} = 165.9, 135.6, 127.4\) (2C), 127.2, 119.0, 118.9, 114.2, 112.6, 61.1, 31.1, 14.2.
C. EXPERIMENTAL PART

IR (cm⁻¹): ν = 3409, 3067, 2976, 2931, 2870, 2361, 2190, 1911, 1716, 1630, 1594, 1545, 1521, 1492, 1468, 1445, 1418, 1367, 1334, 1292, 1255, 1156, 1110, 1027, 974, 952, 938, 882, 858, 815, 798, 776, 765, 736, 720.

MS (70 eV, El) m/z (%) = 352 (47), 351 (16), 350 (100) [M⁺], 324 (14), 322 (26), 277 (12), 146 (66), 102 (23), 76 (10).

HRMS for C₁₂H₁₁O₂ClS₄ (349.9330): found: 349.9327.

**Synthesis of (5-chloro-TTF-4-yl)( phenyl)methanone (33b)**

According to TP 2, 4-chloro-TTF (32c; 239 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 0 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of benzoyl chloride (169 mg, 1.2 mmol) and Pd(PPh₃)₄ (116 mg, 0.10 mmol) in dry THF (4 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 1 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH₂Cl₂, 3:1) yielding 33b as dark red solid (285 mg, 83%).

m.p.: 100.9 – 103.0 °C.

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 7.83 (d, J = 7.7 Hz, 2H), 7.65 – 7.56 (m, 1H), 7.52 – 7.44 (m, 2H), 6.47 – 6.27 (m, 2H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 186.1, 136.4, 133.6, 129.6, 129.3, 128.6, 125.9, 119.3, 118.7, 118.3. (One quaternary carbon not observed).

IR (cm⁻¹): ν = 3067, 2361, 1902, 1715, 1624, 1596, 1578, 1548, 1520, 1509, 1444, 1314, 1307, 1274, 1255, 1175, 1104, 1077, 1023, 1001, 973, 949, 932, 843, 812, 795, 778, 728, 710, 693.

MS (70 eV, El) m/z (%) = 344 (39), 343 (13), 342 (80) [M⁺], 146 (42), 105 (100), 102 (16), 77 (63), 51 (15).
C. EXPERIMENTAL PART

HRMS for \( \text{C}_{13}\text{H}_7\text{OCIS}_4 \) (341.9068): found: 341.9062.

**Synthesis of 4-chloro-5-(4-methoxyphenyl)-TTF (33c)**

According to **TP 2**, 4-chloro-TTF (32c; 239 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl\( \cdot \)LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. ZnCl\(_2\) solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 0 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodoanisole (187 mg, 0.8 mmol), Pd(dba\(_2\)) (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 15 h and was then quenched with sat. aq. NH\(_4\)Cl solution (5 mL), extracted with CH\(_2\)Cl\(_2\) (3 x 10 mL) and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH\(_2\)Cl\(_2\), 3:1) yielding 33c as orange solid (269 mg, 78%).

\textbf{m.p.:} 109.2 – 111.2 °C.

\( ^1\text{H-NMR} \) (600 MHz, CDCl\(_3\)) \( \delta / \text{ppm} = 7.49 \) (d, \( J = 8.0 \) Hz, 2H), 6.93 (d, \( J = 8.0 \) Hz, 2H), 6.57 (br. s, 2H), 3.84 (s, 3H).

\( ^{13}\text{C-NMR} \) (151 MHz, CDCl\(_3\)) \( \delta / \text{ppm} = 160.1, 148.9, 148.8, 130.3, 123.5, 123.4, 119.0, 114.0, 111.1, 111.0, 55.3. \)

\( \text{IR (cm}^{-1}\text{):} \bar{\nu} = 3065, 2994, 2966, 2929, 2834, 2363, 1606, 1583, 1570, 1550, 1503, 1462, 1436, 1416, 1296, 1249, 1178, 1152, 1114, 1107, 1092, 1033, 1012, 982, 930, 890, 827, 799, 777, 766, 750, 735. \)

**MS** (70 eV, El) \( m/z \% = 346 \) (48), 345 (17), 344 (100) \([\text{M}^+]\), 299 (44), 166 (10), 151 (12), 146 (29), 123 (10), 102 (40), 76 (12).

HRMS for \( \text{C}_{13}\text{H}_9\text{OCIS}_4 \) (343.9225): found: 343.9214.
Synthesis of 4-(5-chloro-TTF-4-yl)benzonitrile (33d)

According to TP 2, 4-chloro-TTF (32c; 239 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at 0 °C and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodobenzonitrile (183 mg, 0.8 mmol), Pd(dba)₂ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 13 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH₂Cl₂, 3:1) yielding 33d as dark red solid (313 mg, 92%).

m.p.: 208.7 – 209.9 °C.

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 7.75 – 7.61 (m, 4H), 6.38 (br. s, 2H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 135.1, 132.4, 129.4, 126.8, 119.1, 119.0, 118.2, 117.1, 114.6, 112.6. (One quaternary carbon not observed).

IR (cm⁻¹): ν = 3068, 2362, 2230, 1602, 1574, 1544, 1520, 1496, 1399, 1310, 1264, 1203, 1105, 1019, 990, 950, 893, 840, 810, 800, 780, 734.

MS (70 eV, EI) m/z (%) = 341 (48), 340 (17), 339 (100) [M⁺], 296 (26), 294 (58), 161 (18), 146 (29), 102 (47), 76 (18).

HRMS for C₁₃H₆NCIS₄ (338.9072): found: 338.9074.
C. EXPERIMENTAL PART

Synthesis of diethyl TTF-4,5-dicarboxylate (33e)

According to TP 3, ethyl TTF-4-carboxylate (32g; 276 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -20 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of ethyl cyanoformate (119 mg, 1.2 mmol) in dry THF (2 mL) at -60 °C. The reaction mixture was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 2:1) yielding 33e as dark red solid (226 mg, 65%).

m.p.: 65.5 – 67.0 °C.

^1H-NMR (600 MHz, CDCl₃) δ/ppm = 6.43 (br. s, 2H), 4.29 (q, J = 7.1 Hz, 4H), 1.33 (t, J = 7.3 Hz, 6H).

^13C-NMR (151 MHz, CDCl₃) δ/ppm = 159.6, 132.2, 119.0, 116.4, 110.0, 62.7, 13.9.

IR (cm⁻¹): δ = 3094, 3069, 2987, 2972, 2932, 2906, 2361, 1736, 1687, 1567, 1541, 1518, 1476, 1446, 1394, 1367, 1286, 1271, 1218, 1113, 1087, 1031, 1016, 982, 925, 864, 849, 800, 775, 752, 734, 716, 676.

MS (70 eV, EI) m/z (%) = 350 (19), 349 (16), 348 (91) [M⁺], 276 (16), 250 (19), 249 (11), 248 (100), 203 (15), 148 (11), 146 (84), 102 (21), 88 (13), 76 (13).

HRMS for C₁₂H₁₂O₄S₄ (347.9618): found: 347.9614.

Synthesis of ethyl 5-(phenylthio)-TTF-4-carboxylate (33f)

According to TP 3, ethyl TTF-4-carboxylate (32g; 276 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -20 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of S-phenyl benzenethiosulfonate (300 mg, 1.2 mmol) in dry THF (2 mL)
C. EXPERIMENTAL PART

at -40 °C. The reaction mixture was allowed to warm up to -20 °C within 6 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 3:1) yielding 33f as red solid (226 mg, 59%).

m.p.: 108.7 – 109.8 °C.

1H-NMR (400 MHz, CDCl₃) δ/ppm = 7.69 – 7.62 (m, 2H), 7.52 – 7.45 (m, 1H), 7.45 – 7.37 (m, 2H), 6.30 (d, J = 6.4 Hz, 1H), 6.22 (d, J = 6.4 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H).

13C-NMR (101 MHz, CDCl₃) δ/ppm = 160.3, 148.4, 135.5, 130.9, 130.6, 129.2, 119.1, 118.6, 114.8, 113.8, 105.0, 61.8, 14.3.

IR (cm⁻¹): ν = 3067, 2975, 2903, 2359, 1948, 1682, 1574, 1557, 1522, 1496, 1472, 1452, 1440, 1390, 1364, 1243, 1175, 1163, 1118, 1078, 1022, 999, 945, 916, 888, 865, 828, 792, 776, 749, 734, 701, 686.

MS (70 eV, EI) m/z (%) = 384 (98) [M⁺], 356 (30), 218 (87), 146 (58), 141 (51), 134 (87), 121 (70), 110 (96), 109 (100), 102 (34), 77 (50).


Synthesis of ethyl 5-(methylthio)-TTF-4-carboxylate (33g)

According to TP 3, ethyl TTF-4-carboxylate (32g; 276 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -20 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of S-methyl methanethiosulfonate (151 mg, 1.2 mmol) in dry THF (2 mL) at -20 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 3:1) yielding 33g as red solid (209 mg, 65%).

m.p.: 102.5 – 103.4 °C.
C. EXPERIMENTAL PART

$^{1}$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 6.41 – 6.27 (m, 2H), 4.26 (q, $J$ = 7.1 Hz, 2H), 2.60 (s, 3H), 1.33 (q, $J$ = 7.1 Hz, 3H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 160.2, 148.0, 119.3, 118.6, 115.3, 113.6, 61.6, 18.2, 14.3. (One quaternary carbon not observed).

IR (cm$^{-1}$): $\tilde{\nu}$ = 3057, 2982, 2937, 2737, 2361, 1675, 1547, 1519, 1488, 1463, 1438, 1422, 1388, 1363, 1240, 1168, 1119, 1081, 1026, 966, 931, 888, 830, 798, 777, 749, 734, 659.

MS (70 eV, EI) m/z (%) = 324 (25), 323 (16), 322 (100) [M$^+$], 295 (37), 235 (17), 178 (14), 146 (53), 102 (30), 88 (16).

HRMS for C$_{10}$H$_{10}$O$_2$S$_5$ (321.9284): found: 321.9285.

Synthesis of (3-chlorophenyl)(5-iodo-TTF-4-yl)methanone (33h)

According to TP 4, TTF-4-yl-(3-chlorophenyl)methanone (32i; 343 mg, 1.0 mmol) was dissolved in dry THF (6.7 mL). TMP$_2$Zn·2MgCl$_2$·2LiCl (5; 1.69 mL, 1.1 mmol, 0.65 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (305 mg, 1.2 mmol) in dry THF (2 mL) at -50 °C. The reaction mixture was allowed to warm up to 0 °C within 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 3:1) yielding 33h as dark purple solid (389 mg, 83%).

m.p.: 135.9 – 136.8 °C.

$^{1}$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 7.82 (s, 1H), 7.73 (d, $J$ = 7.7 Hz, 1H), 7.59 (d, $J$ = 8.0 Hz, 1H), 7.44 (t, $J$ = 7.8 Hz, 1H), 6.36 (br. s, 2H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 186.1, 140.0, 137.3, 135.0, 133.6, 130.1, 129.5, 127.8, 119.2, 118.8, 112.9, 106.0, 92.7.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3084, 3064, 2921, 2852, 1886, 1633, 1589, 1566, 1520, 1457, 1420, 1377, 1278, 1243, 1227, 1168, 1101, 1083, 997, 966, 916, 890, 858, 795, 766, 738, 675.
4.5 Preparation of Trifunctionalized TTF-Derivatives

**Synthesis of diethyl 4'-iodo-TTF-4,5-dicarboxylate (34c)**

According to TP 5, diethyl TTF-4,5-dicarboxylate (33e; 348 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at -30 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (355 mg, 1.4 mmol) in dry THF (2 mL) at -60 °C. The reaction mixture was stirred at -60 °C for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 1:1) yielding 34c as red solid (427 mg, 90%).

**m.p.:** 58.8 – 60.6 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 6.44 (s, 1H), 4.30 (q, $J$ = 7.1 Hz, 4H), 1.33 (t, $J$ = 7.0 Hz, 6H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 159.4, 159.4, 132.1, 132.1, 124.0, 117.2, 106.0, 63.5, 62.8 (2C), 13.9 (2C).

IR (cm$^{-1}$): $\tilde{\nu}$ = 3088, 2988, 2942, 2359, 1702, 1573, 1558, 1538, 1512, 1466, 1448, 1392, 1368, 1301, 1243, 1188, 1118, 1090, 1028, 1012, 978, 918, 872, 856, 809, 786, 760, 743, 663.

**MS** (70 eV, El) $m/z$ (%) = 476 (21), 475 (17), 474 (100) [M$^+$], 402 (14), 374 (37), 290 (23), 272 (31), 247 (10), 218 (14), 190 (30), 145 (12), 101 (36), 88 (29), 69 (20), 57 (10), 45 (22).

**HRMS** for C$_{12}$H$_{11}$O$_4$S$_4$ (473.8585): found: 473.8582.
C. EXPERIMENTAL PART

Synthesis of diethyl 4’-(cyclohex-2-en-1-yl)-TTF-4,5-dicarboxylate (34d)

According to TP 5, diethyl TTF-4,5-dicarboxylate (33e; 348 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at -30 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of 3-bromocyclohexene (225 mg, 1.4 mmol) and CuCN·2LiCl (0.20 mL, 0.20 mmol, 1.0 M in THF) in dry THF (2 mL) at -40 °C. The reaction mixture was stirred for 1.5 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 2:1) yielding 34d as dark red oil (356 mg, 83%).

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 5.95 (s, 1H), 5.90 – 5.84 (m, 1H), 5.67 – 5.61 (m, 1H), 4.29 (q, J = 7.1 Hz, 4H), 3.22 (br. s, 1H), 2.07 – 1.98 (m, 2H), 1.92 – 1.85 (m, 1H), 1.76 – 1.55 (m, 3H), 1.33 (t, J = 7.1 Hz, 6H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 159.7 (2C), 141.8, 132.2 (2C), 130.1, 127.1, 117.2, 112.2, 103.0, 62.6 (2C), 37.8, 29.5, 24.8, 20.1, 13.9 (2C).

IR (cm⁻¹): ν = 3063, 3022, 2981, 2933, 2858, 2834, 2361, 2342, 1709, 1569, 1531, 1444, 1390, 1366, 1235, 1115, 1088, 1027, 917, 896, 884, 857, 810, 758, 746, 723, 709, 689.

MS (70 eV, EI) m/z (%) = 430 (19), 429 (21), 428 (100) [M⁺], 356 (11), 328 (31), 190 (20).

HRMS for C₁₈H₂₀O₄S₄ (428.0244): found: 428.0240.

Synthesis of diethyl 4’-(4-(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (34e)

According to TP 5, diethyl TTF-4,5-dicarboxylate (33e; 348 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at -30 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was...
added to a solution of ethyl 4-iodobenzoate (221 mg, 0.8 mmol), Pd(dba)$_2$ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 1 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH$_2$Cl$_2$, 7:3) yielding 34e as dark red solid (467 mg, 94%).

m.p.: 128.9 – 130.4 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) δ/ppm = 8.03 (d, $J$ = 8.1 Hz, 2H), 7.43 (d, $J$ = 8.1 Hz, 2H), 6.69 (br. s, 1H), 4.39 (q, $J$ = 7.2 Hz, 2H), 4.31 (q, $J$ = 7.2 Hz, 4H), 1.40 (t, $J$ = 7.2 Hz, 3H), 1.34 (t, $J$ = 7.2 Hz, 6H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) δ/ppm = 165.8, 159.5 (2C), 135.9, 135.2, 132.2, 132.2, 130.2 (2C), 130.1, 126.0 (2C), 115.8, 114.3, 105.9, 62.7 (2C), 61.2, 14.3, 13.9 (2C).

IR (cm$^{-1}$): $\tilde{\nu}$ = 2982, 2360, 2341, 1718, 1705, 1606, 1571, 1556, 1466, 1408, 1394, 1364, 1317, 1277, 1253, 1212, 1184, 1127, 1108, 1084, 1033, 926, 850, 828, 772, 743, 692, 668.

MS (70 eV, El) m/z (%) = 498 (21), 497 (25), 496 (100) [M$^+$], 424 (13), 396 (21), 368 (19), 294 (13), 266 (11).

HRMS for C$_{21}$H$_{20}$O$_6$S$_4$ (496.0143): found: 496.0138.

**Synthesis of diethyl 4'-(4-cyanophenyl)-TTF-4,5-dicarboxylate (34f)**

![Chemical Structure](attachment:image.png)

According to **TP 5**, diethyl TTF-4,5-dicarboxylate (33e; 348 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at -30 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of 4-iodobenzonitrile (183 mg, 0.8 mmol), Pd(dba)$_2$ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 1 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH$_2$Cl$_2$, 3:7) yielding 34f as dark red solid (297 mg, 66%).
**C. EXPERIMENTAL PART**

**m.p.:** 175.8 – 177.7 °C.

**$^1$H-NMR** (600 MHz, CDCl$_3$) $\delta$/ppm = 7.66 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 6.72 (br. s, 1H), 4.31 (q, $J = 7.0$ Hz, 4H), 1.35 (t, $J = 7.0$ Hz, 6H).

**$^{13}$C-NMR** (151 MHz, CDCl$_3$) $\delta$/ppm = 159.4 (2C), 136.0, 134.2, 132.7 (2C), 132.1 (2C), 126.6 (2C), 118.3, 117.3, 113.3, 111.8, 62.8 (2C), 13.9 (2C). (One quaternary carbon not observed).

**IR** (cm$^{-1}$): $\tilde{\nu} = 3071, 2978, 2930, 2360, 2222, 1733, 1694, 1600, 1579, 1560, 1544, 1474, 1450, 1410, 1367, 1283, 1255, 1201, 1176, 1119, 1088, 1041, 924, 869, 855, 838, 829, 774, 758, 709, 685.

**MS** (70 eV, EI) $m/z$ (%) = 451 (32), 450 (36) [M+H$^+\$], 377 (31), 351 (21), 350 (20), 349 (100), 304 (10), 260 (19), 248 (11), 247 (65), 171 (13), 170 (14), 159 (21), 146 (10), 146 (24), 127 (54), 88 (11), 76 (21).

**HRMS** for C$_{19}$H$_{16}$O$_4$NS$_4$ (M+H$^+$; 449.9962): found: 449.9933.

**Synthesis of diethyl 4'-{(4-methoxyphenyl)-TTF-4,5-dicarboxylate (34g)}**

According to TP 5, diethyl TTF-4,5-dicarboxylate (33e; 348 mg, 1.0 mmol) was dissolved in dry THF (4 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at -30 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of 4-iodoanisole (187 mg, 0.8 mmol), Pd(dba)$_2$ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 1 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 3:2) yielding 34g as red solid (332 mg, 73%).

**m.p.:** 96.5 – 101.9 °C.

**$^1$H-NMR** (600 MHz, CDCl$_3$) $\delta$/ppm = 7.33 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.35 (s, 1H), 4.30 (q, $J = 7.0$ Hz, 4H), 3.83 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 6H).
C. EXPERIMENTAL PART

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 159.9, 159.6, 159.6, 135.8, 132.2, 132.2, 127.7 (2C), 124.9, 115.9, 114.2 (2C), 110.9, 104.5, 62.7 (2C), 55.4, 13.9 (2C).

IR (cm$^{-1}$): $\bar{\nu}$ = 3056, 2981, 2964, 2934, 2841, 2360, 2342, 1730, 1719, 1650, 1626, 1608, 1577, 1561, 1472, 1462, 1442, 1418, 1392, 1362, 1343, 1302, 1178, 1094, 1029, 1020, 928, 922, 884, 859, 850, 831, 304, 782, 773, 746, 708, 694, 671.

MS (70 eV, EI) m/z (%) = 456 (21), 455 (26), 454 (100) [M$^+$], 382, (17), 357, (10), 355 (40), 265 (14), 252 (28), 149 (12), 146 (16), 132 (31), 89 (13), 76 (17).

HRMS for C$_{19}$H$_{18}$O$_5$S$_4$ (454.0037): found: 454.0029.

4.6 Preparation of Tetrafunctionalized TTF-Derivatives

Synthesis of diethyl 4'-4(ethoxycarbonyl)phenyl)-5'-iodo-TTF-4,5-dicarboxylate (35a)

According to TP 6, diethyl 4'-4(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (34e; 497 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (355 mg, 1.4 mmol) in dry THF (6 mL) at -20 °C. The reaction mixture was stirred for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 1:2) yielding 35a as red solid (548 mg, 88%).

m.p.: 138.2 – 140.1 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 8.08 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 4.40 (q, $J = 7.0$ Hz, 2H), 4.34 – 4.27 (m, 4H), 1.41 (t, $J = 7.1$ Hz, 3H), 1.36 – 1.30 (m, 6H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 165.7, 159.4 (2C), 136.9, 134.0, 132.2, 132.1, 131.3, 129.9 (2C), 129.2 (2C), 115.7, 107.4, 64.3, 62.8 (2C), 61.3, 14.3, 13.9 (2C).
IR (cm⁻¹): $\tilde{\nu} = 2978, 2930, 2361, 2340, 1714, 1604, 1583, 1550, 1464, 1388, 1367, 1293, 1257, 1185, 1097, 1024, 944, 920, 860, 843, 811, 773, 752, 700, 671.$

**MS** (70 eV, EI) m/z (%) = 622 (9) [M⁺], 292 (8), 290 (6), 250 (6), 249 (6), 234 (6), 233 (5), 206 (5), 204 (9), 190 (8), 161 (8), 149 (9).

HRMS for C$_{21}$H$_{19}$O$_{6}$S$_{4}$ (621.9109): found: 621.9120.

**Synthesis of diethyl 4’-(4-cyanophenyl)-5’-ido-TTF-4,5-dicarboxylate (35b)**

According to TP 6, diethyl 4’-(4-cyanophenyl)-TTF-4,5-dicarboxylate (34f; 450 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl-LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (355 mg, 1.4 mmol) in dry THF (2 mL) at -20 °C. The reaction mixture was stirred for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH$_2$Cl$_2$, 2:3) yielding 35b as reddish brown solid (437 mg, 76%).

**m.p.:** 141.9 – 144.0 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) δ/ppm = 7.71 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 2H), 4.34 – 4.26 (m, 4H), 1.37 – 1.29 (m, 6H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) δ/ppm = 159.3 (2C), 137.2, 132.9, 132.5 (2C), 132.1 (2C), 129.9 (2C), 118.0, 114.8, 113.1, 108.3, 65.7, 62.8 (2C), 13.9 (2C).

IR (cm⁻¹): $\tilde{\nu} = 2985, 2361, 2342, 2228, 1736, 1688, 1603, 1573, 1557, 1545, 1479, 1444, 1392, 1365, 1288, 1229, 1116, 1086, 1030, 984, 922, 837, 771, 750, 715, 668.$

**MS** (70 eV, EI) m/z (%) = 577 (17), 576 (23), 575 (100) [M⁺], 451 (13), 450 (15), 449 (46), 377 (13), 372 (10), 349 (40), 290 (55), 247 (23), 190 (43), 170 (11), 159 (24), 158 (13), 146 (25), 127 (24), 114 (16), 88 (22), 76 (12).

HRMS for C$_{19}$H$_{14}$O$_{6}$NIS$_4$ (574.8850): found: 574.8854.
Synthesis of diethyl 4',5'-bis(4-(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (35c)

According to TP 6, diethyl 4'-{(4-(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (34e; 497 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl-LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of ethyl 4-iodobenzoate (221 mg, 0.8 mmol), Pd(dba)₂ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 12 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 1:4) yielding 35c as red solid (580 mg, 90%).

m.p.: 131.7 – 133.9 °C.

¹H-NMR (600 MHz, CDCl₃) δ/ ppm = 7.91 (d, J = 8.5 Hz, 4H), 7.24 (d, J = 8.5 Hz, 4H), 4.36 (q, J = 7.1 Hz, 4H), 4.31 (q, J = 7.1 Hz, 4H), 1.38 (t, J = 7.1 Hz, 6H), 1.34 (t, J = 7.1 Hz, 6H).

¹³C-NMR (151 MHz, CDCl₃) δ/ ppm = 165.7, 159.5, 136.3, 132.3, 130.6, 129.6, 129.0, 111.9, 106.3, 62.8, 61.2, 14.3, 13.9.

IR (cm⁻¹): ν = 2981, 2361, 1710, 1604, 1573, 1446, 1407, 1366, 1269, 1178, 1099, 1018, 860, 758, 698, 668.

MS (70 eV, EI) m/z (%) = 646 (26), 645 (40), 644 (100) [M⁺], 572 (17), 146 (12).

HRMS for C₃₀H₂₆O₈S₄ (644.0667): found: 644.0656.
Synthesis of diethyl 4',5'-bis(4-cyanophenyl)-TTF-4,5-dicarboxylate (35d)

According to TP 6, diethyl 4’-(4-cyanophenyl)-TTF-4,5-dicarboxylate (34f; 450 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl-LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of 4-iodobenzonitrile (183 mg, 0.8 mmol), Pd(dba)$_2$ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 12 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with CH$_2$Cl$_2$ (3 × 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH$_2$Cl$_2$, 1:4) yielding 35d as red solid (347 mg, 63%).

m.p.: 162.8 – 165.5 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) δ/ppm = 7.56 (d, $J = 8.2$ Hz, 4H), 7.28 (d, $J = 8.5$ Hz, 4H), 4.31 (q, $J = 7.1$ Hz, 4H), 1.34 (t, $J = 7.1$ Hz, 6H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) δ/ppm = 159.3, 136.1, 132.7, 132.2, 129.7, 117.9, 112.8, 110.0, 108.3, 62.9, 13.9. (One quaternary carbon not observed).

IR (cm$^{-1}$): $\tilde{\nu}$ = 2360, 2340, 2226, 1743, 1570, 1243, 1091, 1026, 850, 814, 758, 668.

MS (70 eV, El) m/z (%) = 552 (26), 551 (34), 550 (100) [M$^+$], 478 (28), 451 (11), 450 (31), 348 (27), 260 (26), 229 (10), 228 (49), 215 (12), 146 (14), 146 (31), 76 (23).

HRMS for C$_{26}$H$_{18}$O$_4$N$_2$S$_4$ (550.0149): found: 550.0144.
Synthesis of diethyl 4',5'-bis(4-methoxyphenyl)-TTF-4,5-dicarboxylate (35e)

According to TP 6, diethyl 4'-((4-cyanophenyl)-TTF-4,5-dicarboxylate (34g; 455 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl-LiCl (4; 1.04 mL, 1.3 mmol, 1.25 m in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of 4-iodoanisole (187 mg, 0.8 mmol), Pd(dba)$_2$ (17.3 mg, 0.03 mmol) and tfp (13.9 mg, 0.06 mmol) in dry THF (2 mL) at 25 °C. The reaction mixture was stirred for 12 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH$_2$Cl$_2$, 2:3) yielding 35e as red solid (353 mg, 63%).

m.p.: 117.1 – 125.0 °C.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$/ppm = 7.13 (d, $J = 8.2$ Hz, 4H), 6.77 (d, $J = 8.5$ Hz, 4H), 4.30 (q, $J = 7.1$ Hz, 4H), 3.78 (s, 6H), 1.34 (t, $J = 7.1$ Hz, 6H).

$^{13}$C-NMR (151 MHz, CDCl$_3$) $\delta$/ppm = 159.5, 143.3, 132.3, 130.5, 130.4, 129.0, 128.4, 125.4, 114.0, 62.7, 55.2, 14.0.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3006, 2982, 2961, 2927, 2853, 2837, 1730, 1715, 1650, 1626, 1603, 1570, 1537, 1509, 1499, 1461, 1447, 1415, 1391, 1370, 1343, 1293, 1245, 1188, 1173, 1113, 1094, 1024, 982, 953, 915, 873, 847, 833, 811, 806, 759, 694, 666.

MS (70 eV, El) $m/z$ (%) = 562 (22), 561 (32), 560 (100) [M$^+$], 371 (11), 270 (16), 238 (21), 223 (24).

HRMS for C$_{26}$H$_{24}$O$_6$S$_4$ (560.0456): found: 560.0455.
Synthesis of diethyl 4’-(2-(ethoxycarbonyl)allyl)-5’-(4-(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (35f)

According to TP 6, diethyl 4’-(4-(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (34e; 497 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of ethyl 2-(bromomethyl)acrylate 38 (154 mg, 0.8 mmol) and CuCN∙2LiCl (0.20 mL, 0.20 mmol, 1.0 M in THF) in dry THF (2 mL) at -40 °C. The reaction mixture was stirred at 25 °C for 48 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 1:4) yielding 35f as red oil (323 mg, 53%).

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 8.05 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 6.34 (s, 1H), 5.74 (s, 1H), 4.39 (q, J = 7.1 Hz, 2H), 4.33 – 4.25 (m, 4H), 4.25 – 4.17 (m, 2H), 3.41 (s, 2H), 1.44 – 1.37 (m, 3H), 1.37 – 1.21 (m, 9H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 165.8, 165.8, 159.6, 159.6, 136.9, 136.2, 132.3, 132.2, 130.8, 130.0 (2C), 129.2, 128.7 (2C), 128.5, 127.4, 113.2, 104.8, 62.7 (2C), 61.2, 61.2, 31.8, 14.3, 14.1, 13.9 (2C).

IR (cm⁻¹): ν = 2981, 2937, 2905, 2361, 2341, 1711, 1631, 1606, 1574, 1534, 1505, 1464, 1445, 1404, 1391, 1367, 1328, 1270, 1242, 1175, 1146, 1092, 1021, 952, 916, 857, 815, 758, 731, 700.

MS (70 eV, EI) m/z (%) = 610 (22), 609 (30), 608 (100) [M⁺], 538 (14), 537 (12), 536 (40), 508 (15), 424 (20), 190 (12), 146 (11).

HRMS for C₂₇H₂₈O₈S₄ (608.0667): found: 608.0664.
C. EXPERIMENTAL PART

Synthesis of diethyl 4'-benzoyl-5'-(4-(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (35g)

According to TP 6, diethyl 4'-(4-(ethoxycarbonyl)phenyl)-TTF-4,5-dicarboxylate (34e; 497 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of benzoyl chloride (197 mg, 1.4 mmol) and Pd(PPh₃)₄ (116 mg, 0.10 mmol) in dry THF (4 mL) at 25 °C. The reaction mixture was stirred for 2.5 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 1:4) yielding 35g as red solid (511 mg, 85%).

m.p.: 69.9 – 72.8 °C.

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 7.77 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.20 – 7.15 (m, 2H), 4.36 – 4.28 (m, 6H), 1.38 – 1.31 (m, 9H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 187.9, 165.4, 159.3 (2C), 142.2, 135.7, 135.3, 133.3, 132.5, 131.8 (2C), 129.5 (2C), 129.3 (2C), 129.2 (2C), 128.2 (2C), 128.0, 110.4, 109.1, 62.8 (2C), 61.2, 14.2, 13.9 (2C).

IR (cm⁻¹): ν = 2985, 2360, 2341, 1715, 1632, 1579, 1446, 1366, 1274, 1252, 1173, 1094, 1016, 916, 863, 810, 768, 758, 718, 693, 657.

MS (70 eV, El) m/z (%) = 602 (25), 601 (36), 600 (100) [M⁺], 528 (15), 500 (13), 262 (12), 190 (13), 105 (82), 77 (37).

HRMS for C₂₈H₂₄O₇S₄ (600.0405): found: 600.0405.
Synthesis of diethyl 4'-((3-chlorobenzoyl)-5'-((4-cyanophenyl)-TTF-4,5-dicarboxylate (35h)

According to TP 6, diethyl 4'-((4-cyanophenyl)-TTF-4,5-dicarboxylate (34f; 450 mg, 1.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl·LiCl (4; 1.04 mL, 1.3 mmol, 1.25 m in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of 3-chlorobenzoyl chloride (245 mg, 1.4 mmol) and Pd(PPh3)4 (116 mg, 0.10 mmol) in dry THF (4 mL) at 25 °C. The reaction mixture was stirred for 3 h and was then quenched with sat. aq. NH4Cl solution (5 mL), extracted with CH2Cl2 (3 x 10 mL) and dried over anhydrous Na2SO4. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH2Cl2, 1:4) yielding 35h as red solid (470 mg, 80%).

m.p.: 47.4 – 49.3 °C.

1H-NMR (600 MHz, CDCl3) δ/ppm = 7.50 – 7.39 (m, 4H), 7.38 – 7.27 (m, 3H), 7.20 – 7.12 (m, 1H), 4.32 (q, J = 7.1 Hz, 4H), 1.34 (t, J = 7.1 Hz, 6H).

13C-NMR (151 MHz, CDCl3) δ/ppm = 185.9, 159.3, 159.2, 142.5, 137.2, 135.4, 134.5, 133.2, 132.5, 132.1 (2C), 131.7, 131.6, 129.9 (2C), 129.7, 129.3, 127.2, 117.6, 113.6, 110.8, 108.9, 62.9, 62.9, 13.9 (2C).

IR (cm⁻¹): ν = 3430, 3065, 2982, 2938, 2360, 2341, 2229, 1722, 1634, 1604, 1580, 1560, 1548, 1493, 1471, 1444, 1419, 1392, 1367, 1239, 1115, 1088, 1026, 945, 911, 852, 825, 796, 731, 717, 706, 681.

MS (70 eV, EI) m/z (%) = 590 (19), 589 (69) [M+2H⁺], 588 (37), 489 (11), 487 (22), 290 (11), 190 (20), 174 (11), 154 (13), 146 (17), 139 (100), 111 (42), 88 (10), 76 (21), 75 (13).

HRMS for C26H20O5NS4 (M+2H⁺; 588.9913): found: 588.9745.
5. Selective Functionalization of 1,4-Dithiin Using TMP-Bases: Access to New Heterocycles

5.1 Typical Procedures

Typical Procedure 1 for the magnesiation of 1,4-dithiin (38) with TMPMgCl-LiCl (2) (TP 1):

A dry and argon flushed Schlenk-flask was charged with a solution of 1,4-dithiin (38; 1.0 equiv) in dry THF (0.5 M). TMPMgCl-LiCl (2; 1.1 equiv, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF using undecane as internal standard.

Typical Procedure 2 for the zincation of monofunctionalized 1,4-dithiin derivatives (40) with TMPZnCl-LiCl (4) (TP 2):

A dry and argon flushed Schlenk-flask was charged with a solution of the corresponding monofunctionalized 1,4-dithiin derivative (1.0 equiv) in dry THF (0.5 M). TMPZnCl-LiCl (4; 1.1 equiv, 1.33 M in THF) was added dropwise at the indicated temperature and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with iodine in dry THF.

Typical Procedure 3 for the preparation of 1,4-dithiin-fused quinolines (TP 3):

According to the literature, the corresponding aldehyde (1.3 equiv) was added to a solution of 2-(1,4-dithiin-2-yl)aniline (40o; 1.0 equiv) and TFA (2 equiv) in EtOH (0.25 M) at 25 °C. The reaction mixture was heated using a Biotage Initiator 2.5 system (130 °C, 100 W, 15 min) and was then allowed to cool to 25 °C. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq. NH₄Cl solution.

Typical Procedure 4 for Sonogashira reactions (TP 4):

The corresponding iodinated 1,4-dithiin (1.0 equiv) was added to a solution of the alkyne (1.5 equiv), Cul (2 mol%) and Pd(PPh₃)₂Cl₂ (1 mol%) in NEt₃ (0.2 M) at 25 °C. The reaction mixture was stirred until full conversion of the 1,4-dithiine derivative was detected. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq. NH₄Cl solution.
Typical Procedure 5 for electrophilic cyclizations with iodine (TP 5):

According to the literature, a solution of iodine (1.2 equiv) in dry CH₂Cl₂ (0.15 M) was added dropwise to a solution of the corresponding alkynylated ethyl 1,4-dithiane-2-carboxylate (1.0 equiv) in dry CH₂Cl₂ (0.08 M) at 25 °C. The reaction mixture was stirred for the indicated time. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq. Na₂S₂O₃ solution.

5.2 Preparation of 1,4-Dithiin

According to the literature, thionyl chloride (18.5 g, 11.3 mL, 156 mmol) was added to a solution of 1,4-dithiane-2,5-diol (37; 6.77 g, 44.4 mmol) in dry DMF (250 mL) at 0 °C. After the addition, the reaction mixture was stirred at 25 °C for 2 h. The product which co-distills with DMF, was distilled under reduced pressure (100 °C, 270 mbar). After reducing half of the volume, more dry DMF (100 mL) was added to the reaction flask and the distillation was continued until a black residue was left. The distilled DMF was extracted with water (150 mL) and Et₂O (400 mL). The organic layer was washed with water (3 x 150 mL), sat. aq. NaHCO₃ solution (2 x 100 mL) and sat. aq. NaCl solution (100 mL). The organic layer was dried over anhydrous MgSO₄ and, after filtration, the solvent was evaporated in vacuo. 1,4-Dithiin (38) was obtained as yellow liquid (4.18 g, 81%) and was used without further purification.

¹H-NMR (200 MHz, CDCl₃) δ/ppm = 6.18 (s, 4H).

5.3 Preparation of Monofunctionalized 1,4-Dithiin-Derivatives

Synthesis of 2-iodo-1,4-dithiin (40a)

According to TP 1, 1,4-dithiin (38; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to
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a solution of iodine (177 mg, 0.7 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane) yielding 40a as yellow liquid (114 mg, 67%).

1H-NMR (300 MHz, CDCl₃) δ/ppm = 6.52 – 6.46 (m, 2H), 6.24 (d, J = 6.6 Hz, 1H).

13C-NMR (75 MHz, CDCl₃) δ/ppm = 125.9, 122.7, 121.7, 72.9.

IR (cm⁻¹): ν = 3025, 2921, 1678, 1598, 1554, 1534, 1469, 1273, 1217, 1134, 885, 839, 794, 768, 732, 668, 566.

MS (70 eV, EI) m/z (%) = 242 (69) [M⁺], 115 (100), 89 (21), 71 (78), 57 (30), 45 (56).

HRMS for C₄H₃IS₂ (241.8721): found: 241.8723.

Synthesis of 2-bromo-1,4-dithiin (40b)

According to TP 1, 1,4-dithiin (38; 116 mg, 5.0 mmol) was dissolved in dry THF (10 mL). TMPMgCl·LiCl (2; 4.95 mL, 5.5 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of 1,2-dibromotetrachloroethane (1.14 g, 3.5 mmol) in dry THF (5 mL) at -78 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (10 mL), extracted with Et₂O (3 x 80 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane) yielding 40b as yellow liquid (529 mg, 77%).

1H-NMR (400 MHz, CDCl₃) δ/ppm = 6.52 – 6.46 (m, 2H), 6.23 (d, J = 6.5 Hz, 1H).

13C-NMR (101 MHz, CDCl₃) δ/ppm = 126.0, 122.8, 121.9, 73.0.

IR (cm⁻¹): ν = 3031, 1563, 1555, 1524, 1503, 1493, 1468, 1446, 1413, 1322, 1275, 1218, 1188, 1135, 1091, 1070, 1031, 1011, 919, 886, 860, 827, 799, 773, 752, 701, 668.

MS (70 eV, EI) m/z (%) = 196 (53), 194 (47) [M⁺], 115 (100), 71 (41), 57 (10), 45 (16).

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**Synthesis of 2-chloro-1,4-dithiin (40c)**

According to **TP 1**, 1,4-dithiin (38; 813 mg, 7.0 mmol) was dissolved in dry THF (14 mL). TMPMgCl·LiCl (2; 6.94 mL, 7.7 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of benzenesulfonyl chloride (865 mg, 4.9 mmol) in dry THF (5 mL) at -78 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (10 mL), extracted with Et₂O (3 x 80 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 40c as yellow liquid (413 mg, 56%).

**¹H-NMR** (400 MHz, CDCl₃) δ/ppm = 6.35 (d, J = 6.7, 1H), 6.32 (d, J = 6.7 Hz, 1H), 6.14 (s, 1H).

**¹³C-NMR** (101 MHz, CDCl₃) δ/ppm = 123.0, 122.6, 122.3, 117.3.

**IR** (cm⁻¹): ν = 3035, 2922, 2179, 1601, 1579, 1548, 1528, 1455, 1402, 1278, 1206, 1136, 1065, 971, 928, 896, 818, 770, 668.

**MS** (70 eV, EI) m/z (%) = 152 (21), 150 (52) [M⁺], 115 (87), 105 (13), 89 (14), 88 (17), 79 (12), 71 (45), 58 (23), 57 (52), 45 (100).

**HRMS** for C₄H₃ClS₂ (149.9365): found: 149.9355.

**Synthesis of 1,4-dithiin-2-carbonitrile (40d)**

According to **TP 1**, 1,4-dithiin (38; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of p-toluenesulfonyl cyanide (127 mg, 0.7 mmol) in dry THF (2 mL) at -60 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/Et₂O, 95:5) yielding 40d as orange liquid (59 mg, 60%).
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\[ ^1H\text{-NMR} \ (300 \text{ MHz, CDCl}_3) \delta/\text{ppm} = 7.13 \ (s, 1H), 6.37 - 6.21 \ (m, 2H). \]

\[ ^{13}C\text{-NMR} \ (75 \text{ MHz, CDCl}_3) \delta/\text{ppm} = 140.0, 122.0, 121.1, 114.4, 105.3. \]

IR (cm\(^{-1}\)): \( \tilde{\nu} = 3034, 2924, 2217, 1654, 1594, 1558, 1525, 1447, 1313, 1281, 1240, 1176, 1140, 1084, 1054, 999, 958, 932, 892, 851, 805, 785, 674, 661. \)

MS (70 eV, EI) m/z (%) = 141 (100) [M\(^+\)], 114 (19), 96 (13), 71 (27), 45 (33).

HRMS for C\(_5\)H\(_3\)NS\(_2\) (140.9707): found: 140.9694.

**Synthesis of ethyl 2-(methylthio)-1,4-dithiin (40e)**

![Structural diagram of ethyl 2-(methylthio)-1,4-dithiin](image)

According to TP 1, 1,4-dithiin (38; 349 mg, 3.0 mmol) was dissolved in dry THF (6 mL). TMPMgCl\(\cdot\)LiCl (2; 2.97 mL, 3.3 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of S-methyl methanethiosulfonate (265 mg, 2.1 mmol) in dry THF (3 mL) at -60 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH\(_4\)Cl solution (10 mL), extracted with Et\(_2\)O (3 x 70 mL) and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 40e as yellow liquid (254 mg, 75%).

\[ ^1H\text{-NMR} \ (400 \text{ MHz, CDCl}_3) \delta/\text{ppm} = 6.46 - 6.39 \ (m, 1H), 6.36 \ (d, J = 6.6 \text{ Hz, 1H}), 5.97 \ (s, 1H), 2.40 \ (s, 3H). \]

\[ ^{13}C\text{-NMR} \ (101 \text{ MHz, CDCl}_3) \delta/\text{ppm} = 132.9, 124.6, 122.7, 114.5, 18.0. \]

IR (cm\(^{-1}\)): \( \tilde{\nu} = 3027, 2986, 2915, 2849, 2823, 1669, 1573, 1543, 1515, 1427, 1417, 1312, 1278, 1228, 1133, 970, 954, 900, 813, 779, 764, 742, 669. \)

MS (70 eV, EI) m/z (%) = 164 (13), 163 (18), 162 (85) [M\(^+\)], 149 (16), 147 (52), 116 (36), 115 (52), 103 (61), 97 (18), 91 (15), 85 (29), 83 (16), 71 (44), 71 (32), 69 (26), 58 (16), 57 (59), 57 (14), 55 (29), 47 (14), 45 (59), 44 (100), 43 (46), 43 (25), 41 (26).

HRMS for C\(_5\)H\(_6\)S\(_3\) (161.9632): found: 161.9630.
**C. EXPERIMENTAL PART**

**Synthesis of 2-(phenylthio)-1,4-dithiin (40f)**

\[
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{Ph} \\
\text{S} \\
\text{S}
\end{array}
\]

According to **TP 1**, 1,4-dithiin (38; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl•LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of S-phenyl benzenethiosulfonate (175 mg, 0.7 mmol) in dry THF (1 mL) at -60 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane) yielding **40f** as yellow liquid (121 mg, 77%).

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 7.47 – 7.28 (m, 5H), 6.39 – 6.25 (m, 3H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 133.5, 130.6, 129.23, 128.7, 127.8, 123.1, 122.7, 122.6.


**MS** (70 eV, EI) m/z (%) = 224 (97) [M⁺], 134 (22), 121 (25), 115 (100), 109 (28), 103 (20), 77 (25), 71 (25), 45 (21).

**HRMS** for C₁₀H₈S₃ (223.9788): found: 223.9765.

**Synthesis of (1,4-dithiin-2-yl)(phenyl)methanol (40g)**

\[
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{OH} \\
\text{Ph}
\end{array}
\]

According to **TP 1**, 1,4-dithiin (38; 58 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPMgCl•LiCl (2; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of benzaldehyde (37 mg, 0.35 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash...
C. EXPERIMENTAL PART

Column chromatography on silica gel (hexane/EtOAc, 7:1) yielding 40g as yellowish solid (75 mg, 97%).

m.p.: 64.9 – 68.3 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$/ppm = 7.47 – 7.29 (m, 5H), 6.34 (d, $J = 6.8$ Hz, 1H), 6.28 (s, 1H), 6.20 (d, $J = 6.8$ Hz, 1H), 5.36 (s, 1H), 2.60 (br. s, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$/ppm = 140.3, 139.6, 128.5, 128.3, 126.6, 123.7, 121.9, 118.3, 75.7.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3791, 3271, 3029, 3016, 2894, 2666, 1957, 1887, 1728, 1711, 1598, 1587, 1573, 1564, 1537, 1492, 1461, 1446, 1392, 1372, 1322, 1301, 1267, 1218, 1187, 1177, 1157, 1142, 1092, 1070, 1031, 1011, 919, 892, 859, 827, 794, 777, 748, 699, 687, 672.

MS (70 eV, El) m/z (%) = 223 (15), 222 (100) [M$^+$], 116 (60), 107 (23), 105 (36), 103 (13), 79 (54), 77 (64), 71 (36), 58 (11), 45 (23).

HRMS for C$_{11}$H$_{10}$OS$_2$ (222.0173): found: 222.0169.

Synthesis of ethyl 1,4-dithiin-2-carboxylate (40h)

According to TP 1, 1,4-dithiin (38; 697 mg, 6.0 mmol) was dissolved in dry THF (12 mL). TMPMgCl-LiCl (2; 5.95 mL, 6.6 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of ethyl cyanoformate (417 mg, 4.2 mmol) in dry THF (6 mL) at -60 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH$_4$Cl solution (10 mL), extracted with Et$_2$O (3 x 70 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/Et$_2$O, 95:5) yielding 40h as red liquid (704 mg, 89%).

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 7.27 (s, 1H), 6.17 (d, $J = 7.2$ Hz, 1H), 6.02 (d, $J = 7.2$ Hz, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.2$ Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 161.1, 133.8, 125.6, 122.0, 119.6, 62.0, 14.1.
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IR (cm⁻¹): \( \tilde{\nu} = 3037, 2980, 2932, 2904, 1702, 1573, 1533, 1464, 1444, 1391, 1366, 1292, 1243, 1218, 1171, 1111, 1094, 1040, 994, 889, 850, 830, 790, 731, 666 \).

MS (70 eV, EI) m/z (%) = 190 (12), 189 (12), 188 (100) [M⁺], 162 (10), 160 (91), 143 (16), 142 (26), 115 (22), 114 (18), 111 (19).


Synthesis of ethyl 2-(1,4-dithin-2-yl)-2-oxoacetate (40i)

According to TP 1, 1,4-dithiin (38; 232 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (2; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before ethyl 2-chloro-2-oxoacetate (191 mg, 1.4 mmol) was added. The reaction mixture was stirred at -40 °C for 3 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 2:1) yielding 40i as red liquid (170 mg, 56%).

¹H-NMR (400 MHz, CDCl₃) \( \delta/\text{ppm} = 7.73 \) (s, 1H), 6.15 (d, J = 7.2 Hz, 1H), 5.97 (d, J = 7.6 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.43 – 1.32 (m, 3H).

¹³C-NMR (101 MHz, CDCl₃) \( \delta/\text{ppm} = 177.3, 161.8, 143.3, 129.8, 121.5, 118.4, 62.8, 14.0 \).

IR (cm⁻¹): \( \tilde{\nu} = 3039, 2982, 2937, 1725, 1659, 1562, 1521, 1469, 1444, 1390, 1368, 1310, 1286, 1253, 1138, 1008, 904, 857, 825, 789, 730, 669, 645, 563 \).

MS (70 eV, EI) m/z (%) = 216 (76) [M⁺], 143 (67), 116 (10), 115 (100), 111 (10), 89 (12), 71 (43), 45 (22).

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Synthesis of 1-(1,4-dithiin-2-yl)-2,2-dimethylpropan-1-one (40j)

According to TP 1, 1,4-dithiin (38; 232 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl-LiCl (2; 1.98 mL, 2.24 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN₂LiCl solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before pivaloyl chloride (169 mg, 1.4 mmol) was added. The reaction mixture was stirred at 25 °C for 20 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/Et₂O, 96:4) yielding 40j as red solid (84 mg, 62%).

m.p.: 102.5 - 103.1 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 6.95 (s, 1H), 6.29 (d, J = 6.8 Hz, 1H), 6.25 (d, J = 6.8 Hz, 1H), 1.27 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 201.3, 134.1, 129.9, 122.8, 122.4, 44.1, 27.6.

IR (cm⁻¹): ν = 3091, 2954, 2357, 1752, 1692, 1637, 1562, 1527, 1468, 1461, 1395, 1365, 1292, 1260, 1210, 1126, 1019, 937, 898, 872, 854, 823, 792, 769, 736, 676, 663.

MS (70 eV, El) m/z (%) = 200 (80) [M⁺], 144 (17), 143 (41), 116 (30), 115 (56), 71 (28), 69 (11), 57 (100), 45 (13), 41 (34).

HRMS for C₉H₁₂O₃S₂ (200.0330): found: 200.0327.

Synthesis of (3-chlorophenyl)(1,4-dithiin-2-yl)methanone (40k)

According to TP 1, 1,4-dithiin (38; 58 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPMgCl-LiCl (2; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was
added and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before 3-chlorobenzoyl chloride (61 mg, 0.35 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/Et₂O, 94:6) yielding 40k as red oil (71 mg, 80%).

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.69 – 7.63 (m, 1H), 7.59 – 7.50 (m, 2H), 7.44 – 7.37 (m, 1H), 6.98 (s, 1H), 6.27 (d, J = 7.5 Hz, 1H), 6.10 (d, J = 7.4 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 187.2, 138.6, 138.0, 134.8, 133.8, 132.5, 129.8, 129.0, 127.2, 122.5, 119.7.

IR (cm⁻¹): v = 3061, 3033, 2924, 1715, 1640, 1590, 1563, 1524, 1470, 1416, 1280, 1260, 1229, 1167, 1112, 1073, 998, 897, 873, 794, 710, 667, 650, 577, 558.

MS (70 eV, El) m/z (%) = 256 (28), 254 (62) [M⁺], 139 (100), 111 (59), 75 (22).

HRMS for C₁₁H₇ClO₂S₂ (253.9627): found: 253.9623.

Synthesis of (1,4-dithiin-2-y1)(phenyl)methanone (40l)

According to TP 1, 1,4-dithiin (38; 1.16 g, 10.0 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (2; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before benzoyl chloride (984 mg, 7.0 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 50 mL), extracted with Et₂O (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/Et₂O, 94:6) yielding 40l as red liquid (1.20 g, 78%).

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 7.76 – 7.63 (m, 2H), 7.63 – 7.51 (m, 1H), 7.51 – 7.36 (m, 2H), 6.95 (s, 1H), 6.28 (d, J = 7.5 Hz, 1H), 6.10 (d, J = 7.2 Hz, 1H).
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$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 188.6, 137.0, 136.9, 134.2, 132.5, 129.1, 128.4, 122.6, 119.7.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3092, 3035, 2973, 2955, 2928, 2868, 2360, 1748, 1693, 1638, 1563, 1528, 1468, 1396, 1366, 1261, 1126, 1020, 938, 900, 872, 858, 770, 737, 666.

MS (70 eV, EI) m/z (%) = 220 (40) [M$^+$], 105 (100), 77 (63).

HRMS for C$_{11}$H$_8$OS$_2$ (220.0017): found: 220.0014.

**Synthesis of cyclopropyl(1,4-dithiin-2-yl)methanone (40m)**

![Chemical structure of 40m](image)

According to TP 1, 1,4-dithiin (38; 232 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (2; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl$_2$ solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN$\cdot$2LiCl solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before cyclopropanecarbonyl chloride (146 mg, 1.4 mmol) was added. The reaction mixture was stirred at 25 °C for 20 h and was then quenched with aq. NH$_4$Cl/NH$_3$ solution (8:1, 5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/Et$_2$O, 9:1) yielding 40m as red oil (168 mg, 65%).

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$/ppm = 7.30 (s, 1H), 6.19 (d, $J = 7.3$ Hz, 1H), 6.05 (d, $J = 7.3$ Hz, 1H), 2.33 (sep, $J = 4.5$ Hz, 1H), 1.15 – 1.06 (m, 2H), 0.98 – 0.93 (m, 2H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$/ppm = 192.4, 135.0, 133.0, 122.2, 119.5, 17.1, 11.7.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3033, 2360, 2086, 1645, 1561, 1528, 1438, 1418, 1385, 1292, 1198, 1161, 1128, 1090, 1061, 1029, 984, 925, 878, 792, 718.

MS (70 eV, EI) m/z (%) = 203 (98), 186 (12), 185 (13), 184 (100) [M$^+$], 116 (51), 115 (20), 111 (10), 105 (12), 85 (11), 71 (30), 69 (88), 45 (32), 44 (13), 41 (61).

HRMS for C$_8$H$_6$OS$_2$ (184.0017): found: 184.0014.
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Synthesis of 2-(cyclohex-2-en-1-yl)-1,4-dithiin (40n)

According to TP 1, 1,4-dithiin (38; 58 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPMgCl·LiCl (2; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN·2LiCl solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before 3-bromocyclohexene (56 mg, 0.35 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with aq. NH₄Cl/NH₃ solution (8:1, 5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 40n as yellow liquid (50 mg, 73%).

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 6.34 (d, J = 6.8 Hz, 1H), 6.29 (d, J = 6.8 Hz, 1H), 5.91 (s, 1H), 5.89 – 5.81 (m, 1H), 5.63 – 5.55 (m, 1H), 3.12 – 3.03 (m, 1H), 2.09 – 1.96 (m, 2H), 1.93 – 1.79 (m, 1H), 1.75 – 1.47 (m, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 142.4, 129.8, 127.7, 123.4, 122.6, 115.6, 42.4, 28.6, 25.0, 20.1.


MS (70 eV, EI) m/z (%) = 196 (20) [M⁺], 79 (23), 77 (21), 53 (34), 52 (22), 45 (100).

HRMS for C₁₀H₁₂S₂ (196.0380): found: 196.0386.

Synthesis of 2-(1,4-dithiin-2-yl)aniline (40o)

According to TP 1, 1,4-dithiin (38; 1.16 g, 10.0 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (2; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -40 °C and the
reaction mixture was stirred for 0.5 h. ZnCl₂ solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added over 1 h to a solution of 2-iodoaniline (1.75 g, 8.0 mmol), Pd(dba)₂ (173 mg, 0.3 mmol) and tfp (139 mg, 0.6 mmol) in dry THF (7 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 6 h and was then quenched with sat. aq. NH₄Cl solution (50 mL), extracted with Et₂O (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 7:1) yielding 40o as yellow oil (1.56 g, 94%).

^1H-NMR (400 MHz, CDCl₃) δ/ppm = 7.20 – 7.09 (m, 2H), 6.78 – 6.68 (m, 2H), 6.49 – 6.42 (m, 1H), 6.41 – 6.35 (m, 1H), 6.20 (s, 1H), 3.70 (br. s, 2H).

^13C-NMR (101 MHz, CDCl₃) δ/ppm = 143.9, 135.0, 130.7, 129.7, 123.0, 122.8, 122.8, 119.1, 118.5, 116.0.

IR (cm⁻¹): v = 3435, 3352, 3204, 3024, 2923, 2853, 2620, 1936, 1669, 1611, 1575, 1533, 1486, 1450, 1365, 1302, 1281, 1256, 1211, 1157, 1138, 1054, 1032, 1007, 939, 910, 855, 792, 777, 746, 673, 655, 634, 577, 558.

MS (70 eV, El) m/z (%) = 207 (90) [M⁺], 190 (37), 174 (94), 173 (51), 130 (55), 117 (100), 90 (61), 89 (47), 77 (16), 63 (17), 58 (11), 57 (11), 45 (40), 43 (11).

HRMS for C₁₀H₉NS₂ (207.0176): found: 207.0162.

Synthesis of 2-(m-tolyl)-1,4-dithiine (40p)

According to TP 1, 1,4-dithiin (38; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl-LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl₂ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of 3-iodotoluene (174 mg, 0.8 mmol), Pd(dba)₂ (17 mg, 0.03 mmol) and tfp (14 mg, 0.06 mmol) in dry THF (1 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were
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Evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 40p as yellow oil (140 mg, 85%).

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.41 – 7.32 (m, 2H), 7.29 – 7.20 (m, 1H), 7.19 – 7.10 (m, 1H), 6.49 – 6.38 (m, 2H), 6.34 (s, 1H), 2.38 (s, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 138.2, 138.0, 137.0, 129.4, 128.4, 127.7, 124.2, 123.4, 122.8, 115.8, 21.4.

IR (cm$^{-1}$): ν = 3028, 2952, 2917, 2857, 1726, 1673, 1600, 1583, 1531, 1481, 1454, 1432, 1417, 1376, 1312, 1278, 1253, 1230, 1164, 1135, 1093, 1038, 998, 969, 953, 903, 885, 846, 795, 771, 756, 671.

MS (70 eV, El) m/z (%) = 208 (10), 207 (15), 206 (100) [M$^+$], 205 (21), 191 (33), 190 (16), 174 (10), 173 (23), 161 (21), 147 (12), 135 (18), 129 (18), 115 (41), 45 (12).

HRMS for C$_{11}$H$_{10}$S$_2$ (206.0224): found: 206.0219.

Synthesis of ethyl 4-(1,4-dithiin-2-yl)benzoate (40q)

According to TP 1, 1,4-dithiin (38; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (2; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. ZnCl$_2$ solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added to a solution of ethyl 4-iodobenzoate (221 mg, 0.8 mmol), Pd(dba)$_2$ (17 mg, 0.03 mmol) and tfp (14 mg, 0.06 mmol) in dry THF (1 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/Et$_2$O, 95:5) yielding 40q as yellow solid (186 mg, 87%).

m.p.: 82.6 – 84.0 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 8.04 – 7.98 (m, 2H), 7.65 – 7.58 (m, 2H), 6.48 (s, 1H), 6.46 – 6.42 (m, 1H), 6.42 – 6.39 (m, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H).
C. EXPERIMENTAL PART

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 166.0, 141.2, 136.6, 130.3, 129.8, 126.8, 123.5, 122.4, 118.8, 61.1, 14.3.

IR (cm$^{-1}$): v = 3031, 2978, 1937, 1701, 1603, 1530, 1474, 1443, 1404, 1363, 1283, 1271, 1249, 1183, 1124, 1110, 1019, 917, 862, 831, 800, 777, 763, 688, 659, 634, 567.

MS (70 eV, EI) m/z (%) = 266 (11), 265 (17), 264 (100) [M$^+$], 236 (20), 191 (39), 190 (20), 158 (13), 147 (16), 115 (11).

HRMS for C$_{13}$H$_{12}$O$_2$S$_2$ (264.0279): found: 264.0271.

5.4 Preparation of Difunctionalized 1,4-Dithiin-Derivatives

Synthesis of 2,3-diiodo-1,4-dithiin (41a)

According to TP 2, 2-iodo-1,4-dithiin (40a; 242 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPZnCl-LiCl (4; 0.83 mL, 1.1 mmol, 1.33 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (177 mg, 0.7 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane) yielding 41a as yellow solid (175 mg, 68%).

m.p.: 84.9 – 86.4 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 6.42 (s, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 123.5, 84.9.

IR (cm$^{-1}$): v = 3024, 2962, 1592, 1544, 1485, 1260, 1092, 1020, 885, 872, 790, 757, 671.

MS (70 eV, EI) m/z (%) = 368 (58) [M$^+$], 241 (95), 127 (21), 114 (100), 88 (49), 61 (13), 45 (13), 43 (17).

HRMS for C$_4$H$_{12}$I$_2$S$_2$ (367.7687): found: 367.7680.
Synthesis of 2-chloro-3-iodo-1,4-dithiin (41b)

According to TP 2, 2-chloro-1,4-dithiin (40c; 80 mg, 0.53 mmol) was dissolved in dry THF (1 mL). TMPZnCl-LiCl (4; 0.43 mL, 0.57 mmol, 1.33 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (94 mg, 0.37 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane) yielding 41b as yellow solid (73 mg, 71%).

m.p.: 55.0 – 56.3 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 6.54 (d, J = 6.3 Hz, 1H), 6.34 (d, J = 6.3 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 125.8, 123.6, 122.9, 74.0.

IR (cm⁻¹): ν = 3033, 2921, 1591, 1550, 1518, 1354, 1275, 1260, 1133, 922, 879, 817, 787, 736, 712, 675, 586, 558.

MS (70 eV, EI) m/z (%) = 278 (30), 276 (67) [M⁺], 151 (38), 149 (100), 107 (14), 105 (40), 88 (28), 79 (16), 58 (12).

HRMS for C₄H₂IClS₂: found: 275.8330.

Synthesis of 3-iodo-1,4-dithiin-2-carbonitrile (41c)

According to TP 2, 1,4-dithiin-2-carbonitrile (40d; 93 mg, 0.66 mmol) was dissolved in dry THF (3 mL). TMPZnCl-LiCl (4; 0.55 mL, 0.73 mmol, 1.33 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (117 mg, 0.46 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column
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chromatography on silica gel (i)hexane/CH₂Cl₂, 2:1) yielding 41c as orange liquid (106 mg, 86%).

¹H-NMR (600 MHz, CDCl₃) δ/ppm = 6.63 (d, J = 6.3 Hz, 1H), 6.32 (d, J = 6.3 Hz, 1H).

¹³C-NMR (151 MHz, CDCl₃) δ/ppm = 124.3, 122.1, 116.0, 109.0, 96.6.


MS (70 eV, EI) m/z (%) = 267 (84) [M⁺], 142 (10), 141 (14), 140 (100), 127 (13), 114 (10), 96 (61), 82 (10), 45 (15).

HRMS for C₅H₂NIS₂ (266.8673): found: 266.8675.

Synthesis of ethyl 3-iodo-1,4-dithiin-2-carboxylate (41d)

Ethyl 1,4-dithiin-2-carboxylate (40h; 1.09 g, 5.81 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (2; 5.76 mL, 6.39 mmol, 1.11 M in THF) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of iodine (1.03 g, 4.07 mmol) in dry THF (6 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na₂S₂O₃ solution (50 mL), extracted with Et₂O (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i)hexane/CH₂Cl₂, 2:1) yielding 41d as orange liquid (793 mg, 62%).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 6.61 (d, J = 6.2 Hz, 1H), 6.25 (d, J = 6.2 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 162.2, 126.6, 124.4, 123.5, 83.2, 62.5, 14.0.

IR (cm⁻¹): ν = 3033, 2979, 2934, 1710, 1601, 1558, 1510, 1463, 1443, 1388, 1365, 1212, 1113, 1093, 1030, 889, 851, 795, 761, 676.

MS (70 eV, EI) m/z (%) = 314 (100) [M⁺], 159 (69), 144 (10), 115 (16), 114 (20), 88 (21), 71 (13), 58 (10), 45 (14).
HRMS for C\textsubscript{7}H\textsubscript{7}O\textsubscript{2}I\textsubscript{2} (313.8932): found: 313.8929.

**Synthesis of ethyl 2-(3-iodo-1,4-dithiin-2-yl)-2-oxoacetate (41e)**

![Structure of ethyl 2-(3-iodo-1,4-dithiin-2-yl)-2-oxoacetate](image)

According to TP 2, ethyl 2-(1,4-dithiin-2-yl)-2-oxoacetate (40i; 216 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPZnCl·LiCl (4; 0.83 mL, 1.1 mmol, 1.33 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (178 mg, 0.7 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution (5 mL), extracted with Et\textsubscript{2}O (3 x 10 mL) and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (\textit{h}exane/CH\textsubscript{2}Cl\textsubscript{2}, 2:1) yielding 41e as red oil (120 mg, 50%).

\[ ^1H-NMR \ (400 \text{ MHz, } \text{CDCl}_3) \delta/\text{ppm} = 6.61 \text{ (d, } J = 6.1 \text{ Hz, } 1\text{H}), \ 6.42 \text{ (d, } J = 6.2 \text{ Hz, } 1\text{H}), \ 4.40 \text{ (q, } J = 7.2 \text{ Hz, } 2\text{H}), \ 1.45 - 1.35 \text{ (m, } 3\text{H}). \]

\[ ^{13}C-NMR \ (101 \text{ MHz, CDCl}_3) \delta/\text{ppm} = 180.9, \ 161.0, \ 127.6, \ 126.1, \ 122.5, \ 89.4, \ 63.0, \ 13.9. \]

\[ \text{IR (cm}^{-1}) : \nu = 3038, 2980, 2934, 2869, 1727, 1682, 1549, 1471, 1444, 1389, 1367, 1297, 1254, 1170, 1096, 1007, 964, 913, 890, 849, 790, 761, 678, 649, 575. \]

\[ \text{MS (70 eV, EI) } m/z (\%) = 342 \text{ (43 [M}^+]), 269 \text{ (76), 241 (100), 187 (49), 149 (37), 142 (34), 127 (23), 114 (90), 88 (65), 86 (26), 72 (22), 71 (20), 69 (43), 59 (27), 58 (26), 57 (24), 55 (23), 45 (39), 44 (21), 43 (30), 41 (36).} \]

HRMS for C\textsubscript{8}H\textsubscript{7}O\textsubscript{3}I\textsubscript{2} (341.8881): found: 341.8871.

**Synthesis of (3-chlorophenyl)(3-iodo-1,4-dithiin-2-yl)methanone (41f)**

![Structure of (3-chlorophenyl)(3-iodo-1,4-dithiin-2-yl)methanone](image)

According to TP 2, (3-chlorophenyl)(1,4-dithiin-2-yl)methanone (40k; 127 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPZnCl·LiCl (4; 0.41 mL, 0.55 mmol, 1.33 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc
reagent was added to a solution of iodine (89 mg, 0.35 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH$_2$Cl$_2$, 2:1) yielding 41f as orange liquid (92 mg, 69%).

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.89 – 7.82 (m, 1H), 7.73 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.44 (t, $J = 7.9$ Hz, 1H), 6.71 – 6.62 (m, 1H), 6.59 – 6.52 (m, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ/ppm = 189.9, 135.3, 135.1, 134.3, 132.3, 130.2, 129.7, 128.1, 126.1, 122.2, 76.8.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3064, 3029, 2922, 2849, 1950, 1885, 1779, 1667, 1595, 1567, 1522, 1515, 1497, 1465, 1419, 1371, 1312, 1288, 1265, 1231, 1162, 1135, 1096, 1077, 1043, 998, 975, 911, 887, 824, 801, 787, 762, 719, 685, 657.

MS (70 eV, El) m/z (%) = 382 (41), 381 (15), 380 (100) [M$^+$], 254 (11), 253 (11), 218 (45), 190 (54), 139 (99), 114 (11), 111 (72), 88 (12), 75 (36), 50 (12).

HRMS for C$_{11}$H$_6$OClI$_2$ (379.8593): found: 379.8598.

Synthesis of (3-iodo-1,4-dithiin-2-yl)(phenyl)methanone (41g)

According to TP 2, (1,4-dithiin-2-yl)(phenyl)methanone (40I; 220 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPZnCl-LiCl (4; 0.83 mL, 1.1 mmol, 1.33 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (178 mg, 0.7 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/CH$_2$Cl$_2$, 2:1) yielding 41g as orange oil (189 mg, 78%).

$^1$H-NMR (300 MHz, CDCl$_3$) δ/ppm = 7.94 – 7.83 (m, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 6.66 (d, $J = 6.2$ Hz, 1H), 6.54 (d, $J = 6.2$ Hz, 1H).
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$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 191.2, 134.4, 133.4, 133.0, 128.9, 125.9, 122.4, 75.8.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3031, 2923, 1963, 1594, 1578, 1447, 1311, 1234, 1175, 1160, 1130, 1055, 1022, 999, 974, 935, 894, 806, 782, 727, 677.

MS (70 eV, EI) $m/z$ (%) = 348 (11), 347 (13), 346 (98) $[\text{M}^+], 220$ (13), 219 (14), 191 (16), 190 (25), 147 (21), 105 (100), 77 (72), 51 (26), 43 (45).

HRMS for C$_{11}$H$_7$OIS$_2$ (345.8983): found: 345.8976.

Synthesis of 2-allyl-3-bromo-1,4-dithiin (41h)

According to TP 2, 2-bromo-1,4-dithiin (40b; 316 mg, 1.6 mmol) was dissolved in dry THF (3 mL). TMPZnCl-LiCl (4; 1.34 mL, 1.78 mmol, 1.33 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. CuCN2LiCl solution (1.94 mL, 1.94 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before allyl chloride (137 mg, 1.1 mmol) was added. The reaction mixture was stirred at -40 °C for 1 h and was then quenched with aq. NH$_4$Cl/NH$_3$ solution (8:1, 5 mL), extracted with Et$_2$O (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated $in$ vacuo. The crude product was purified by flash column chromatography on silica gel ($i$hexane) yielding 41h as yellow liquid (191 mg, 74%).

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 6.52 – 6.43 (m, 1H), 6.43 – 6.33 (m, 1H), 5.85 – 5.68 (m, 1H), 5.23 – 5.15 (m, 1H), 5.15 – 5.09 (m, 1H), 3.23 (dt, $J$ = 6.3, 1.5 Hz, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 132.1, 132.0, 123.7, 123.4, 117.7, 103.2, 41.5.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3032, 3018, 2925, 2853, 2832, 1718, 1648, 1585, 1563, 1556, 1520, 1492, 1466, 1433, 1413, 1341, 1275, 1214, 1180, 1162, 1133, 1090, 1053, 1029, 1012, 979, 966, 915, 899, 885, 865, 822, 798, 780, 778, 741, 730, 705, 668, 654.

MS (70 eV, EI) $m/z$ (%) = 236 (78), 234 (75) $[\text{M}^+], 195$ (16), 193 (16), 155 (28), 153 (11), 140 (14), 127 (13), 125 (10), 123 (19), 122 (100), 121 (38), 111 (23), 97 (20), 95 (11), 85 (14), 83 (14), 81 (10), 71 (22), 69 (32), 57 (28), 55 (16), 45 (27), 44 (14), 43 (28), 41 (21).

HRMS for C$_7$H$_7$BrS$_2$ (233.9171): found: 233.9178.
Synthesis of (1,4-dithio-2,3-diyl)bis((3-chlorophenyl)methanone) (41i)

According to TP 2, (3-chlorophenyl)(1,4-dithio-2-yl)methanone (40k; 127 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPZnCl-LiCl (4; 0.41 mL, 0.55 mmol, 1.33 M in THF) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of 3-chlorobenzoyl chloride (61 mg, 0.35 mmol) and Pd(PPh3)4 (58 mg, 0.05 mmol) in dry THF (1 mL) at 25 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. NH4Cl solution (5 mL), extracted with Et2O (3 x 10 mL) and dried over anhydrous Na2SO4. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 7:1) yielding 41i as red oil (72 mg, 52%).

1H-NMR (300 MHz, CDCl3) δ/ppm = 7.68 – 7.62 (m, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.35 (t, J = 7.9 Hz, 2H), 6.65 (s, 2H).

13C-NMR (75 MHz, CDCl3) δ/ppm = 188.5, 139.9, 136.8, 134.9, 133.8, 129.9, 129.0, 127.5, 125.1.

IR (cm⁻¹): v = 3065, 2949, 2924, 2854, 1744, 1661, 1590, 1568, 1522, 1470, 1421, 1281, 1228, 1164, 1114, 1100, 1073, 1042, 998, 979, 942, 893, 855, 795, 722, 676.

MS (70 eV, El) m/z (%) = 394 (27), 392 (34) [M⁺], 360 (16), 249 (22), 139 (100), 111 (49), 75 (16).

HRMS for C18H10O2Cl2S2 (391.9499): found: 391.9503.
Synthesis of (1,4-dithiin-2,3-diyl)bis(phenylmethanone) (41j)

According to TP 2, (1,4-dithiin-2-yl)(phenyl)methanone (40l; 220 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPZnCl-LiCl (4; 0.83 mL, 1.1 mmol, 1.33 m in THF) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of benzyol chloride (98 mg, 0.7 mmol) and Pd(PPh₃)₄ (116 mg, 0.1 mmol) in dry THF (1 mL) at 25 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with Et₂O (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 6:1) yielding 41j as red oil (134 mg, 59%).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 7.68 (d, J = 7.2 Hz, 4H), 7.53 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.7 Hz, 4H), 6.66 (s, 2H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 190.0, 139.5, 135.5, 133.8, 129.4, 128.5, 125.2.

IR (cm⁻¹): ν = 3043, 2920, 2849, 1722, 1708, 1682, 1659, 1631, 1595, 1573, 1548, 1530, 1445, 1312, 1294, 1252, 1241, 1177, 1095, 1072, 1036, 1018, 996, 955, 935, 901, 836, 797, 747, 718, 689, 675, 663.

MS (70 eV, EI) m/z (%) = 325 (10), 324 (50) [M⁺], 105 (100), 77 (56).

HRMS for C₁₈H₁₂O₂S₂ (324.0279): found: 324.0273.
5.5 Preparation of 1,4-Dithiin-Fused Quinolines

Synthesis of 5-(furan-2-yl)-[1,4]dithiino[2,3-c]quinoline (42a)

According to TP 3, furural (62 mg, 0.65 mmol) was added to a solution of 2-(1,4-dithiin-2-yl)aniline (400; 104 mg, 0.5 mmol) and TFA (114 mg, 1.0 mmol) in EtOH (0.2 mL) at 25 °C. The reaction mixture was heated using a Biotage Initiator 2.5 system (130 °C, 100 W, 15 min). The reaction mixture was allowed to cool to 25 °C and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 95:5) yielding 42a as yellow solid (74 mg, 52%).

m.p.: 118.3 – 121.6 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 8.29 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.61 – 7.53 (m, 1H), 7.38 (d, J = 3.5 Hz, 1H), 6.71 (d, J = 6.6 Hz, 1H), 6.67 – 6.57 (m, 2H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 151.3, 146.4, 146.1, 144.3, 142.6, 130.1, 129.7, 127.4, 126.5, 126.1, 126.0, 124.2, 123.6, 114.4, 111.6.

IR (cm⁻¹): ν = 3127, 3096, 3050, 3031, 2922, 2852, 1613, 1566, 1546, 1526, 1488, 1474, 1435, 1396, 1373, 1343, 1314, 1297, 1241, 1224, 1176, 1128, 1099, 1024, 999, 947, 930, 884, 875, 859, 842, 802, 771, 756, 732, 720, 699, 678, 654.

MS (70 eV, El) m/z (%) = 285 (12), 284 (20), 283 (100) [M⁺], 282 (11), 254 (32), 251 (11), 250 (14), 223 (21), 222 (17), 210 (15).

HRMS for C₁₅H₉ONS₂ (283.0126): found: 283.0129.
Synthesis of 5-(thiophen-2-yl)-[1,4]dithiino[2,3-c]quinoline (42b)

According to TP 3, thiophene-2-carbaldehyde (73 mg, 0.65 mmol) was added to a solution of 2-(1,4-dithiin-2-yl)aniline (40o; 104 mg, 0.5 mmol) and TFA (114 mg, 1.0 mmol) in EtOH (0.2 mL) at 25 °C. The reaction mixture was heated using a Biotage Initiator 2.5 system (130 °C, 100 W, 15 min). The reaction mixture was allowed to cool to 25 °C and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc/NEt₃, 98:2:0.05) yielding 42b as yellow solid (90 mg, 60%).

m.p.: 128.8 – 131.2 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 8.28 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 3.7, 1.0 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.61 – 7.51 (m, 2H), 7.24 – 7.16 (m, 1H), 6.71 (d, J = 6.6 Hz, 1H), 6.60 (d, J = 6.6 Hz, 1H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 149.8, 146.3, 142.6, 142.5, 130.0, 130.0, 129.5, 128.8, 127.4, 127.2, 126.6, 126.3, 125.9, 124.1, 123.5.

IR (cm⁻¹): ν = 3079, 3064, 3021, 2923, 2852, 1607, 1579, 1558, 1544, 1531, 1474, 1447, 1425, 1374, 1356, 1336, 1307, 1292, 1235, 1221, 1156, 1134, 1070, 1051, 971, 916, 894, 882, 858, 849, 836, 799, 774, 760, 743, 729, 706, 687, 656.

MS (70 eV, El) m/z (%) = 301 (14), 300 (25), 299 (100) [M⁺], 298 (46), 267 (14), 266 (45), 222 (10).

HRMS for C₁₅H₉NS₃ (298.9897): found: 298.9889.
Synthesis of 5-(pyridin-3-yl)-[1,4]dithiino[2,3-c]quinoline (42c)

According to TP 3, nicotinaldehyde (43 mg, 0.4 mmol) was added to a solution of 2-(1,4-dithiin-2-yl)aniline (40o; 104 mg, 0.5 mmol) and TFA (114 mg, 1.0 mmol) in EtOH (0.2 mL) at 25 °C. The reaction mixture was heated using a Biotage Initiator 2.5 system (130 °C, 100 W, 15 min). The reaction mixture was allowed to cool to 25 °C and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/EtOAc, 1:1) yielding 42c as yellow solid (62 mg, 53%).

m.p.: 163.2 – 165.8 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 8.97 (s, 1H), 8.78 – 8.70 (m, 1H), 8.39 – 8.28 (m, 1H), 8.19 – 8.10 (m, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.77 (t, J = 7.2 Hz, 1H), 7.65 (t, J = 7.3 Hz, 1H), 7.47 (dd, J = 7.6, 4.9 Hz, 1H), 6.66 – 6.54 (m, 2H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 153.9, 150.1, 149.8, 146.5, 142.9, 137.0, 135.2, 130.3, 129.8, 127.8, 126.7, 126.3, 126.2, 123.6, 123.5, 123.0.


MS (70 eV, El) m/z (%) = 295 (14), 294 (69) [M⁺], 293 (19), 270 (10), 269 (16), 268 (100), 261 (15).

HRMS for C₁₆H₁₀N₂S₂ (294.0285): found 294.0281.
C. EXPERIMENTAL PART

Synthesis of 5-phenyl-[1,4]dithiino[2,3-c]quinoline (42d)

According to TP 3, benzaldehyde (69 mg, 0.64 mmol) was added to a solution of 2-(1,4-dithiin-2-yl)aniline (40o; 104 mg, 0.5 mmol) and TFA (114 mg, 1.0 mmol) in EtOH (0.2 mL) at 25 °C. The reaction mixture was heated using a Biotage Initiator 2.5 system (130 °C, 100 W, 15 min). The reaction mixture was allowed to cool to 25 °C and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc/NEt₃, 98:2:0.05) yielding 42d as yellow solid (79 mg, 54%).

m.p.: 175.8 – 179.7 °C.

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 8.31 (d, J = 8.2 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.78 – 7.47 (m, 7H), 6.62 – 6.55 (m, 1H), 6.55 – 6.48 (m, 1H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 157.1, 146.4, 141.6, 139.4, 129.9, 129.8, 129.2, 129.0, 128.2, 127.3, 127.1, 126.7, 126.2, 123.5, 123.1.

IR (cm⁻¹): ν = 3050, 3029, 3015, 2921, 2852, 1949, 1921, 1894, 1834, 1806, 1770, 1731, 1699, 1600, 1578, 1545, 1533, 1493, 1474, 1448, 1441, 1374, 1339, 1330, 1312, 1286, 1251, 1235, 1173, 1162, 1151, 1134, 1092, 1074, 1024, 1000, 993, 976, 948, 921, 902, 893, 863, 844, 818, 803, 781, 771, 751, 711, 702, 685, 656.

MS (70 eV, El) m/z (%) = 295 (12), 294 (23), 293 (100) [M⁺], 292 (59), 280 (12), 267 (22), 261 (10), 260 (39), 259 (10), 190 (14), 111 (10).

HRMS for C₁₇H₁₁NS₂ (293.0333): found: 293.0330.
5.6 Preparation of Alkynylated 1,4-Dithiin-Derivatives

**Synthesis of 3-(3-oxooct-1-yn-1-yl)-1,4-dithiin-2-carbonitrile (43a)**

![Chemical Structure](image)

According to TP 4, 2-chloro-3-iodo-1,4-dithiin (41c; 533 mg, 2.0 mmol) was added to a solution of 1-octyne (330 mg, 3.0 mmol), Cul (7.6 mg, 0.04 mmol) and Pd(PPh₃)₂Cl₂ (14 mg, 0.02 mmol) in NEt₃ (10 mL) at 25 °C. The reaction mixture was stirred at this temperature for 4 h and was then quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (Hexane/CH₂Cl₂, 2:1) yielding 43a as orange oil (454 mg, 91%).

**¹H-NMR** (400 MHz, CDCl₃) δ/ppm = 6.50 – 6.34 (m, 2H), 2.47 (t, J = 7.1 Hz, 2H), 1.67 – 1.53 (m, 2H), 1.49 – 1.18 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H).

**¹³C-NMR** (101 MHz, CDCl₃) δ/ppm = 136.4, 124.1, 121.9, 114.5, 106.6, 104.2, 75.3, 31.2, 28.4, 27.9, 22.4, 19.9, 14.0.

**IR** (cm⁻¹): ν = 3039, 2927, 2857, 2208, 1552, 1519, 1464, 1457, 1423, 1377, 1346, 1324, 1278, 1215, 1137, 1108, 1080, 1069, 1042, 987, 961, 890, 796, 782, 723.

**MS** (70 eV, El) m/z (%): 251 (13), 250 (18), 249 (100) [M⁺], 206 (13), 192 (13), 180 (14), 178 (20), 173 (15), 165 (18), 160 (10), 153 (10), 152 (12), 146 (13), 134 (18), 45 (18), 43 (13), 41 (20).

**HRMS** for C₁₃H₁₅NS₂ (249.0646): found: 249.0641.

**Synthesis of ethyl 3-(3-oxooct-1-yn-1-yl)-1,4-dithiin-2-carboxylate (43b)**

![Chemical Structure](image)

According to TP 4, ethyl 3-iodo-1,4-dithiin-2-carboxylate (41d; 1.13 g, 3.6 mmol) was added to a solution of 1-octyne (593 mg, 5.4 mmol), Cul (14 mg, 0.07 mmol) and Pd(PPh₃)₂Cl₂ (25 mg, 0.04 mmol) in NEt₃ (18 mL) at 25 °C. The reaction mixture was stirred at this temperature for
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4 h and was then quenched with sat. aq. NH₄Cl solution (10 mL), extracted with EtOAc (3 x 70 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/EtOAc, 9:1) yielding 43b as orange oil (817 mg, 77%).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 6.38 (s, 2H), 4.28 (q, J = 7.0 Hz, 2H), 2.44 (t, J = 7.1 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.49 – 1.24 (m, 9H), 0.90 (t, J = 6.8 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 161.7, 128.5, 128.2, 123.7, 123.6, 102.7, 61.9, 31.3, 28.6, 28.1, 22.5, 20.1, 14.1, 14.0. (One signal not observed; possible coincidental isochronicity).

IR (cm⁻¹): ν = 3035, 2954, 2929, 2857, 2208, 1701, 1562, 1530, 1464, 1444, 1426, 1389, 1365, 1325, 1260, 1233, 1181, 1110, 1094, 1044, 1016, 960, 898, 864, 830, 797, 760, 723, 676.

MS (70 eV, El) m/z (%) = 298 (11), 297 (19), 296 (100) [M⁺], 198 (13), 197 (25), 171 (10), 153 (50), 143 (15), 43 (36), 41 (10).

HRMS for C₁₅H₂₀O₂S₂ (296.0905): found: 296.0900.

Synthesis of ethyl 3-(phenylethynyl)-1,4-dithiin-2-carboxylate (43c)

According to TP 4, ethyl 3-iodo-1,4-dithiin-2-carboxylate (41d; 742 mg, 2.4 mmol) was added to a solution of phenylacetylene (686 mg, 3.6 mmol), Cul (9 mg, 0.05 mmol) and Pd(PPh₃)₂Cl₂ (17 mg, 0.03 mmol) in NEt₃ (12 mL) at 25 °C. The reaction mixture was stirred at this temperature for 3 h and was then quenched with sat. aq. NH₄Cl solution (10 mL), extracted with EtOAc (3 x 70 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/EtOAc, 9:1) yielding 43c as red oil (634 mg, 93%).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 7.52 (dd, J = 7.5, 2.1 Hz, 2H), 7.42 – 7.32 (m, 3H), 6.47 – 6.39 (m, 2H), 4.33 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 161.5, 131.9, 129.9, 129.4, 128.4, 127.3, 124.1, 123.6, 122.1, 99.2, 85.3, 62.1, 14.2.
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IR (cm⁻¹): ν = 3033, 2979, 2935, 2902, 2869, 2190, 1698, 1597, 1558, 1528, 1485, 1466, 1441, 1388, 1365, 1293, 1212, 1176, 1157, 1133, 1114, 1088, 1069, 1020, 990, 915, 889, 849, 796, 754, 717, 686.

MS (70 eV, El) m/z (%): 290 (11), 289 (19), 288 (100) [M⁺], 260 (11), 259 (17), 243 (12), 229 (12), 216 (28), 215 (28), 214 (17), 171 (47), 145 (47), 145 (21), 113 (11).

HRMS for C₁₅H₁₂O₂S₂ (288.0279): found: 288.0273.

Synthesis of ethyl 3-((trimethylsilyl)ethynyl)-1,4-dithiin-2-carboxylate (43d)

According to TP 4, ethyl 3-iodo-1,4-dithiin-2-carboxylate (41d; 283 mg, 0.9 mmol) was added to a solution of trimethylsilylacetylene (133 mg, 1.34 mmol), Cul (3 mg, 0.02 mmol) and Pd(PPh₃)₂Cl₂ (6 mg, 0.01 mmol) in NEt₃ (4.5 mL) at 25 °C. The reaction mixture was stirred at this temperature for 3 h and was then quenched with sat. aq. NH₄Cl solution (10 mL), extracted with EtOAc (3 x 70 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane/CH₂Cl₂, 2:1) yielding 43d as red oil (206 mg, 80%).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 6.38 (s, 2H), 4.30 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 0.24 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 161.5, 131.3, 126.5, 123.8 (2C), 106.2, 99.0, 62.1, 14.1, -0.4.

IR (cm⁻¹): ν = 3036, 2960, 2900, 2134, 1703, 1603, 1560, 1524, 1464, 1444, 1408, 1389, 1365, 1247, 1226, 1171, 1122, 1095, 1035, 992, 972, 838, 797, 758, 725, 676, 659.

MS (70 eV, El) m/z (%): 286 (15), 285 (20), 284 (100) [M⁺], 241 (19), 225 (44), 197 (33), 177 (10), 135 (10), 123 (15), 121 (16), 121 (14), 75 (10), 73 (25).

HRMS for C₁₂H₁₆O₂S₂Si (284.0361): found: 284.0356.
5.7 Iodine-Mediated Electrophilic Cyclizations

Synthesis of 7-hexanoyl-8-iodo-5H-[1,4]dithiino[2,3-c]pyran-5-one (44a)

According to TP 5, a solution of iodine (841 mg, 3.3 mmol) in dry CH₂Cl₂ (22 mL) was added dropwise to a solution of ethyl 3-(3-oxooct-1-yn-1-yl)-1,4-dithiin-2-carboxylate (43b; 817 mg, 2.8 mmol) in dry CH₂Cl₂ (35 mL) at 25 °C. The reaction mixture was stirred at this temperature for 2 h and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (ihexane/CH₂Cl₂, 2:1) yielding 44a as red oil (972 mg, 88%).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 6.33 (d, J = 7.2 Hz, 1H), 6.11 (d, J = 7.2 Hz, 1H), 2.87 – 2.75 (m, 2H), 1.67 (quin, J = 7.5 Hz, 2H), 1.44 – 1.22 (m, 6H), 0.98 – 0.82 (m, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ/ppm = 163.0, 156.9, 153.4, 125.2, 121.4, 113.9, 74.1, 37.3, 31.3, 28.7, 27.0, 22.4, 14.0.

IR (cm⁻¹): ν = 3035, 2952, 2925, 2854, 1697, 1574, 1554, 1489, 1463, 1377, 1351, 1333, 1252, 1175, 1144, 1105, 1029, 977, 891, 858, 792, 745, 723, 673.

MS (70 eV, El) m/z (%) = 396 (10), 395 (17), 394 (100) [M⁺], 324 (34), 295 (10), 197 (24), 127 (23), 43 (23), 41 (10).

HRMS for C₁₃H₁₆O₂I₂S₂ (393.9558): found: 393.9553.

Synthesis of 8-iodo-7-phenyl-5H-[1,4]dithiino[2,3-c]pyran-5-one (44b)

According to TP 5, a solution of iodine (236 mg, 0.93 mmol) in dry CH₂Cl₂ (6 mL) was added dropwise to a solution of ethyl 3-(phenylethynyl)-1,4-dithiin-2-carboxylate (43c; 223 mg, 0.77 mmol) in dry CH₂Cl₂ (10 mL) at 25 °C. The reaction mixture was stirred at this temperature
for 12 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i.hexane/CH$_2$Cl$_2$, 1:1) yielding 44b as red solid (250 mg, 84%).

**m.p.:** 198.6 – 202.4 °C.

$^1$H-NMR (400 MHz, CDCl$_3$) δ/ppm = 7.64 (dd, $J = 7.5$, 1.9 Hz, 2H), 7.52 – 7.41 (m, 3H), 6.36 (d, $J = 7.2$ Hz, 1H), 6.16 (d, $J = 7.2$ Hz, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) δ/ppm = 158.8, 156.5, 153.9, 133.7, 130.9, 129.5, 128.2, 125.3, 121.8, 115.5, 73.9.

IR (cm$^{-1}$): $\tilde{\nu}$ = 3035, 1705, 1598, 1578, 1564, 1549, 1495, 1476, 1442, 1363, 1318, 1299, 1277, 1229, 1171, 1150, 1077, 1058, 1027, 1013, 939, 922, 901, 829, 788, 773, 743, 699, 680, 659.

MS (70 eV, EI) m/z (%) = 388 (11), 387 (17), 386 (100) [M$^+$], 358 (10), 259 (16), 231 (40), 203 (32), 145 (12), 105 (53), 77 (47), 51 (12).

HRMS for C$_{13}$H$_7$O$_2$I$_2$ (385.8932): found: 385.8926.

**Synthesis of (E)-7-(iodo(trimethylsilyl)methylene)-[1,4]dithiino[2,3-c]furan-5(7H)-one (44c)**

![Chemical structure]

According to TP 5, a solution of iodine (193 mg, 0.76 mmol) in dry CH$_2$Cl$_2$ (5 mL) was added dropwise to a solution of ethyl 3-((trimethylsilyl)ethynyl)-1,4-dithiin-2-carboxylate (43d; 180 mg, 0.63 mmol) in dry CH$_2$Cl$_2$ (8 mL) at 25 °C. The reaction mixture was stirred at this temperature for 3 h and was then quenched with sat. aq. Na$_2$S$_2$O$_3$ solution (5 mL), extracted with CH$_2$Cl$_2$ (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i.hexane/EtOAc, 95:5) yielding 44c as dark red oil (195 mg, 81%).

$^1$H-NMR (400 MHz, CDCl$_3$) δ/ppm = 5.80 (s, 1H), 5.78 (s, 1H), 0.33 (s, 9H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) δ/ppm = 162.1, 151.2, 144.7, 122.6, 118.3, 117.8, 92.2, 0.4.
IR (cm$^{-1}$): $\tilde{\nu} = 3508, 3038, 2953, 2896, 2849, 2441, 2219, 2004, 1940, 1748, 1597, 1572, 1515, 1458, 1408, 1322, 1291, 1247, 1224, 1125, 1007, 991, 860, 839, 816, 777, 758, 745, 711, 664, 653.$

**MS** (70 eV, El) $m/z$ (%) = 384 (15), 383 (17), 382 (100) [M$^+$], 240 (15), 212 (10), 196 (21), 181 (14), 153 (15), 73 (78).

**HRMS** for C$_{10}$H$_{11}$O$_2$Si$_2$ (381.9014): found: 381.9017.

### 5.8 Preparation of a 1,4-Dithiin-Fused Pyridazine

**Synthesis of 5,8-bis(3-chlorophenyl)-[1,4]dithiino[2,3-d]pyridazine (45)**

![Diagram](attachment:image.png)

Hydrazine monohydrate (195 mg, 3.9 mmol) was added to a solution of (1,4-dithiin-2,3-diyl)bis((3-chlorophenyl)methanone) (41i; 511 mg, 1.3 mmol) in THF (2.6 mL) at 0 °C. The reaction mixture was stirred at this temperature for 1 h and was then quenched with sat. aq. NH$_4$Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 7:1) yielding 45 as orange solid (314 mg, 62%).

**m.p.:** 116.9 – 119.0 °C.

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$/ppm = 7.72 (d, $J = 1.7$ Hz, 2H), 7.62 – 7.43 (m, 6H), 6.33 (s, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$/ppm = 156.6, 137.2, 135.5, 134.4, 129.9, 129.6 (2C), 127.8, 123.7.

IR (cm$^{-1}$): $\tilde{\nu} = 3064, 3029, 2923, 2853, 1950, 1885, 1819, 1779, 1595, 1566, 1520, 1497, 1465, 1419, 1371, 1312, 1289, 1264, 1230, 1161, 1137, 1095, 1077, 1043, 998, 975, 911, 887, 824, 801, 787, 762, 719, 685, 668, 657.
MS (70 eV, EI) m/z (%) = 390 (76), 389 (42), 388 (100) [M+], 387 (24), 363 (64), 632 (21), 361 (84), 355 (20), 290 (34), 272 (34), 270 (44), 200 (65), 43 (21).

HRMS for C\textsubscript{18}H\textsubscript{10}N\textsubscript{2}Cl\textsubscript{2}S\textsubscript{2} (387.9662): found: 387.9666.

5.9 Preparation of 1,4-Dithiin-Fused Pyrazines

**Synthesis of pyrazine-2,3-dithiol (47)**

\[
\begin{array}{c}
\text{N} \\
\text{SH}
\end{array}
\]

According to the literature\textsuperscript{74} 2,3-dichloropyrazine (46; 745 mg, 5.0 mmol) and NaHS\textsubscript{x}H\textsubscript{2}O (2.34 g, 5.0 mmol) were dissolved in H\textsubscript{2}O (15 mL). The reaction mixture was heated to 120 °C for 5 h. The resulting precipitate was filtered, washed with H\textsubscript{2}O (20 mL) and then dissolved in NaOH (2 M; 20 mL). Remaining solids were removed by filtration and the filtrate was acidified with AcOH (50 mL). The resulting precipitate was filtered, washed with H\textsubscript{2}O and dried under high vacuum yielding 47 as yellow solid (434 mg, 60%).

The analytical data matches those reported in the literature\textsuperscript{76}.

**Synthesis of [1,4]dithiino[2,3-b:5,6-b']dipyrazine (48)**

\[
\begin{array}{c}
\text{N} \\
\text{S} & \text{S} \\
\text{N} & \text{N}
\end{array}
\]

2,3-Dichloropyrazine (46; 74 mg, 0.50 mmol), K\textsubscript{2}CO\textsubscript{3} (346 mg, 2.5 mmol) and pyrazine-2,3-dithiol (47; 94 mg, 0.65 mmol) were suspended in DMF. The reaction mixture was stirred at 80 °C for 18 h and was then quenched with H\textsubscript{2}O (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After filtration, the solvents were evaporated \textit{in vacuo}. The crude product was purified by flash column chromatography on silica gel (\textit{hexane}/EtOAc, 8:1) yielding 48 as yellowish solid (84 mg, 76%).

m.p.: 130.4 – 136.2 °C.

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) δ/ppm = 8.22 (s, 4H).

13C-NMR (75 MHz, CDCl3) δ/ppm = 150.7, 141.8.

IR (cm⁻¹): ν = 2922, 2853, 1918, 1805, 1528, 1463, 1417, 1401, 1335, 1269, 1164, 1135, 1083, 1058, 959, 847, 818.

MS (70 eV, EI) m/z (%) = 222 (11), 221 (10), 220 (100) [M⁺], 176 (26), 142 (13), 117 (19), 88 (11), 83 (13), 70 (14).


Synthesis of 2,3-dichloro-5-(trimethylsilyl)pyrazine (49)

2,3-Dichloropyrazine (46; 1.49 g, 10.0 mmol) was dissolved in dry THF (20 mL). Trimethylsilyl chloride (5.43 g, 50.0 mmol) was added and the reaction mixture was cooled to -78 °C. TMP Li (1; 17.5 mL, 11.0 mmol, 0.63 M in THF) was added dropwise and the reaction mixture was stirred for 0.5 h. The resulting solution was quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/Et₂O, 96:4) yielding 49 as colorless liquid (1.68 g, 76%).

1H-NMR (300 MHz, CDCl3) δ/ppm = 8.33 (s, 1H), 0.36 (s, 9H).

13C-NMR (75 MHz, CDCl3) δ/ppm = 161.6, 148.5, 147.4, 145.4, -2.1.

IR (cm⁻¹): ν = 2959, 2901, 1740, 1484, 1390, 1337, 1268, 1251, 1214, 1166, 1120, 1062, 1040, 916, 871, 840, 823, 768, 756, 748, 700.

MS (70 eV, EI) m/z (%) = 220 (9) [M⁺], 207 (37), 84 (9), 73 (71), 72 (16), 45 (15), 43 (10).

HRMS for C7H10N2Cl2Si (219.9990): found: 219.9979.

Synthesis of 2,3-dichloro-5,6-bis(trimethylsilyl)pyrazine (50a)

2,3-Dichloropyrazine (46; 149 mg, 1.0 mmol) was dissolved in dry THF (2 mL). Trimethylsilyl chloride (543 mg, 5.0 mmol) was added and the reaction mixture was cooled to -78 °C. TMP Li
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(1; 3.46 mL, 2.2 mmol, 0.63 M in THF) was added dropwise and the reaction mixture was stirred for 0.5 h. The resulting solution was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 50a as colorless solid (151 mg, 52%).

**m.p.:** 60.2 – 63.8 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 0.40 (s, 18H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 166.4, 145.9, 0.2.

**IR (cm⁻¹):** ν = 2956, 2900, 1502, 1409, 1348, 1282, 1264, 1247, 1168, 1092, 1068, 944, 897, 833, 754, 695, 659.

**MS** (70 eV, El) m/z (%) = 292 (21) [M⁺], 292 (12), 279 (23), 277 (24), 257 (30), 163 (23), 163 (25), 158 (29), 104 (27), 76 (24), 73 (100), 72 (24), 44 (29), 43 (20).

**HRMS** for C₁₀H₁₈N₂Cl₂Si₂ (292.0386): found: 292.0381.

**Synthesis of 2,3-dichloro-5,6-bis(triethylsilyl)pyrazine (50b)**

2,3-Dichloropyrazine (46; 1.49 g, 10.0 mmol) was dissolved in dry THF (20 mL). Triethylsilyl chloride (7.54 g, 50.0 mmol) was added and the reaction mixture was cooled to -78 °C. TMLi (1; 35 mL, 22.0 mmol, 0.63 M in THF) was added dropwise and the reaction mixture was stirred for 0.5 h. The resulting solution was quenched with sat. aq. NH₄Cl solution (50 mL), extracted with EtOAC (3 x 100 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i-hexane) yielding 50b as colorless liquid (2.55 g, 68%).

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 1.07 – 0.80 (m, 30H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 165.8, 145.6, 7.5, 4.2.

**IR (cm⁻¹):** ν = 2955, 2911, 2876, 1458, 1413, 1380, 1281, 1238, 1171, 1085, 1065, 1000, 970, 957, 886, 720, 660.
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**MS** (70 eV, El) m/z (%) = 378 (14), 376 (19) [M⁺], 351 (18), 350 (23), 349 (75), 348 (33), 347 (100), 341 (13), 321 (15), 319 (15), 228 (13), 226 (31), 121 (19), 117 (17), 115 (20), 114 (33), 95 (12), 87 (55), 86 (25), 59 (63), 58 (11), 57 (10), 341 (13), 321 (15), 228 (13), 226 (31), 121 (19), 117 (17), 115 (20), 114 (33), 95 (12), 87 (55), 86 (25), 59 (63), 58 (11), 57 (10).

**HRMS** for C₁₆H₃₆N₂Cl₂Si₂ (376.1325): found: 376.1317.

**Synthesis of 2,3-dibromo-5,6-bis(trimethylsilyl)pyrazine (50c)**

![Structure of 2,3-dibromo-5,6-bis(trimethylsilyl)pyrazine](image)

2,3-Dibromopyrazine (54; 357 mg, 1.5 mmol) was dissolved in dry THF (6 mL). Trimethylsilyl chloride (815 mg, 7.5 mmol) was added and the reaction mixture was cooled to -78 °C. TMPLi (1; 6.0 mL, 3.3 mmol, 0.63 M in THF) was added dropwise and the reaction mixture was stirred for 0.5 h. The resulting solution was quenched with sat. aq. NH₄Cl solution (5 mL), extracted with EtOAC (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*hexane*) yielding 50c as colorless solid (151 mg, 63%).

m.p.: 92.7 – 95.2 °C.

**¹H-NMR** (300 MHz, CDCl₃) δ/ppm = 0.44 (s, 18H).

**¹³C-NMR** (75 MHz, CDCl₃) δ/ppm = 164.9, 146.7, -1.7.

**IR** (cm⁻¹): δ = 2957, 2899, 1459, 1409, 1320, 1250, 1234, 1205, 1190, 1100, 1056, 833, 755, 698.

**MS** (70 eV, El) m/z (%) = 367 (39), 365 (15) [M-Ch₃⁺], 303 (86), 302 (11), 139 (23), 137 (23), 112 (14), 111 (14), 105 (10), 97 (27), 85 (18), 83 (21), 81 (17), 75 (11), 74 (21), 73 (100), 71 (23), 70 (13), 69 (31), 59 (21), 57 (35), 56 (10), 55 (29), 45 (15), 45 (13), 44 (15), 43 (30), 43 (23), 41 (27).

**HRMS** for C₉H₁₅N₂Br₂Si₂ (364.9141): found: 364.9146.
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Synthesis of 2,3-bis(trimethylsilyl)-[1,4]dithiino[2,3-\textit{b}:5,6-\textit{b}']dipyrazine (51a)

A suspension of 2,3-dichloro-5,6-bis(trimethylsilyl)pyrazine (50a; 291 mg, 1.0 mmol), \( \text{K}_2\text{CO}_3 \) (691 mg, 5.0 mmol) and pyrazine-1,2-dithiol (47; 187 mg, 1.3 mmol) in DMF (10 mL) was stirred at 80 °C for 6 h. The reaction mixture was quenched with water (5 mL), extracted with \( \text{EtOAc} \) (3 x 10 mL) and dried over anhydrous \( \text{Na}_2\text{SO}_4 \). After filtration, the solvents were evaporated \textit{in vacuo}. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 9:1) yielding 51a as yellow solid (139 mg, 38%).

\textbf{m.p.:} 101.6 – 103.0 °C.

\textbf{\( ^1\text{H-NMR} \) (600 MHz, CDCl\textsubscript{3}) \( \delta/ppm = 8.19 \text{ (s, 2H)}, 0.37 \text{ (s, 18H)}. \)

\textbf{\( ^{13}\text{C-NMR} \) (151 MHz, CDCl\textsubscript{3}) \( \delta/ppm = 165.2, 151.8, 147.8, 141.3, 0.19. \)

\textbf{IR (cm\textsuperscript{-1}):} \( \tilde{\nu} = 2953, 2897, 1456, 1421, 1408, 1348, 1277, 1248, 1179, 1146, 1088, 1062, 906, 835, 824, 755, 697, 660. \)

\textbf{MS (70 eV, El) \( m/z \) (%) = 366 (19), 365 (30), 364 (100) [M\textsuperscript{+}], 350 (10), 349 (36), 291 (20), 259 (14), 166 (63), 88 (14), 73 (48), 45 (11).}

\textbf{HRMS for C\textsubscript{14}H\textsubscript{20}N\textsubscript{4}S\textsubscript{2}Si\textsubscript{2} (364.0668):} found: 364.0662.

Synthesis of 2,3-bis(triethylsilyl)-[1,4]dithiino[2,3-\textit{b}:5,6-\textit{b}']dipyrazine (51b)

A suspension of 2,3-dichloro-5,6-bis(triethylsilyl)pyrazine (50b; 1.76 g, 4.67 mmol), \( \text{K}_2\text{CO}_3 \) (3.23 g, 23.4 mmol) and pyrazine-1,2-dithiol (47; 876 mg, 6.07 mmol) in DMF (10 mL) was stirred at 80 °C for 6 h. The reaction mixture was quenched with water (5 mL), extracted with \( \text{EtOAc} \) (3 x 10 mL) and dried over anhydrous \( \text{Na}_2\text{SO}_4 \). After filtration, the solvents were evaporated \textit{in vacuo}. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 8:1) yielding 51b as yellow solid (1.07 g, 51%).

\textbf{m.p.:} 58.1 – 58.2 °C.

\textbf{\( ^1\text{H-NMR} \) (600 MHz, CDCl\textsubscript{3}) \( \delta/ppm = 8.18 \text{ (s, 2H)}, 1.00 – 0.93 \text{ (m, 18H)}, 0.93 – 0.86 \text{ (m, 12H).} \)
C. EXPERIMENTAL PART

\[ \text{\textsuperscript{13}C-NMR} \ (151 \text{ MHz, CDCl}_3) \, \delta/\text{ppm} = 164.5, 151.8, 147.5, 141.3, 7.6, 4.2. \]

IR (cm\(^{-1}\)):
\[ v = \begin{align*} 
2953, & \ 2933, \ 2873, \ 1538, \ 1500, \ 1454, \ 1414, \ 1378, \ 1345, \ 1277, \ 1235, \ 1180, \ 1146, \\
1076, & \ 1061, \ 998, \ 970, \ 901, \ 844, \ 719, \ 704. 
\end{align*} \]

MS (70 eV, EI) \( m/z \) (%):
\[ m/z = \begin{align*} 
450 & \ (16), \ 449 \ (28), \ 448 \ (84) \ [M^+] , \ 421 \ (21), \ 420 \ (37), \ 419 \ (100), \ 333 \ (12), \ 167 \ (12), \ 166 \ (23), \ 153 \ (12), \ 87 \ (17), \ 59 \ (20). 
\end{align*} \]

HRMS for \( \text{C}_{20}\text{H}_{32}\text{N}_4\text{S}_2\text{Si}_2 \): found: 448.1603.

**Synthesis of 2,3-diiodo-[1,4]dithiino[2,3-b:5,6-b']dipyrazine (52a)**

ICI (0.16 mL, 487 mg, 3.0 mmol) was added dropwise to a solution of 2,3-bis(triethylsilyl)-[1,4]dithiino[2,3-b:5,6-b']dipyrazine (51b; 224 mg, 0.5 mmol) in \( \text{CH}_2\text{Cl}_2 \) (1 mL) at 25 °C. The reaction mixture was stirred at 50 °C for 4 h and was then quenched with sat. aq. \( \text{Na}_2\text{S}_2\text{O}_3 \) solution (5 mL), extracted with \( \text{CH}_2\text{Cl}_2 \) (3 \times 10 mL) and dried over anhydrous \( \text{Na}_2\text{SO}_4 \). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (i hexane/EtOAc, 9:1) yielding 52a as yellow solid (158 mg, 74%).

m.p.: 149.6 – 155.3 °C.

\[ \text{'H-NMR} \ (300 \text{ MHz, CDCl}_3) \, \delta/\text{ppm} = 8.23 \ (s, 2H). \]

\[ \text{\textsuperscript{13}C-NMR} \ (75 \text{ MHz, CDCl}_3) \, \delta/\text{ppm} = 149.9, 149.0, 142.0, 126.0. \]

IR (cm\(^{-1}\)):
\[ v = \begin{align*} 
2956, & \ 2923, \ 2849, \ 1694, \ 1500, \ 1469, \ 1415, \ 1374, \ 1346, \ 1302, \ 1260, \ 1195, \ 1170, \\
1153, & \ 1134, \ 1078, \ 1050, \ 910, \ 845. 
\end{align*} \]

MS (70 eV, EI) \( m/z \) (%):
\[ m/z = \begin{align*} 
473 \ (11), \ 472 \ (100) \ [M^+] , \ 166 \ (14), \ 88 \ (14), \ 84 \ (13), \ 83 \ (11), \ 70 \ (24). 
\end{align*} \]

HRMS for \( \text{C}_8\text{H}_2\text{I}_2\text{N}_4\text{S}_2 \) (471.7810): found: 471.7802.
C. EXPERIMENTAL PART

Synthesis of 2,3-dibromo-[1,4]dithiino[2,3-b:5,6-b']dipyrazine (52b)

Bromine (0.5 mL, 1.55 g, 39 mmol) was added dropwise to a solution of 2,3-bis(triethylsilyl)-[1,4]dithiino[2,3-b:5,6-b']dipyrazine (51b; 112 mg, 0.25 mmol) in CH₂Cl₂ (0.5 mL) at 25 °C. The reaction mixture was stirred for 20 h and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 9:1) yielding 52b as yellow solid (57 mg, 60%).

m.p.: 141.6 – 144.7 °C.

¹H-NMR (300 MHz, CDCl₃) δ/ppm = 8.24 (s, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 149.7, 148.4, 142.1, 139.6.

IR (cm⁻¹): ν = 2956, 2922, 2853, 2604, 1919, 1462, 1418, 1349, 1264, 1197, 1175, 1139, 1078, 1052, 875, 808, 735.

MS (70 eV, El) m/z (%): 380 (56), 379 (13), 378 (100), 376 (51) [M⁺], 336 (10), 334 (19), 218 (42), 108 (16), 88 (20), 84 (14), 83 (19), 82 (15), 70 (39), 52 (12).

HRMS for C₈H₂Br₂N₄S₂ (375.8088): found: 375.8098.

Synthesis of 2,3-dichloro-5,6-diiodopyrazine (52c)

ICl (3.04 mL, 9.74 g, 60 mmol) was added dropwise to a solution of 2,3-dichloro-5,6-bis(trimethylsilyl)pyrazine (50a; 1.46 g, 5.0 mmol) in CH₂Cl₂ (10 mL) at 25 °C. The reaction mixture was stirred at 50 °C for 4 h and was then quenched with sat. aq. Na₂S₂O₃ solution (5 mL), extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/CH₂Cl₂, 9:1) yielding 52c as yellow solid (1.24 g, 62%).

m.p.: 127.6 – 131.9 °C.

¹³C-NMR (75 MHz, CDCl₃) δ/ppm = 145.3, 125.3.
C. EXPERIMENTAL PART

IR (cm$^{-1}$): $\nu = 2956, 2923, 2845, 1477, 1461, 1346, 1289, 1277, 1258, 1194, 1128, 1044, 933, 878, 843, 803, 658$.

MS (70 eV, EI) $m/z$ (%) = 407 (12), 405 (26), 402 (12), 400 (18) [$\text{M}^+$], 273 (12), 147 (15), 127 (23), 81 (11), 73 (100), 71 (16), 69 (20), 57 (25), 55 (20), 44 (52), 43 (20), 43 (54), 41 (23).

HRMS for $\text{C}_4\text{Cl}_2\text{I}_2\text{N}_2$ (399.7528): found: 399.7535.
E. APPENDIX
1. X-Ray Data for Compounds 15e, 15m, 27a, 27b, 32g, 35c and 35d

Single crystals of compounds 15e, 15m, 27a, 27b, 32g, 35c, and 35d, suitable for X-ray diffraction, were obtained by slow evaporation of heptane-, THF- or CH₂Cl₂-solutions solutions. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-Kα radiation (λ = 0.71071 Å).

Data collection was performed with the CrysAlis CCD software, CrysAlis RED software was used for data reduction. Absorption correction using the SCALE3 ABSPACK multiscan method was applied. The structures were solved with SHELXS-97, refined with SHELXL-97 and finally checked using PLATON. Details for data collection and structure refinement are summarized in Table 10, Table 17 and Table 24.

CCDC-1016850 (for 15e), CCDC-1016851 (for 15m), CCDC-1425229 (for 32g), CCDC-1425230 (for 35c) and CCDC-1425228 (for 35d) contain supplementary crystallographic data for this thesis. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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79 SCALE3 ABSPACK – An Oxford Diffraction Program (1.0.4, gui:1.0.3) (C), Oxford Diffraction, Ltd., 2005.
### Quinoxalines

**Table 10:** Details for X-ray data collection and structure refinement for compounds 15e and 15m.

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<tr>
<th></th>
<th>15e</th>
<th>15m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C(<em>{30})H(</em>{16})N(_2)O(_2)</td>
<td>C(<em>{30})H(</em>{16})N(_2)S(_2)</td>
</tr>
<tr>
<td>Formula mass</td>
<td>436.45</td>
<td>468.57</td>
</tr>
<tr>
<td>T[K]</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>Crystal size [mm]</td>
<td>0.43 × 0.15 × 0.10</td>
<td>0.23 × 0.13 × 0.06</td>
</tr>
<tr>
<td>Crystal description</td>
<td>yellow rod</td>
<td>yellow block</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P21)</td>
<td>(P21/c)</td>
</tr>
<tr>
<td>a [Å]</td>
<td>12.4504(11)</td>
<td>15.3378(10)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>5.6333(4)</td>
<td>14.1481(8)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>15.8276(11)</td>
<td>10.3748(5)</td>
</tr>
<tr>
<td>α [°]</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>β [°]</td>
<td>98.584(7)</td>
<td>94.934(5)</td>
</tr>
<tr>
<td>γ [°]</td>
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<td>90.0</td>
</tr>
<tr>
<td>V [Å(^3)]</td>
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<td>2243.0(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
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<tr>
<td>(\rho_{\text{calc.}}) [g cm(^{-3})]</td>
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<td>1.388</td>
</tr>
<tr>
<td>(\mu) [mm(^{-1})]</td>
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<td>0.260</td>
</tr>
<tr>
<td>(F(000))</td>
<td>452</td>
<td>968</td>
</tr>
<tr>
<td>(\Theta) range [°]</td>
<td>4.26 – 28.28</td>
<td>4.20 – 25.35</td>
</tr>
<tr>
<td>Index ranges</td>
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<td>(-18 \leq h \leq 18)</td>
</tr>
<tr>
<td></td>
<td>(-7 \leq k \leq 7)</td>
<td>(-16 \leq k \leq 17)</td>
</tr>
<tr>
<td></td>
<td>(-16 \leq l \leq 21)</td>
<td>(-12 \leq l \leq 12)</td>
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<td>Reflns. collected</td>
<td>6781</td>
<td>14332</td>
</tr>
<tr>
<td>Reflns. obsd.</td>
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<td>2689</td>
</tr>
<tr>
<td>Reflns. unique</td>
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<td>4067</td>
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<tr>
<td>(R_{\text{int}} = 0.0274)</td>
<td>(R_{\text{int}} = 0.0782)</td>
<td></td>
</tr>
<tr>
<td>(R_1, wR_2) (2(σ) data)</td>
<td>0.0572, 0.1008</td>
<td>0.0503, 0.0974</td>
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<tr>
<td>(R_1, wR_2) (all data)</td>
<td>0.1064, 0.1279</td>
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<td>GOOF on (F^2)</td>
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<tr>
<td>Peak/hole [e Å(^{-3})]</td>
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<td>0.393 / -0.369</td>
</tr>
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</table>
Figure 10: Molecular structure of compound 15e in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.

Table 11: Selected bond lengths (Å) of compound 15e.

<table>
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<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
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<td>C6 – N1</td>
<td>1.377(3)</td>
<td>C8 – C9</td>
<td>1.444(3)</td>
</tr>
<tr>
<td>C6 – C1</td>
<td>1.410(4)</td>
<td>C27 – C28</td>
<td>1.384(4)</td>
</tr>
<tr>
<td>C6 – C5</td>
<td>1.414(3)</td>
<td>C13 – C12</td>
<td>1.384(4)</td>
</tr>
<tr>
<td>C2 – C1</td>
<td>1.391(4)</td>
<td>C16 – C15</td>
<td>1.193(3)</td>
</tr>
<tr>
<td>C2 – C3</td>
<td>1.399(3)</td>
<td>C16 – C17</td>
<td>1.441(3)</td>
</tr>
<tr>
<td>O2 – C24</td>
<td>1.361(3)</td>
<td>C9 – C10</td>
<td>1.389(4)</td>
</tr>
<tr>
<td>O2 – C26</td>
<td>1.388(3)</td>
<td>C29 – C30</td>
<td>1.383(4)</td>
</tr>
<tr>
<td>C5 – N2</td>
<td>1.373(3)</td>
<td>C29 – C28</td>
<td>1.383(4)</td>
</tr>
<tr>
<td>C5 – C4</td>
<td>1.411(4)</td>
<td>C17 – C18</td>
<td>1.391(4)</td>
</tr>
<tr>
<td>C25 – C30</td>
<td>1.374(4)</td>
<td>C18 – C19</td>
<td>1.379(3)</td>
</tr>
<tr>
<td>C25 – O1</td>
<td>1.385(3)</td>
<td>C10 – C11</td>
<td>1.387(4)</td>
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<tr>
<td>C25 – C26</td>
<td>1.393(3)</td>
<td>C12 – C11</td>
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<td>C1 – C7</td>
<td>1.435(3)</td>
<td>C21 – C20</td>
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<tr>
<td>C4 – C3</td>
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<tr>
<td>C4 – C15</td>
<td>1.434(3)</td>
<td>C7 – C8</td>
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<td>1.363(3)</td>
<td>C22 – C21</td>
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<td>N2 – C24</td>
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<td>C22 – C17</td>
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<td>C14 – C13</td>
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<tr>
<td>C23 – C24</td>
<td>1.436(3)</td>
<td>C14 – C9</td>
<td>1.392(4)</td>
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Table 12: Selected bond angles (°) of compound 15e.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
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<tbody>
<tr>
<td>N1 – C6 – C1</td>
<td>119.3(2)</td>
</tr>
<tr>
<td>N1 – C6 – C5</td>
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</tr>
<tr>
<td>C1 – C6 – C5</td>
<td>120.2(3)</td>
</tr>
<tr>
<td>C1 – C2 – C3</td>
<td>120.7(3)</td>
</tr>
<tr>
<td>C24 – O2 – C26</td>
<td>117.1(2)</td>
</tr>
<tr>
<td>N2 – C5 – C4</td>
<td>118.7(2)</td>
</tr>
<tr>
<td>N2 – C5 – C6</td>
<td>121.1(3)</td>
</tr>
<tr>
<td>C4 – C5 – C6</td>
<td>120.2(3)</td>
</tr>
<tr>
<td>C30 – C25 – O1</td>
<td>118.2(2)</td>
</tr>
<tr>
<td>C30 – C25 – C26</td>
<td>120.3(3)</td>
</tr>
<tr>
<td>O1 – C25 – C26</td>
<td>121.5(2)</td>
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<tr>
<td>C2 – C1 – C6</td>
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<td>C2 – C1 – C7</td>
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<tr>
<td>N1 – C23 – O1</td>
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<td>N1 – C23 – C4</td>
<td>123.2(2)</td>
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<td>O1 – C23 – C4</td>
<td>120.7(2)</td>
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<td>O2 – C26 – C25</td>
<td>121.6(2)</td>
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<tr>
<td>N2 – C24 – C2</td>
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<tr>
<td>C1 – C6 – C5</td>
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</tr>
<tr>
<td>N1 – C6 – C5</td>
<td>178.2(2)</td>
</tr>
<tr>
<td>C1 – C6 – C5</td>
<td>-0.9(4)</td>
</tr>
<tr>
<td>C3 – C2 – C1</td>
<td>-0.4(4)</td>
</tr>
<tr>
<td>C3 – C2 – C7</td>
<td>-179.7(3)</td>
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<td>1.0(4)</td>
</tr>
<tr>
<td>N1 – C6 – C1</td>
<td>1.1(4)</td>
</tr>
<tr>
<td>C5 – C6 – C1</td>
<td>-179.8(2)</td>
</tr>
</tbody>
</table>

Table 13: Selected torsion angles (°) of compound 15e.

<table>
<thead>
<tr>
<th>Torsion</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1 – C6 – C5 – N2</td>
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</tr>
<tr>
<td>O1 – C25 – C26 – O2</td>
<td>-0.1(4)</td>
</tr>
<tr>
<td>C1 – C6 – C5 – N2</td>
<td>-179.5(2)</td>
</tr>
<tr>
<td>O2 – C26 – C27 – C28</td>
<td>179.8(2)</td>
</tr>
<tr>
<td>N1 – C6 – C5 – C4</td>
<td>178.2(2)</td>
</tr>
<tr>
<td>C25 – C26 – C27 – C28</td>
<td>1.4(4)</td>
</tr>
<tr>
<td>C1 – C6 – C5 – C4</td>
<td>-0.9(4)</td>
</tr>
<tr>
<td>C5 – N2 – C24 – O2</td>
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</tr>
<tr>
<td>C3 – C2 – C1 – C6</td>
<td>-0.4(4)</td>
</tr>
<tr>
<td>C5 – N2 – C24 – C23</td>
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</tr>
<tr>
<td>C3 – C2 – C1 – C7</td>
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</tr>
<tr>
<td>C26 – O2 – C24 – N2</td>
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</tr>
<tr>
<td>N1 – C6 – C1 – C2</td>
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<tr>
<td>C26 – O2 – C24 – C23</td>
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<td>C5 – C6 – C1 – C2</td>
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<td>N1 – C23 – C24 – N2</td>
<td>-0.9(4)</td>
</tr>
<tr>
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</tr>
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<td>O1 – C23 – C24 – N2</td>
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<tr>
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<tr>
<td>N1 – C23 – C24 – O2</td>
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<td>Length (Å)</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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<td>-178.4(2)</td>
</tr>
<tr>
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<td>0.3(4)</td>
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<td>177.2(3)</td>
</tr>
<tr>
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<td>-0.2(4)</td>
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<tr>
<td>C4–C5–N2–C24</td>
<td>-177.9(2)</td>
</tr>
<tr>
<td>C6–C5–N2–C24</td>
<td>0.8(4)</td>
</tr>
<tr>
<td>C1–C6–N1–C23</td>
<td>178.5(2)</td>
</tr>
<tr>
<td>C5–C6–N1–C23</td>
<td>-0.6(4)</td>
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<td>C6–N1–C23–O1</td>
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<td>C6–N1–C23–C24</td>
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<td>C24–O2–C26–C27</td>
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<td>C30–C25–C26–C27</td>
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<tr>
<td>O1–C25–C26–C27</td>
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</tr>
<tr>
<td>C30–C25–C26–O2</td>
<td>179.7(3)</td>
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Figure 11: Molecular structure of compound 15m in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50 % probability level.

Table 14: Selected bond lengths (Å) of compound 15m.

<table>
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<tr>
<th>Bond</th>
<th>Length</th>
<th>Bond</th>
<th>Length</th>
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<td>C29 – C28</td>
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</tr>
<tr>
<td>S1 – C30</td>
<td>1.773(3)</td>
<td>C8 – C7</td>
<td>1.196(4)</td>
</tr>
<tr>
<td>S2 – C25</td>
<td>1.756(3)</td>
<td>C8 – C9</td>
<td>1.437(4)</td>
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<tr>
<td>S2 – C24</td>
<td>1.763(3)</td>
<td>C12 – C13</td>
<td>1.369(4)</td>
</tr>
<tr>
<td>N2 – C24</td>
<td>1.307(4)</td>
<td>C12 – C11</td>
<td>1.380(4)</td>
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<tr>
<td>N2 – C3</td>
<td>1.379(3)</td>
<td>C9 – C10</td>
<td>1.387(4)</td>
</tr>
<tr>
<td>N1 – C23</td>
<td>1.310(3)</td>
<td>C9 – C14</td>
<td>1.393(4)</td>
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<td>N1 – C4</td>
<td>1.369(4)</td>
<td>C13 – C14</td>
<td>1.374(4)</td>
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<tr>
<td>C23 – C24</td>
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<td>C17 – C22</td>
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<td>C25 – C26</td>
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<td>C10 – C11</td>
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<tr>
<td>C25 – C30</td>
<td>1.389(4)</td>
<td>C26 – C27</td>
<td>1.374(4)</td>
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<tr>
<td>C16 – C15</td>
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<td>C20 – C21</td>
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<td>C16 – C17</td>
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<td>C28 – C27</td>
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<td>C30 – C29</td>
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<td>C2 – C1</td>
<td>1.388(4)</td>
<td>C5 – C6</td>
<td>1.372(4)</td>
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<tr>
<td>C2 – C3</td>
<td>1.421(4)</td>
<td>C5 – C15</td>
<td>1.421(4)</td>
</tr>
<tr>
<td>C2 – C7</td>
<td>1.430(4)</td>
<td>C18 – C19</td>
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<td>C4 – C3</td>
<td>1.396(4)</td>
<td>C18 – C17</td>
<td>1.398(4)</td>
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### Table 15: Selected bond angles (°) of compound 15m.

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<td>C13 – C12 – C11</td>
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<td>C25 – S2 – C24</td>
<td>101.7(1)</td>
<td>C10 – C9 – C14</td>
</tr>
<tr>
<td>C24 – N2 – C3</td>
<td>116.5(2)</td>
<td>C10 – C9 – C8</td>
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<tr>
<td>C23 – N1 – C4</td>
<td>116.6(2)</td>
<td>C14 – C9 – C8</td>
</tr>
<tr>
<td>N1 – C23 – C24</td>
<td>122.0(3)</td>
<td>C12 – C13 – C14</td>
</tr>
<tr>
<td>N1 – C23 – S1</td>
<td>115.1(2)</td>
<td>C22 – C17 – C18</td>
</tr>
<tr>
<td>C24 – C23 – S1</td>
<td>122.8(2)</td>
<td>C22 – C17 – C16</td>
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<tr>
<td>N2 – C24 – C23</td>
<td>122.4(2)</td>
<td>C18 – C17 – C16</td>
</tr>
<tr>
<td>N2 – C24 – S2</td>
<td>116.1(2)</td>
<td>C13 – C14 – C9</td>
</tr>
<tr>
<td>C23 – C24 – S2</td>
<td>121.2(2)</td>
<td>C11 – C10 – C9</td>
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<tr>
<td>C26 – C25 – C30</td>
<td>119.4(3)</td>
<td>C8 – C7 – C2</td>
</tr>
<tr>
<td>C26 – C25 – S2</td>
<td>117.9(2)</td>
<td>C10 – C11 – C12</td>
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<td>C30 – C25 – S2</td>
<td>122.7(2)</td>
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</tr>
<tr>
<td>C15 – C16 – C17</td>
<td>175.7(3)</td>
<td>C5 – C6 – C1</td>
</tr>
<tr>
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<td>C19 – C20 – C21</td>
</tr>
<tr>
<td>C29 – C30 – S1</td>
<td>117.3(2)</td>
<td>C27 – C28 – C29</td>
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<td>C1 – C2 – C3</td>
<td>117.9(3)</td>
<td>C22 – C21 – C20</td>
</tr>
<tr>
<td>C1 – C2 – C7</td>
<td>120.5(3)</td>
<td>C21 – C22 – C17</td>
</tr>
<tr>
<td>C3 – C2 – C7</td>
<td>121.6(2)</td>
<td>C16 – C15 – C5</td>
</tr>
<tr>
<td>N1 – C4 – C3</td>
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<td>C19 – C18 – C17</td>
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<td>N1 – C4 – C5</td>
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<tr>
<td>C2 – C1 – C6</td>
<td>121.5(3)</td>
<td>N2 – C3 – C2</td>
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<td>C6 – C5 – C15</td>
<td>122.2(2)</td>
<td>C4 – C3 – C2</td>
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<td>C6 – C5 – C4</td>
<td>118.3(3)</td>
<td>C30 – C29 – C28</td>
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<tr>
<td>C15 – C5 – C4</td>
<td>119.5(3)</td>
<td>C7 – C8 – C9</td>
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### Table 16: Selected torsion angles (°) of compound 15m.

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</tr>
</thead>
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<td>-175.4(3)</td>
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<td></td>
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<tr>
<td>C4 – N1 – C23 – S1</td>
<td>-176.7(2)</td>
<td>N1 – C4 – C3 – C2</td>
<td>-177.9(3)</td>
<td></td>
<td></td>
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<tr>
<td>C30 – S1 – C23 – N1</td>
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<td>C5 – C4 – C3 – C2</td>
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<tr>
<td>C30 – S1 – C23 – C24</td>
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<td>C1 – C2 – C3 – N2</td>
<td>177.0(3)</td>
<td></td>
<td></td>
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<tr>
<td>C3 – N2 – C24 – C23</td>
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<td>C7 – C2 – C3 – N2</td>
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<tr>
<td>C3 – N2 – C24 – S2</td>
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<td>C1 – C2 – C3 – C4</td>
<td>-1.4(4)</td>
<td></td>
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<tr>
<td>N1 – C23 – C24 – N2</td>
<td>3.7(4)</td>
<td>C7 – C2 – C3 – C4</td>
<td>179.7(3)</td>
<td></td>
<td></td>
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<tr>
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<td>179.7(2)</td>
<td>C25 – C30 – C29 – C28</td>
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<td></td>
<td></td>
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<tr>
<td>N1 – C23 – C24 – S2</td>
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<td>S1 – C30 – C29 – C28</td>
<td>176.1(2)</td>
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</table>
Tetrathiafulvalenes

Table 17: Details for X-ray data collection and structure refinement for compounds 27a and 27b.

<table>
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<tr>
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<th>27a</th>
<th>27b</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C₆H₂Br₂S₄</td>
<td>C₆H₂Br₂S₄</td>
</tr>
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<td>Formula mass</td>
<td>362.12</td>
<td>362.12</td>
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<tr>
<td>T[K]</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>Crystal size [mm]</td>
<td>0.48 × 0.11 × 0.06</td>
<td>0.13 × 0.06 × 0.03</td>
</tr>
<tr>
<td>Crystal description</td>
<td>orange red rod</td>
<td>Orange red platelet</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pna21</td>
<td>C2/c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>18.5221(11)</td>
<td>19.4634(7)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>3.9448(2)</td>
<td>3.9238(1)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>26.9282(16)</td>
<td>12.6797(4)</td>
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<table>
<thead>
<tr>
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<th>27a</th>
<th>27b</th>
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<td>( \alpha ) [°]</td>
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<td>90</td>
</tr>
<tr>
<td>( \beta ) [°]</td>
<td>90</td>
<td>93.194(3)</td>
</tr>
<tr>
<td>( \gamma ) [°]</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>( V ) [Å³]</td>
<td>1967.5(2)</td>
<td>966.85(5)</td>
</tr>
<tr>
<td>( Z )</td>
<td>8</td>
<td>4</td>
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<tr>
<td>( \rho_{\text{calc}} ) [g cm(^{-3})]</td>
<td>2.445</td>
<td>2.488</td>
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<tr>
<td>( \mu ) [mm(^{-1})]</td>
<td>9.026</td>
<td>9.184</td>
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<tr>
<td>( F(000) )</td>
<td>1376</td>
<td>688</td>
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<tr>
<td>( \Theta ) range [°]</td>
<td>4.38 – 28.28</td>
<td>4.19 – 30.50</td>
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<tr>
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<td>-27 ≤ ( h ) ≤ 27</td>
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<tr>
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<td>-5 ≤ ( k ) ≤ 5</td>
<td>-5 ≤ ( k ) ≤ 5</td>
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<tr>
<td></td>
<td>-34 ≤ ( l ) ≤ 35</td>
<td>-13 ≤ ( l ) ≤ 18</td>
</tr>
<tr>
<td>Reflns. collected</td>
<td>14939</td>
<td>4480</td>
</tr>
<tr>
<td>Reflns. obsd.</td>
<td>3245</td>
<td>1274</td>
</tr>
<tr>
<td>Reflns. unique</td>
<td>4717</td>
<td>1476</td>
</tr>
<tr>
<td></td>
<td>(( R_{\text{int}} = 0.0853 ))</td>
<td>(( R_{\text{int}} = 0.0293 ))</td>
</tr>
<tr>
<td>( R_1 ), ( wR_2 ) (2σ data)</td>
<td>0.0803, 0.1816</td>
<td>0.0238, 0.0492</td>
</tr>
<tr>
<td>( R_1 ), ( wR_2 ) (all data)</td>
<td>0.1222, 0.2242</td>
<td>0.0316, 0.0526</td>
</tr>
<tr>
<td>GOOF on ( F^2 )</td>
<td>1.089</td>
<td>1.043</td>
</tr>
<tr>
<td>Peak/hole [e Å(^{-3})]</td>
<td>5.850 / -1.146</td>
<td>0.494 / -0.573</td>
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Figure 12: Molecular structure of compound 27a in the crystal, view of the two crystallographically independent molecules, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.

Table 18: Selected bond lengths (Å) of compound 27a.

<table>
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<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<td>Br1 – C1</td>
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<tr>
<td>Br4 – C9</td>
<td>1.864(2)</td>
</tr>
<tr>
<td>S7 – C12</td>
<td>1.74(2)</td>
</tr>
<tr>
<td>S7 – C9</td>
<td>1.774(2)</td>
</tr>
<tr>
<td>S5 – C7</td>
<td>1.73(2)</td>
</tr>
<tr>
<td>S5 – C8</td>
<td>1.746(2)</td>
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<tr>
<td>S2 – C3</td>
<td>1.757(2)</td>
</tr>
<tr>
<td>S2 – C2</td>
<td>1.78(3)</td>
</tr>
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<td>S6–C11</td>
<td>1.72(3)</td>
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<tr>
<td>S6–C8</td>
<td>1.792(2)</td>
</tr>
<tr>
<td>S1–C1</td>
<td>1.75(3)</td>
</tr>
<tr>
<td>S3 – C4</td>
<td>1.76(3)</td>
</tr>
<tr>
<td>S8 – C12</td>
<td>1.76(3)</td>
</tr>
<tr>
<td>S8 – C10</td>
<td>1.760(2)</td>
</tr>
<tr>
<td>S4 – C6</td>
<td>1.709(2)</td>
</tr>
<tr>
<td>S4 – C10</td>
<td>1.75(2)</td>
</tr>
<tr>
<td>C4 – C3</td>
<td>1.34(3)</td>
</tr>
<tr>
<td>C2 – C1</td>
<td>1.29(4)</td>
</tr>
<tr>
<td>C6 – C5</td>
<td>1.32(2)</td>
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<tr>
<td>C7 – C11</td>
<td>1.39(4)</td>
</tr>
<tr>
<td>C9 – C10</td>
<td>1.30(2)</td>
</tr>
<tr>
<td>C8–C12</td>
<td>1.37(3)</td>
</tr>
<tr>
<td>S1–C3</td>
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</tr>
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<td>S3–C5</td>
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#### Table 19: Selected bond angles (°) of compound 27a.

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<th>Bond Angles</th>
<th>Value</th>
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</tr>
<tr>
<td>C3 – S2 – C2</td>
<td>94.9(1)</td>
</tr>
<tr>
<td>C11 – S6 – C8</td>
<td>95.7(1)</td>
</tr>
<tr>
<td>C1 – S1 – C3</td>
<td>94.0(1)</td>
</tr>
<tr>
<td>C5 – S3 – C4</td>
<td>95.4(1)</td>
</tr>
<tr>
<td>C12 – S8 – C10</td>
<td>93.7(9)</td>
</tr>
<tr>
<td>C6 – S4 – C4</td>
<td>93.6(1)</td>
</tr>
<tr>
<td>C3 – C4 – S4</td>
<td>123.2(2)</td>
</tr>
<tr>
<td>C3 – C4 – S3</td>
<td>122.5(2)</td>
</tr>
<tr>
<td>S4 – C4 – S3</td>
<td>114.8(2)</td>
</tr>
<tr>
<td>C1 – C2 – S2</td>
<td>116.4(2)</td>
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<tr>
<td>C5 – C6 – S4</td>
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</tr>
<tr>
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<td>122.1(1)</td>
</tr>
<tr>
<td>S4 – C6 – Br2</td>
<td>115.8(9)</td>
</tr>
<tr>
<td>C11 – C7 – S5</td>
<td>118.2(2)</td>
</tr>
<tr>
<td>C11 – C7 – Br3</td>
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<tr>
<td>S5 – C7 – Br3</td>
<td>116.4(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7 – C9 – Br4</td>
<td>115.1(1)</td>
</tr>
<tr>
<td>C2 – C1 – S1</td>
<td>120.2(2)</td>
</tr>
<tr>
<td>C2 – C1 – Br1</td>
<td>125.2(2)</td>
</tr>
<tr>
<td>S1 – C1 – Br1</td>
<td>114.7(2)</td>
</tr>
<tr>
<td>C12 – C8 – S5</td>
<td>122.0(2)</td>
</tr>
<tr>
<td>C12 – C8 – S6</td>
<td>124.0(2)</td>
</tr>
<tr>
<td>S5 – C8 – S6</td>
<td>114.0(9)</td>
</tr>
<tr>
<td>C9 – C10 – S8</td>
<td>117.2(1)</td>
</tr>
<tr>
<td>C4 – C3 – S2</td>
<td>123.7(2)</td>
</tr>
<tr>
<td>C4 – C3 – S1</td>
<td>121.8(2)</td>
</tr>
<tr>
<td>S2 – C3 – S1</td>
<td>114.5(1)</td>
</tr>
<tr>
<td>C6 – C5 – S3</td>
<td>114.0(1)</td>
</tr>
<tr>
<td>C8 – C12 – S7</td>
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<tr>
<td>C8 – C12 – S8</td>
<td>122.8(2)</td>
</tr>
<tr>
<td>S7 – C12 – S8</td>
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</tr>
<tr>
<td>C7 – C11 – S6</td>
<td>116.6(2)</td>
</tr>
<tr>
<td>C10 – C9 – S7</td>
<td>119.5(1)</td>
</tr>
<tr>
<td>C10 – C9 – Br4</td>
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#### Table 20: Selected torsion angles (°) of compound 27a.

<table>
<thead>
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</tr>
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</tr>
<tr>
<td>C5 – S3 – C4 – C3</td>
<td>-177.1(2)</td>
</tr>
<tr>
<td>C5 – S3 – C4 – S4</td>
<td>1.9(1)</td>
</tr>
<tr>
<td>C3 – S2 – C2 – C1</td>
<td>0.6(2)</td>
</tr>
<tr>
<td>C4 – S4 – C6 – C5</td>
<td>-0.3(2)</td>
</tr>
<tr>
<td>C4 – S4 – C6 – Br2</td>
<td>178.8(1)</td>
</tr>
<tr>
<td>C8 – S5 – C7 – C11</td>
<td>-0.4(2)</td>
</tr>
<tr>
<td>C8 – S5 – C7 – Br3</td>
<td>-177.8(1)</td>
</tr>
<tr>
<td>C12 – S7 – C9 – C10</td>
<td>-0.1(2)</td>
</tr>
<tr>
<td>C12 – S7 – C9 – Br4</td>
<td>178.4(1)</td>
</tr>
<tr>
<td>S2 – C2 – C1 – S1</td>
<td>-2.0(3)</td>
</tr>
<tr>
<td>S2 – C2 – C1 – Br1</td>
<td>178.4(1)</td>
</tr>
<tr>
<td>S2 – C2 – C1 – Br1</td>
<td>178.4(1)</td>
</tr>
<tr>
<td>C3 – S1 – C1 – C2</td>
<td>2.7(22)</td>
</tr>
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</tr>
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<td>C7 – S5 – C8 – S6</td>
<td>-1.4(1)</td>
</tr>
<tr>
<td>C11 – S6 – C8 – C12</td>
<td>-177.2(2)</td>
</tr>
<tr>
<td>C11 – S6 – C8 – S5</td>
<td>2.2(1)</td>
</tr>
<tr>
<td>S7 – C9 – C10 – S8</td>
<td>0.0(2)</td>
</tr>
<tr>
<td>Br4 – C9 – C10 – S8</td>
<td>-178.3(8)</td>
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<table>
<thead>
<tr>
<th>Torsion Angles</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>S3 – C4 – C3 – S2</td>
<td>1.3(3)</td>
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<tr>
<td>S4 – C4 – C3 – S1</td>
<td>0.3(3)</td>
</tr>
<tr>
<td>S3 – C4 – C3 – S1</td>
<td>178.7(1)</td>
</tr>
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<td>179.2(2)</td>
</tr>
<tr>
<td>C2 – S2 – C3 – S1</td>
<td>1.2(1)</td>
</tr>
<tr>
<td>C1 – S1 – C3 – C4</td>
<td>179.8(2)</td>
</tr>
<tr>
<td>C1 – S1 – C3 – S2</td>
<td>-2.1(1)</td>
</tr>
<tr>
<td>S4 – C6 – C5 – S3</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>Br2 – C6 – C5 – S3</td>
<td>-177.3(8)</td>
</tr>
<tr>
<td>C4 – S3 – C5 – C6</td>
<td>-2.1(2)</td>
</tr>
<tr>
<td>S5 – C8 – C12 – S7</td>
<td>2.0(2)</td>
</tr>
<tr>
<td>S6 – C8 – C12 – S7</td>
<td>-178.5(1)</td>
</tr>
<tr>
<td>S5 – C8 – C12 – S8</td>
<td>178.6(1)</td>
</tr>
<tr>
<td>S6 – C8 – C12 – S8</td>
<td>-2.2(2)</td>
</tr>
<tr>
<td>C9 – S7 – C12 – C8</td>
<td>176.7(2)</td>
</tr>
<tr>
<td>C9 – S7 – C12 – S8</td>
<td>0.1(1)</td>
</tr>
<tr>
<td>C10 – S8 – C12 – C8</td>
<td>-176.6(2)</td>
</tr>
<tr>
<td>C10 – S8 – C12 – S7</td>
<td>0.0(1)</td>
</tr>
<tr>
<td>S5 – C7 – C11 – S6</td>
<td>2.2(2)</td>
</tr>
<tr>
<td>Br3 – C7 – C11 – S6</td>
<td>179.3(1)</td>
</tr>
</tbody>
</table>
Figure 13: Molecular structure of compound 27b in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50 % probability level.

Table 21: Selected bond lengths (Å) of compound 27b.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Br1 – C3</td>
<td>1.882(2)</td>
<td>S2 – C1</td>
</tr>
<tr>
<td>S1 – C3</td>
<td>1.741(2)</td>
<td>C3 – C4</td>
</tr>
<tr>
<td>S1 – C1</td>
<td>1.762(2)</td>
<td>C1 – C1&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
<tr>
<td>S2 – C4</td>
<td>1.739(2)</td>
<td></td>
</tr>
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</table>

Table 22: Selected bond angles (°) of compound 27b.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>C3 – S1 – C1</td>
<td>93.7(1)</td>
<td>C1&lt;sup&gt;i&lt;/sup&gt; – C1 – S1</td>
</tr>
<tr>
<td>C4 – S2 – C1</td>
<td>95.1(1)</td>
<td>C1&lt;sup&gt;i&lt;/sup&gt; – C1 – S2</td>
</tr>
<tr>
<td>C4 – C3 – S1</td>
<td>119.7(2)</td>
<td>S1 – C1 – S2</td>
</tr>
<tr>
<td>C4 – C3 – Br1</td>
<td>123.4(2)</td>
<td>C3 – C4 – S2</td>
</tr>
<tr>
<td>S1 – C3 – Br1</td>
<td>116.9(1)</td>
<td></td>
</tr>
</tbody>
</table>

Table 23: Selected torsion angles (°) of compound 27b.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 – S1 – C3 – C4</td>
<td>-1.6(2)</td>
<td>C3 – S1 – C1 – C1&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
<tr>
<td>C1 – S1 – C3 – Br1</td>
<td>178.9(1)</td>
<td>C3 – S1 – C1 – S2</td>
</tr>
<tr>
<td>S1 – C3 – C4 – S2</td>
<td>0.6(3)</td>
<td>C4 – S2 – C1 – C1&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
<tr>
<td>Br1 – C3 – C4 – S2</td>
<td>-179.9(1)</td>
<td>C4 – S2 – C1 – S1</td>
</tr>
<tr>
<td>C1 – S2 – C4 – C3</td>
<td>0.7(2)</td>
<td></td>
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### Table 24: Details for X-ray data collection and structure refinement for compounds 32g, 35c and 35d.

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<thead>
<tr>
<th></th>
<th>32g</th>
<th>35c</th>
<th>35d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₉H₈O₂S₄</td>
<td>C₃₀H₂₈O₈S₄</td>
<td>C₂₉H₁₈N₂O₄S₄ · (H₂O)₀.₁₁</td>
</tr>
<tr>
<td><strong>Formula mass</strong></td>
<td>276.39</td>
<td>644.76</td>
<td>552.65</td>
</tr>
<tr>
<td><strong>T[K]</strong></td>
<td>173(2)</td>
<td>173(2)</td>
<td>123(2)</td>
</tr>
<tr>
<td><strong>Crystal size [mm]</strong></td>
<td>0.22 × 0.17 × 0.11</td>
<td>0.37 × 0.26 × 0.11</td>
<td>0.23 × 0.17 × 0.13</td>
</tr>
<tr>
<td><strong>Crystal description</strong></td>
<td>orange red block</td>
<td>dark red block</td>
<td>red block</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>triclinic</td>
<td>Triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a [Å]</strong></td>
<td>7.4753(3)</td>
<td>14.0157(6)</td>
<td>10.4341(5)</td>
</tr>
<tr>
<td><strong>b [Å]</strong></td>
<td>7.5350(3)</td>
<td>15.870(6)</td>
<td>10.5898(6)</td>
</tr>
<tr>
<td><strong>c [Å]</strong></td>
<td>20.4016(12)</td>
<td>16.2834(8)</td>
<td>13.6768(5)</td>
</tr>
<tr>
<td><strong>α [°]</strong></td>
<td>85.359(4)</td>
<td>61.914(5)</td>
<td>70.307(4)</td>
</tr>
<tr>
<td><strong>β [°]</strong></td>
<td>88.611(4)</td>
<td>72.352(4)</td>
<td>86.343(3)</td>
</tr>
<tr>
<td><strong>γ [°]</strong></td>
<td>89.943(4)</td>
<td>82.966(4)</td>
<td>64.261(5)</td>
</tr>
<tr>
<td><strong>V [Å³]</strong></td>
<td>1145.04(9)</td>
<td>3044.2(11)</td>
<td>1275.57(11)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td><strong>ρ_{calcd.} [g cm⁻³]</strong></td>
<td>1.603</td>
<td>1.407</td>
<td>1.439</td>
</tr>
<tr>
<td><strong>μ [mm⁻¹]</strong></td>
<td>0.804</td>
<td>0.361</td>
<td>0.409</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>568</td>
<td>1344</td>
<td>570</td>
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<tr>
<td><strong>Θ range [°]</strong></td>
<td>4.21 – 25.35</td>
<td>4.17 – 25.35</td>
<td>4.09 – 25.35</td>
</tr>
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<td><strong>Index ranges</strong></td>
<td>-8 ≤ h ≤ 9</td>
<td>-12 ≤ h ≤ 12</td>
<td>-12 ≤ h ≤ 12</td>
</tr>
<tr>
<td></td>
<td>-9 ≤ k ≤ 9</td>
<td>-18 ≤ k ≤ 19</td>
<td>-12 ≤ k ≤ 12</td>
</tr>
<tr>
<td></td>
<td>-24 ≤ l ≤ 24</td>
<td>-19 ≤ l ≤ 19</td>
<td>-16 ≤ l ≤ 16</td>
</tr>
<tr>
<td><strong>Refns. collected</strong></td>
<td>8066</td>
<td>22722</td>
<td>17681</td>
</tr>
<tr>
<td><strong>Refns. obsd.</strong></td>
<td>3404</td>
<td>8250</td>
<td>3826</td>
</tr>
<tr>
<td><strong>Refns. unique</strong></td>
<td>4130</td>
<td>11073</td>
<td>4642</td>
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<tr>
<td></td>
<td>(R_int = 0.0347)</td>
<td>(R_int = 0.0284)</td>
<td>(R_int = 0.0344)</td>
</tr>
<tr>
<td><strong>R₁, wR₂ (2σ data)</strong></td>
<td>0.0619, 0.1421</td>
<td>0.0472, 0.1123</td>
<td>0.0307, 0.0748</td>
</tr>
<tr>
<td><strong>R₁, wR₂ (all data)</strong></td>
<td>0.0760, 0.1503</td>
<td>0.0689, 0.1271</td>
<td>0.0410, 0.0803</td>
</tr>
<tr>
<td><strong>GOOF on F²</strong></td>
<td>1.088</td>
<td>1.023</td>
<td>1.032</td>
</tr>
<tr>
<td><strong>Peak/hole [e Å⁻³]</strong></td>
<td>1.379 / -0.461</td>
<td>1.381 / -0.515</td>
<td>0.269 / -0.231</td>
</tr>
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</table>
Figure 14: Molecular structure of compound 32g in the crystal, view of the two crystallographically independent molecules, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.

Table 25: Selected bond lengths (Å) of compound 32g.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
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<tbody>
<tr>
<td>S8 – C15</td>
<td>1.739(5)</td>
</tr>
<tr>
<td>S8 – C13</td>
<td>1.761(5)</td>
</tr>
<tr>
<td>S2 – C2</td>
<td>1.740(6)</td>
</tr>
<tr>
<td>S2 – C3</td>
<td>1.763(5)</td>
</tr>
<tr>
<td>S4 – C5</td>
<td>1.660(6)</td>
</tr>
<tr>
<td>S4 – C4</td>
<td>1.757(5)</td>
</tr>
<tr>
<td>S7 – C14</td>
<td>1.708(5)</td>
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<tr>
<td>S7 – C13</td>
<td>1.772(5)</td>
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<tr>
<td>S1 – C1</td>
<td>1.733(7)</td>
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<tr>
<td>S1 – C3</td>
<td>1.763(5)</td>
</tr>
<tr>
<td>S5 – C11</td>
<td>1.740(5)</td>
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<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<tr>
<td>C12 – C13</td>
<td>1.338(7)</td>
</tr>
<tr>
<td>O3 – C16</td>
<td>1.207(6)</td>
</tr>
<tr>
<td>C10 – C11</td>
<td>1.329(8)</td>
</tr>
<tr>
<td>C7 – C6</td>
<td>1.506(8)</td>
</tr>
<tr>
<td>C17 – C18</td>
<td>1.522(7)</td>
</tr>
<tr>
<td>C5 – C6</td>
<td>1.339(8)</td>
</tr>
<tr>
<td>C8 – C9</td>
<td>1.503(7)</td>
</tr>
<tr>
<td>C2 – C1</td>
<td>1.314(8)</td>
</tr>
<tr>
<td>O4 – C16</td>
<td>1.334(6)</td>
</tr>
<tr>
<td>O4 – C17</td>
<td>1.450(6)</td>
</tr>
<tr>
<td>O2 – C7</td>
<td>1.340(6)</td>
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### Table 26: Selected bond angles (°) of compound 32g.

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<td>94.6(3)</td>
</tr>
<tr>
<td>C5 – S4 – C4</td>
<td>95.5(3)</td>
</tr>
<tr>
<td>C14 – S7 – C13</td>
<td>94.7(2)</td>
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<td>C1 – S1 – C3</td>
<td>94.9(3)</td>
</tr>
<tr>
<td>C11 – S5 – C12</td>
<td>94.5(2)</td>
</tr>
<tr>
<td>C10 – S6 – C12</td>
<td>94.4(2)</td>
</tr>
<tr>
<td>C6 – S3 – C4</td>
<td>93.1(3)</td>
</tr>
<tr>
<td>C16 – O4 – C17</td>
<td>116.6(4)</td>
</tr>
<tr>
<td>C7 – O2 – C8</td>
<td>116.5(4)</td>
</tr>
<tr>
<td>C3 – C4 – S4</td>
<td>123.0(4)</td>
</tr>
<tr>
<td>C3 – C4 – S3</td>
<td>122.8(4)</td>
</tr>
<tr>
<td>S4 – C4 – S3</td>
<td>114.2(3)</td>
</tr>
<tr>
<td>C14 – C15 – C16</td>
<td>125.9(5)</td>
</tr>
<tr>
<td>C14 – C15 – S8</td>
<td>118.1(4)</td>
</tr>
<tr>
<td>C16 – C15 – S8</td>
<td>115.9(3)</td>
</tr>
<tr>
<td>C15 – C14 – S7</td>
<td>118.4(4)</td>
</tr>
<tr>
<td>C13 – C12 – S5</td>
<td>122.5(4)</td>
</tr>
<tr>
<td>C13 – C12 – S6</td>
<td>122.8(4)</td>
</tr>
<tr>
<td>S5 – C12 – S6</td>
<td>114.7(3)</td>
</tr>
<tr>
<td>C4 – C3 – S2</td>
<td>122.7(4)</td>
</tr>
</tbody>
</table>

### Table 27: Selected torsion angles (°) of compound 32g.

<table>
<thead>
<tr>
<th>Torsion</th>
<th>Angle</th>
</tr>
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<tbody>
<tr>
<td>C5 – S4 – C4 – C3</td>
<td>-179.7(5)</td>
</tr>
<tr>
<td>C5 – S4 – C4 – S3</td>
<td>-0.9(3)</td>
</tr>
<tr>
<td>C6 – S3 – C4 – C3</td>
<td>179.8(5)</td>
</tr>
<tr>
<td>C6 – S3 – C4 – S4</td>
<td>1.0(3)</td>
</tr>
<tr>
<td>C13 – S8 – C15 – C14</td>
<td>0.0(4)</td>
</tr>
<tr>
<td>C13 – S8 – C15 – C16</td>
<td>179.6(4)</td>
</tr>
<tr>
<td>C16 – C15 – C14 – S7</td>
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Figure 15: Molecular structure of compound 35c in the crystal, view of the two crystallographically independent molecules, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.
Table 28: Selected bond lengths (Å) of compound 35c.

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Table 29: Selected bond angles (°) of compound 35c.

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Table 30: Selected torsion angles (°) of compound 35c.

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Figure 16: Molecular structure of compound 35d in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.

Table 31: Selected bond lengths (Å) of compound 35d.

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<td>1.501(3)</td>
</tr>
<tr>
<td>C19 – C20</td>
<td>1.476(2)</td>
</tr>
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<td>C22 – C21</td>
<td>1.388(3)</td>
</tr>
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Table 32: Selected bond angles (°) of compound 35d.

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<th>Bond</th>
<th>Angle (°)</th>
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<tbody>
<tr>
<td>C1 – S1 – C2</td>
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<tr>
<td>C10 – S4 – C19</td>
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</tr>
<tr>
<td>C10 – S3 – C11</td>
<td>95.08(8)</td>
</tr>
<tr>
<td>C3 – S2 – C1</td>
<td>94.60(8)</td>
</tr>
<tr>
<td>C4 – O1 – C5</td>
<td>116.43(14)</td>
</tr>
<tr>
<td>C2 – C3 – C4</td>
<td>126.06(16)</td>
</tr>
<tr>
<td>C2 – C3 – S2</td>
<td>117.92(14)</td>
</tr>
<tr>
<td>C4 – C3 – S2</td>
<td>116.01(13)</td>
</tr>
<tr>
<td>C1 – C10 – S3</td>
<td>124.70(14)</td>
</tr>
<tr>
<td>C1 – C10 – S4</td>
<td>121.45(14)</td>
</tr>
<tr>
<td>S3 – C10 – S4</td>
<td>113.83(10)</td>
</tr>
<tr>
<td>C10 – C1 – S1</td>
<td>123.68(14)</td>
</tr>
<tr>
<td>C10 – C1 – S2</td>
<td>121.53(14)</td>
</tr>
<tr>
<td>S1 – C1 – S2</td>
<td>114.8(1)</td>
</tr>
<tr>
<td>C19 – C11 – C12</td>
<td>126.20(16)</td>
</tr>
<tr>
<td>C19 – C11 – S3</td>
<td>117.19(14)</td>
</tr>
<tr>
<td>C12 – C11 – S3</td>
<td>116.62(13)</td>
</tr>
<tr>
<td>C7 – O3 – C8</td>
<td>115.94(14)</td>
</tr>
<tr>
<td>C17 – C12 – C13</td>
<td>119.92(17)</td>
</tr>
<tr>
<td>C17 – C12 – C11</td>
<td>120.76(16)</td>
</tr>
<tr>
<td>C13 – C12 – C11</td>
<td>119.32(16)</td>
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<tr>
<td>O2 – C4 – O1</td>
<td>126.09(16)</td>
</tr>
<tr>
<td>O2 – C4 – C3</td>
<td>125.22(16)</td>
</tr>
<tr>
<td>O1 – C4 – C3</td>
<td>108.63(15)</td>
</tr>
<tr>
<td>C15 – C16 – C17</td>
<td>119.57(18)</td>
</tr>
<tr>
<td>O3 – C8 – C9</td>
<td>110.75(16)</td>
</tr>
<tr>
<td>C11 – C19 – C20</td>
<td>128.84(17)</td>
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</table>
## Table 33: Selected torsion angles (°) of compound 35d.

<table>
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<tr>
<th>Bond Pairs</th>
<th>Angle(°)</th>
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<tbody>
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<td>C1 – S2 – C3 – C2</td>
<td>6.8(2)</td>
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</tr>
<tr>
<td>C11 – S3 – C10 – C1</td>
<td>163.6(2)</td>
</tr>
<tr>
<td>C11 – S3 – C10 – S4</td>
<td>-14.8(1)</td>
</tr>
<tr>
<td>C19 – S4 – C10 – C1</td>
<td>-163.8(2)</td>
</tr>
<tr>
<td>C19 – S4 – C10 – S3</td>
<td>14.6(1)</td>
</tr>
<tr>
<td>S3 – C10 – C1 – S1</td>
<td>2.3(2)</td>
</tr>
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<td>S4 – C10 – C1 – S1</td>
<td>-179.4(1)</td>
</tr>
<tr>
<td>S3 – C10 – C1 – S2</td>
<td>-177.5(1)</td>
</tr>
<tr>
<td>S4 – C10 – C1 – S2</td>
<td>0.7(2)</td>
</tr>
<tr>
<td>C2 – S1 – C1 – C10</td>
<td>-169.3(2)</td>
</tr>
<tr>
<td>C2 – S1 – C1 – S2</td>
<td>10.6(1)</td>
</tr>
<tr>
<td>S3 – S2 – C1 – C10</td>
<td>169.1(2)</td>
</tr>
<tr>
<td>C3 – S2 – C1 – C1</td>
<td>-10.8(1)</td>
</tr>
<tr>
<td>C10 – S3 – C11 – C19</td>
<td>9.3(2)</td>
</tr>
<tr>
<td>C10 – S3 – C11 – C12</td>
<td>-171.0(1)</td>
</tr>
<tr>
<td>C19 – C11 – C12 – C17</td>
<td>122.1(2)</td>
</tr>
<tr>
<td>C3 – C11 – C12 – C17</td>
<td>-57.5(2)</td>
</tr>
<tr>
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</tr>
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<td>C3 – C11 – C12 – C13</td>
<td>123.1(2)</td>
</tr>
<tr>
<td>C5 – C1 – C4 – O2</td>
<td>0.0(3)</td>
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<tr>
<td>C5 – O1 – C4 – C3</td>
<td>-177.4(2)</td>
</tr>
<tr>
<td>C2 – C3 – C4 – O2</td>
<td>69.5(3)</td>
</tr>
<tr>
<td>S2 – C3 – C4 – O2</td>
<td>-109.1(2)</td>
</tr>
<tr>
<td>C2 – C3 – C4 – O1</td>
<td>-113.1(2)</td>
</tr>
<tr>
<td>S2 – C3 – C4 – O1</td>
<td>68.3(2)</td>
</tr>
<tr>
<td>C7 – O3 – C8 – C9</td>
<td>-84.9(2)</td>
</tr>
<tr>
<td>C12 – C11 – C19 – C20</td>
<td>-7.2(3)</td>
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<tr>
<td>S3 – C11 – C19 – C20</td>
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<td>C12 – C11 – C19 – S4</td>
<td>179.9(1)</td>
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<tr>
<td>S3 – C11 – C19 – S4</td>
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<tr>
<td>C10 – S4 – C19 – C11</td>
<td>-8.6(2)</td>
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<tr>
<td>C10 – S4 – C19 – C20</td>
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<td>0.2(3)</td>
</tr>
<tr>
<td>C11 – C12 – C17 – C16</td>
<td>-179.2(2)</td>
</tr>
</tbody>
</table>

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D. APPENDIX

2. List Of Abbreviations

AcOH  acetic acid  
aq   aqueous  
Ar   aryl  
ATR  attenuated total reflection (IR)  
br.  broad  
Bu  butyl  
cat.  catalytic  
δ  chemical shifts in parts per million  
d  doublet  
conc.  concentrated  
dba  trans,trans-dibenzylideneacetone  
DMF  N,N-dimethylformamide  
DMSO  dimethyl sulfoxide  
DTT  1,3-dithiole-2-thione  
E  electrophile  
EI  electron impact ionization  
equiv  equivalent  
ESI  electrospray ionization  
Et  ethyl  
FG  functional group  
GC  gas chromatography  
h  hour  
HRMS  high resolution mass spectrometry  
Pr  iso-propyl  
IR  infra-red  
J  coupling constant (NMR)  
LDA  lithium diisopropylamide  
M  molarity  
m  multiplet  
m.p.  melting point  
Me  methyl  
MeCN  acetonitrile  
Met  metal  
min  minute
### D. APPENDIX

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmol</td>
<td>millimole</td>
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</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
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</tr>
<tr>
<td>MW</td>
<td>microwave</td>
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</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidine</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
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</tr>
<tr>
<td>o</td>
<td>ortho</td>
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<td>p</td>
<td>para</td>
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<td>PEPPSI-(\text{tPr})</td>
<td><a href="3-chloropyridyl">1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene</a>palladium(II) dichloride</td>
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<tr>
<td>Ph</td>
<td>phenyl</td>
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<td>quartet</td>
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<td>sat</td>
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<td>2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl</td>
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<tr>
<td>t</td>
<td>triplet</td>
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<tr>
<td>fBu</td>
<td>(\text{t-}\text{butyl})</td>
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<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
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<tr>
<td>tfp</td>
<td>tris-(2-furyl)phosphine</td>
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</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<td>TLC</td>
<td>thin layer chromatography</td>
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<td>trimethylsilyl</td>
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<td>Tos</td>
<td>4-toluenesulfonyl</td>
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<td>typical procedure</td>
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<td>tetrathiafulvalene</td>
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