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

von
Julia Christine Ruth Nafe
aus
Gera

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Erklärung

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Eidesstattliche Versicherung

Diese Dissertation wurde eigenständig und ohne unerlaubte Hilfsmittel erarbeitet.

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Julia Christine Ruth Nafe

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1. Gutachter: Prof. Dr. Paul Knochel

2. Gutachter: Prof. Dr. Konstantin Karaghiosoff

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Parts of this Ph.D. thesis have been published

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Julia Nafe, Paul Knochel: **„**Selective Metalation of 1,3-Dithiole-2-thiones: An Effective Preparation of New Symmetrically and Nonsymmetrically Tetraarylated Tetrathiafulvalenes”, Synthesis **2015**, DOI: 10.1055/s-0035-1560728.

Julia Nafe, Florian Auras, Konstantin Karaghiosoff, Thomas Bein, Paul Knochel: „Selective Functionalization of Tetrathiafulvalene Using Mg- and Zn-TMP-Bases: Preparation of Mono-, Di-, Tri- and Tetrasubstituted Derivatives“, *Org. Lett.* **2015**, *17*, 5356-5359.

Julia Nafe, Alicia Castello-Mico, Paul Knochel: „Selective Functionalization of 1,4-Dithiin Using TMP-Bases: Access to New Heterocycles“, *manuscript in preparation*.

Für Max

und meine Familie

„Vielleicht geht‘s
auch nicht ums
Happy End,
sondern nur um die
Geschichte selbst“

-Julia Engelmann-

Table of Contents

A. INTRODUCTION

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, heterocylic 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

[1] (a) Nicolaou, K. C.; Chen, J. S.; Edmonds, D. J.; Estrada, A. A. *Angew. Chem. Int. Ed.* **2009**, *121*, 670. (b) Chinchilla, R.; Nájera, C.; Yus, M. *Tetrahedron* **2005**, *61*, 3139.

[2] (a) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T.-Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222. (b) Clarke, T.; Ballantyne, A.; Jamieson, F.; Brabec, C.; Nelson, J.; Durrant, J. *Chem. Commun.* **2009**, 89.

[3] (a) Porter, A. E. A. In *Comprehensive Heterocyclic Chemistry*; Katritsky, A. R.; Rees, C. W. Eds.; Pergamon: Oxford, UK, **1984**, 157. (b) Woo, G. H. C.; Snyder, J. K.; Wan, Z. K. *Prog. Heterocycl. Chem.* **2002**, *14* , 279. For an overview see: (c) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084. (d) Baumann, M.; Baxendale, I. R. *Beilstein J. Org. Chem.* **2013**, *9*, 2265.

[4] (a) Berzelius, J. J. *Jahresber.* **1839**, *18*, 487. (b) Burns, J. Waser, J. *J. Am. Chem. Soc.* **1957**, *79*, 859. (c) Seyferth, D. *Organometallics* **2001**, *20*, 1488.

[5] (a) Gilman, H.; Bebb, R. L. *J. Am. Chem. Soc.* **1939**, *61*, 109. (b) Wittig, G.; Fuhrmann, G. *Chem. Ber.* **1940**, *73*, 1197.

[6] (a) Snieckus, V. *Chem Rev.* **1990**, *90*, 879. (b) Schlosser, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 376.

[7] Chichibabin, A. E.; Zeide, O. A. *J. Russ. Phys. Chem. Soc.* **1914**, *46*, 1216.

[8] Hauser, C. R.; Walker, H. W. *J. Am. Chem. Soc.* **1947**, *69*, 295.

[9] (a) Krasovskiy, A.; Krasovskaya, V.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 2958. (b) Lin, W.; Baron, O.; Knochel, P. *Org. Lett.* **2006**, *8*, 5673. (c) Mosrin, M.; Knochel, P. *Org. Lett.* **2008**, *10*, 2497. (d) Mosrin, M.; Boudet, N.; Knochel, P. *Org. Biomol. Chem.* **2008**, *6*, 3237. (e) Piller, F. M.; Knochel, P. *Synthesis* **2011**, 1751. (f) Haag, B.; Mosrin, M.; Ila, H.; Malakhov, V.; Knochel, P. *Angew. Chem., Int. Ed.* **2011**, *50*, 9794. (g) Kunz, T.; Knochel, P. *Angew. Chem., Int. Ed.* **2012**, *51*, 1958.

[10] García-Álvarez, P.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Klett, J.; Mulvey, R. E.; O'Hara, C. T.; Weatherstone, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 8079.

higher reactivity. In the same way, the more reactive base $TMP_2Mg{\cdot}2LiCl$ (**3**)[11] was developed for less activated substrates, whereas milder bases, such as $TMPZnCl{\cdot}LiCl$ (**4**)[12] and $TMP_2Zn{\cdot}2MgCl{\cdot}2LiCl$ (**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]

[11] (a) Clososki, G. C.; Rohbogner, C. J.; Knochel, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7681. (b) C. J. Rohbogner, G. C. Clososki, P. Knochel, *Angew. Chem., Int. Ed.* **2008**, *47*, 1503. (c) Rohbogner, C. J.; Wagner, A. J.; Clososki, G. C.; Knochel, P. *Org. Synth.* **2009**, *86*, 374.

[12] Klier, L.; Bresser, T. Nigst, T. A.; Karaghiosoff, K.; Knochel, P. *J. Am. Chem. Soc.* **2012**, *134*, 13584. (b) Bresser, T.; Knochel, P. *Angew. Chem. Int. Ed.* **2011**, *50*, 1914. (c) Mosrin, M.; Knochel, P. *Org. Lett.* **2009**, *11*, 1837.

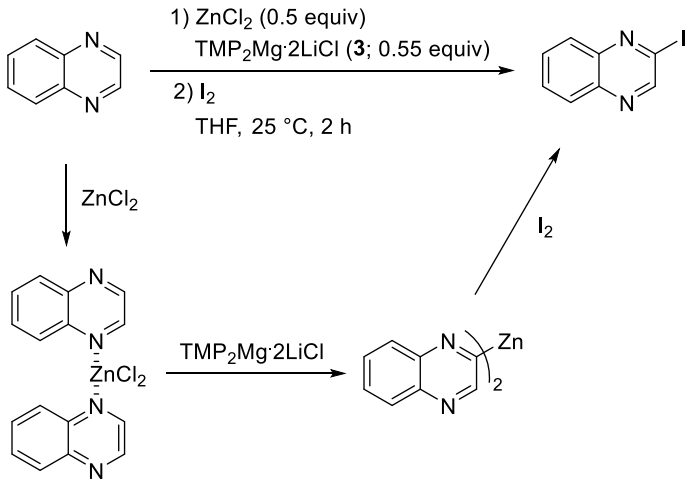
[13] (a) Wunderlich, S. H.; Knochel, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7685. (b) Wunderlich, S. H.; Knochel, P. *Org. Lett.* **2008**, *10*, 4705. (c) Wunderlich, S.; Knochel, P. *Chem. Commun.* **2008**, 6387. (d) Kienle, M.; Dunst, C.; Knochel, P. *Org. Lett.* **2009**, *11*, 5158. (e) Mosrin, M.; Knochel, P. *Chem. Eur. J.* **2009**, *15*, 1468. (f) Dunst, C.; Kienle, M.; Knochel, P. *Synthesis* **2010**, 2313.

[14] Chinchilla, R.; Nájera, C.; Yus, M. *Arkovic* **2007**, *X*, 152.

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 $TMP_2Mg{\cdot}2LiCl$ (**3**; 0.55 equiv) in the presence of $ZnCl_2$ (0.5 equiv).[15] They postulate the formation of an intermediate zinc complex that reacts with $TMP_2Mg{\cdot}2LiCl$ (**3**) furnishing the zinc derivative after fast transmetalation. Quenching with iodine afforded the monofunctionalized quinoxaline-derivative (Scheme 1).

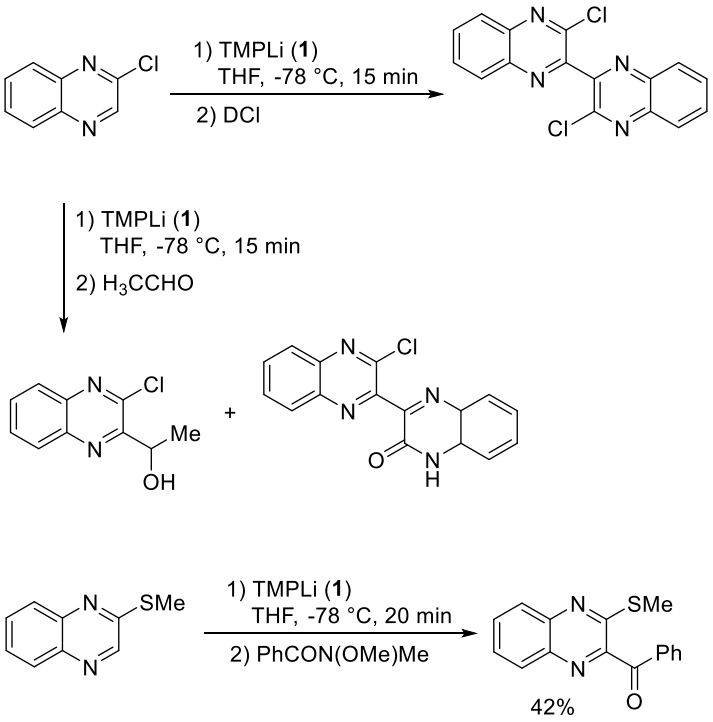


Scheme 1: Postulated mechanism for the preparation of iodinated quinoxaline.

In 1991, *Ward* tried to achieve a selective metalation of different 2-substituted quinoxalines using the stronger base TMPLi (**1**). Treatment of 2-chloroquinoxaline with 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 TMPLi (**1**) to 2-(methylthio)quinoxaline, followed by trapping with PhCON(OMe)Me, afforded the expected product in 42% yield without formation of a dimer (Scheme 2).[16]

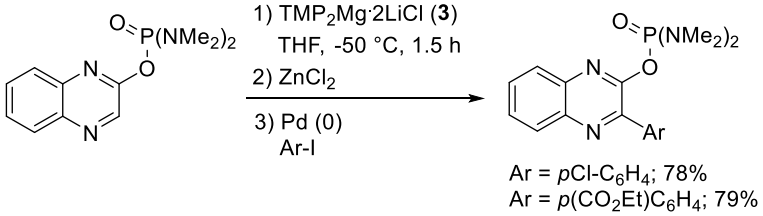
[15] Dong, Z.; Clososki, G. C.; Wunderlich, S. H.; Unsinn, A.; Li, J.; Knochel, P. *Chem. Eur. J.* **2009**, *15*, 457.

[16] (a) Ward, J. S.; Merritt, L. *Heterocycl. Chem.* **1991**, *25*, 765. (b) Tuck, A.; Plé, N.; Mongin, F.; Quéguiner, G. *Tetrahedron* **2001**, *57*, 4489.



Scheme 2: Attempts to achieve a selective metalation of 2-substituted quinoxalines using TMPLi (**1**).

Another difunctionalization was achieved by selective metalation of quinoxalines bearing a phosphorodiamidate group as directing group. The addition of $TMP_2Mg{\cdot}2LiCl$ (**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).[17]

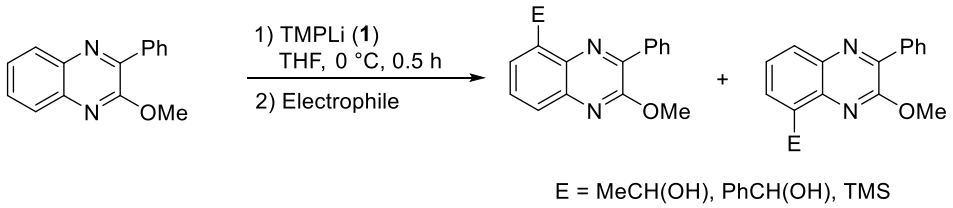


Scheme 3: Selective magnesiation of a 2-substituted quinoxaline followed by Pd-catalyzed cross-couplings.

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).[18]

[17] Rohbogner, C. J.; Wirth, S.; Knochel, P. *Org. Lett.* **2010**, *12*, 1984.

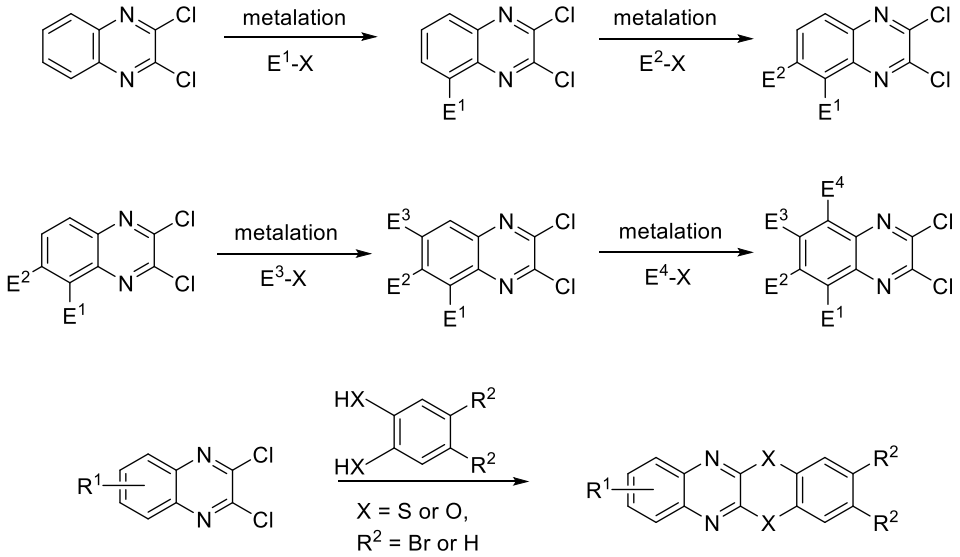
[18] Gautheron, V.; Salliot, I.; Plé, N.; Turck, A.; Quéguiner, G. *Tetrahedron* **1999**, *55*, 5389.



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

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).



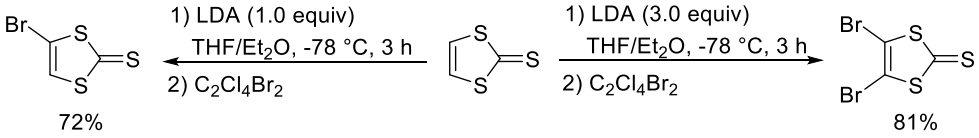
Scheme 5: Desired fully functionalization of 2,3-dichloroquinoxaline followed by anellation reactions.

3. 1,3-Dithiole-2-thione

Dithiolethiones are important *S*-heterocylces 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.[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. *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).[20]



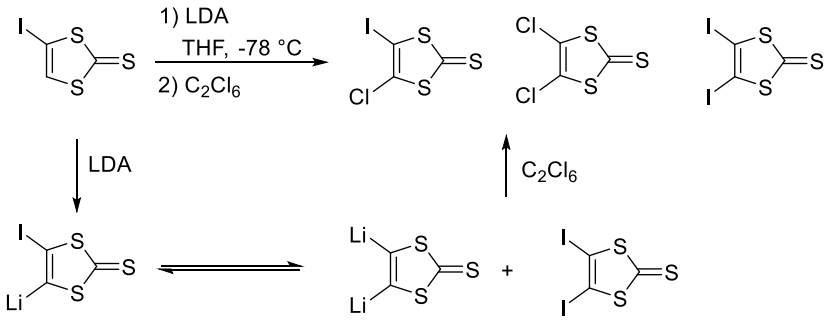
Scheme 6: Preparation of mono- and dibromo-DTT *via* direct metalation of DTT using LDA.

In contrast, *Suizu* and *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 hexachloroethane 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).[21]

[19] (a) Kato, R. *Chem. Rev.* **2004**, *104*, 5319. (b) Wang, H.; Liu, B.; Wan, J.; Xu, J.; Zheng, X. *J. Raman Spectrosc.* **2009**, *40*, 992.

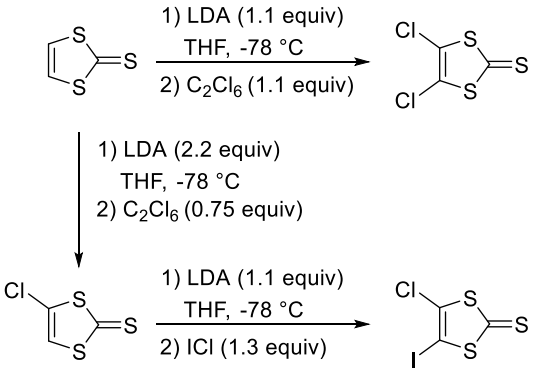
[20] (a) Alberola, A.; Collis, R.; García, F.; Howard, R. E. *Tetrahedron* **2006**, *62*, 8152. (b) Alberola, A.; Bosch-Navarro, C.; Gaviña, P.; Tatay, S. *Synt. Met.* **2010**, *160*, 1979.

[21] Suizu, R.; Imakubo, T. *Org. Biomol. Chem.* **2003**, *1*, 3629.



Scheme 7: Disproportionation of lithiated iodo-DTT leading to a mixture of products.

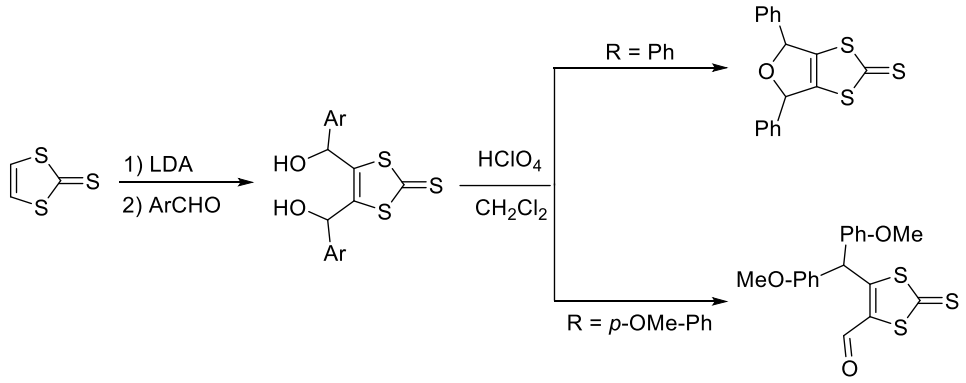
Furthermore, undesired side reactions *via* ring-opening were observed in reactions of DTT with stoichiometric amounts of LDA. Thus, the mono-lithiation of DTT using LDA (1.1 equiv, THF, -78 °C) and subsequent trapping with hexachloroethane (1.1 equiv) furnished dichloro-DTT instead of the desired monochlorinated 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).



Scheme 8: Preparation of chloro-iodo-DTT.

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. Lithiathion 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]

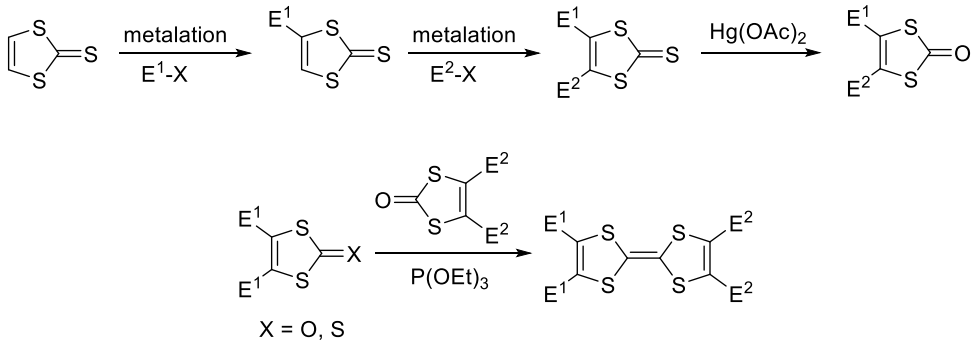
[22] (a) Khan, T.; Skabara, P. J.; Coles, S. J.; Hursthouse, M. B. *Chem. Commun.* **2001**, 369. (b) Vilela, F.; Skabara, P. J.; Mason, C. R.; Westgate, T. D. J.; Luquin, A.; Coles, S. J.; Hursthouse, M. B. *Beilstein J. Org. Chem.* **2010**, *6*, 1002.



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.[23] 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[24] and the related superconducting Fabre-Bechgaard salt,[25] much effort has been made to tune the electronic properties of these materials by modification of the TTF-scaffold (Figure 1).

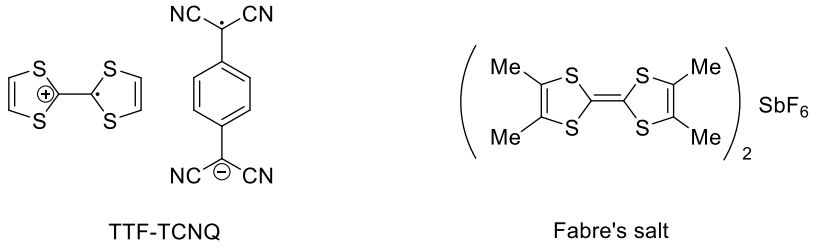
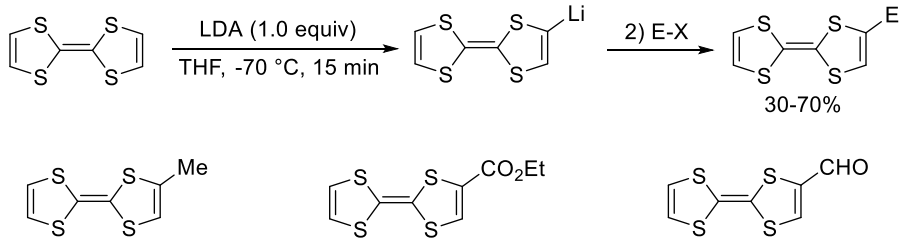


Figure 1: Structures of a conductive TTF-TCNQ CT-complex and the superconducting Fabre-Bechgaard salt.

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).[26]



Scheme 11: Preparation of monosubstituted TTF-derivatives by direct metalation of TTF.

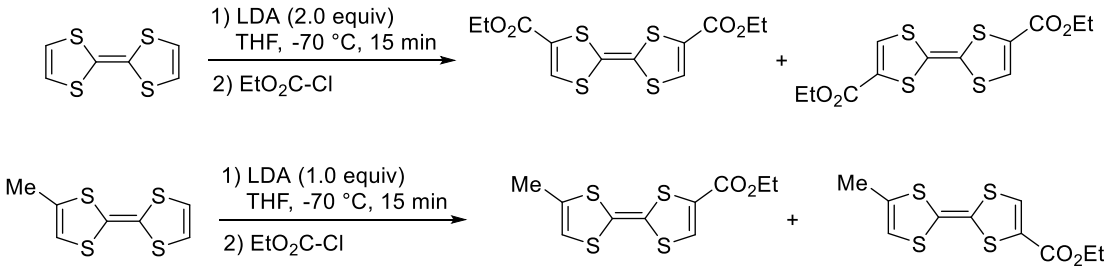
However, the addition of excess LDA (2.0 equiv) to TTF, followed by trapping with ethyl chloroformate resulted in a mixture (1:1) of 4,4'- and 4,5'-disubstituted TTF-derivatives that was not separated. In addition, no regioselectivity was achieved by trapping the lithiated species of 4-methyl-TTF with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

[23] Gorgues, A.; Hudhomme, P.; Sallé, M. *Chem. Rev.* **2004**, *104*, 5151.

[24] (a) Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.

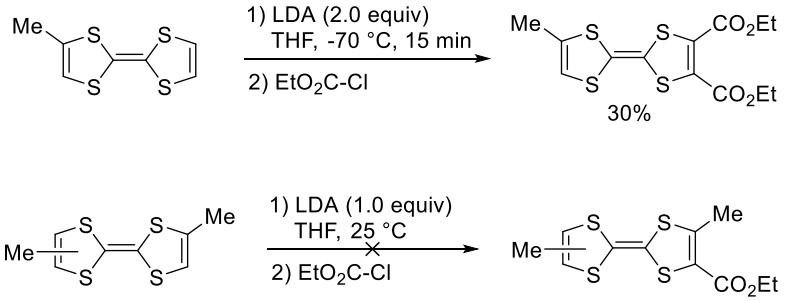
[25] Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, L95.

[26] (a) Green, D. *J. Org. Chem.* **1979**, *44*, 1476. (b) Fabre, J.-M.; Garín, J.; Uriel, S. *Tetrahedron Lett.* **1991**, *32*, 6407. (c) Otsubo, T.; Kochi, Y.; Bitoh, A.; Ogura, F. *Chem. Lett.* **1994**, 2047.



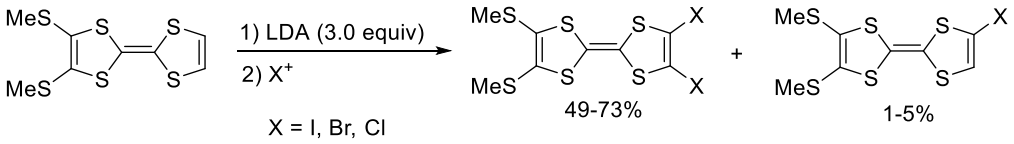
Scheme 12: Isomeric mixture of disubstituted TTF-derivatives.

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).



Scheme 13: Attempts to prepare trifunctionalized TTF-derivatives.

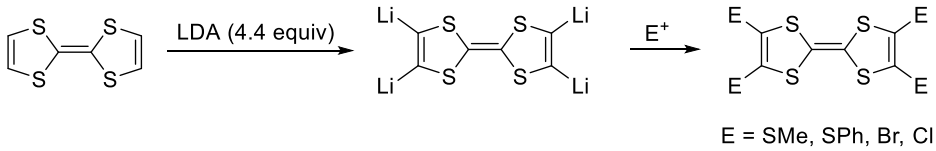
Iyoda et al. reported the successful synthesis of fully functionalized TTF-derivatives by the addition of excess LDA (3.0 equiv) to the dithioether derivative, followed by trapping with halides. Under these conditions, only trace amounts (1-5%) of the trifunctionalized side products were obtained (Scheme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



Scheme 14: Preparation of fully substituted TTF-derivatives.

[27] Iyoda, M.; Kuwatani, Y.; Hara, K.; Ogura, E.; Suzuki, H.; Ito, H.; Mori, T. *Chem. Lett.* **1997**, 599.

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).[28]

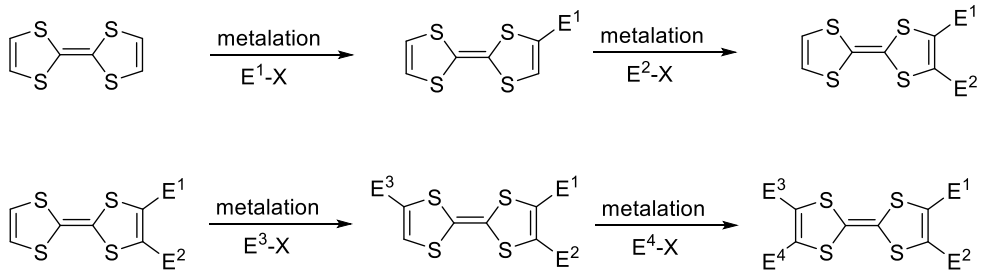


Scheme 15: Preparation of tetrafunctionalized TTF-derivatives in an one-pot procedure.

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.

[28] (a) AAhron-Shalom, E.; Becker, J.Y; Bernstein, J.; Bittner, S.; Shaik, S. *Tetrahedron Lett.* **1985**, *26*, 2783. (b) Hsu, S.-Y.; Chiang, L. Y. *J. Org. Chem.* **1987**, *52*, 3444. (c) Jørgensen, M.; Bechgaard, K. *Synthesis* **1989**, 207.

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 accummulation 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-existance of a diamagnetic ring current, although the strict definition of *Hückel*-aromaticity can not be applied.[29]

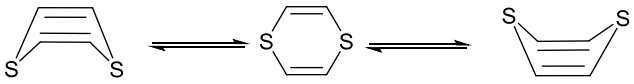


Figure 2: Non-planar conformation of 1,4-dithiin.

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]

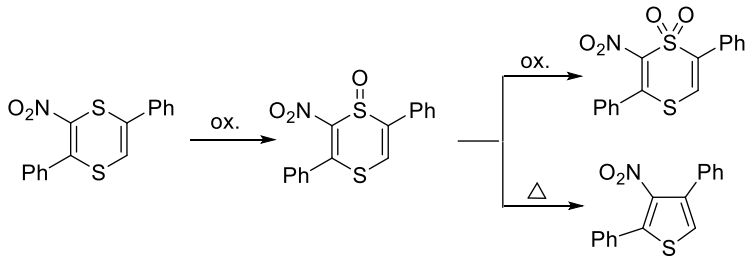
5.1 Reactions of 1,4-Dithiins

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]

[29] (a) Kobayashi, K.; Gajuriel, C. L. *Sulfur Rep.* **1986**, *7*, 123. (b) Büchel, K. H.; Falbe, J.; Hagemann, H.; Hanack, M.; Klamann, D.; Kreher, R.; Kropf, H.; Regitz, M.; Schaumann, E. In *Methods of Organic Chemistry: Heteroarenes IV (Six-Membered Rings and Larger Hetero-Rings with Maximum Unsaturation)*, Vol. E 9a, 4th Edition; Thornton, S. R.; Sturdy, L. A.; Williams, A. L., Eds.; Thieme: Stuttgart, **1997**, 250. (c) Pelloni, S.; Faglioni, F.; Soncini, A.; Ligabue, A.; Lazzeretti, P. *Chem. Phys. Lett.* **2003**, *375*, 583.

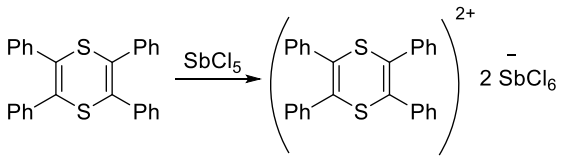
[30] Gollnick, K.; Hartmann, H. *Tetrahedron Lett.* **1982**, *23*, 2651.

[31] Andreu, R.; Garín, J.; Orduna, J.; Royo, J. M. *Tetrahedron Lett.* **2001**, *42*, 875.



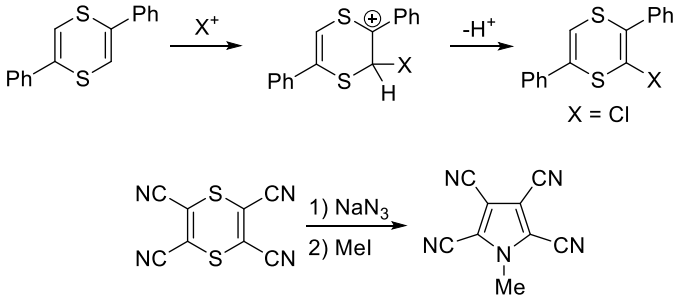
Scheme 17: Oxidation of a dithiin-derivative leading to a sulfoxide and following transformation.

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.

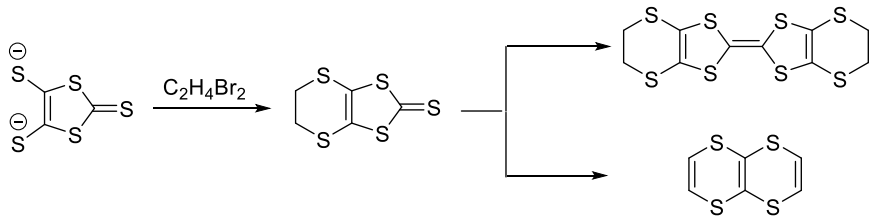
Moreover, 1,4-dithiin reacts readily with electrophiles, as well as with nucleophiles. For example, diphenyl dithiin can undergo electrophilic substitutions such as formylation, nitration and bromination. These reactions are postulated to proceed in an addition-elimination process leading to trisubstituted 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.

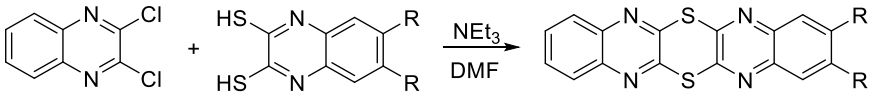
1,4-Dithiin-fused heterocycles are of high interest for material chemistry due to their electronical properties. Most common are these structures in the field of electroconductive materials and in the field of dyes. The alkylation of 1,2-dibromoethane with 2-thioxo-1,3-dithiole-4,5-bis(thiolate) which 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]



Scheme 20: Preparation of dithiin-fused *S*-heterocycles.

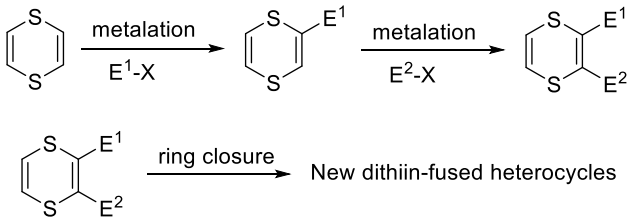
With regards to dyes, dithiin-fused heteroacenes can be obtained by anellation of dichloroquinoxalines with dimercaptoquinoxalines (Scheme 21).[33]



Scheme 21: Preparation of dithiin-fused quinoxalines.

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).



Scheme 22: Desired functionalization of 1,4-dithiin followed by cyclizations leading to new dithiin-fused heterocycles.

[32] Nakano, H.; Nakamura, T.; Nogami, T.; Shirota, Y. *Chem. Lett.* **1987**, 1317.

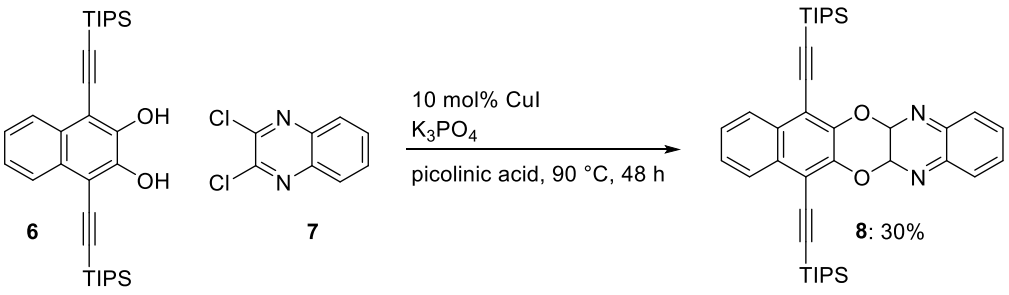
[33] Podsiadly, R.; Sokolowska, J. *Dyes Pigments* **2012**, *92*, 1300.

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,[34] fluorescent dyes,[35] and as building blocks for new materials.[36] Anellation procedures are known to convert quinoxalines into diazadioxacenes that have interesting optical and electronic properties.[37] *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).[37a]



Scheme 23: Copper-based synthesis of diazadioxacenes.

However, the alkynylation is located at the 1,2-diol unit and its preparation involves multiple steps.[37a] 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 electronical properties due to the extended π-system.

[34] (a) Rajule, R.; Bryant, V. C.; Lopez, H.; Luo, X.; Natarajan, A. *Bioorg. Med. Chem.* **2012**, *20*, 2227. (b) Parhi, A. K.; Zhang, Y.; Saionz, K. W.; Pradhan, P.; Kaul, M.; Trivedi, K.; Pilch, D. S.; LaVoie, E. J. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 4968. (c) Betschart, C.; Hintermann, S.; Behnke, D.; Cotesta, S.; Fendt, M.; Gee, C. E.; Jacobson, L. H.; Laue, G.; Ofner, S.; Chaudhari, V.; Badiger, S.; Pandit, C.; Wagner, J.; Hoyer, D. *J. Med. Chem.* **2013**, *56*, 7590.

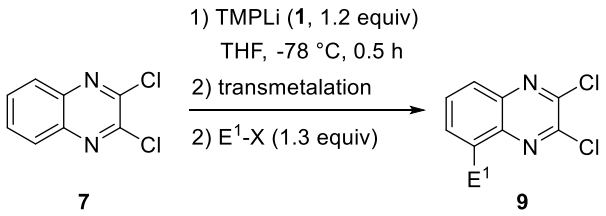
[35] (a) Jaung, J.-Y. *Dyes and Pigments* **2006**, *71*, 245. (b) Achelle, S.; Baudequin, C.; Plé, N. *Dyes and Pigments* **2013**, *98*, 575.

[36] (a) Gao, Z.; Qu, B.; Wu, H.; Yang, H.; Gao, C.; Zhang, L.; Xiao, L.; Chen, Z.; Wei, W.; Gong, Q. *Synthetic Metals* **2013**, *172*, 69. (b) Gao, Z.; Qu, B.; Wu, H.; Gao, C.; Yang, H.; Zhang, L.; Xiao, L.; Chen, Z.; Gong, Q. *J. Appl. Polym. Sci.* **2014**, *131*, 40279; (c) Kitazawa, D.; Watanabe, N.; Yamamoto, S.; Tsukamoto, J. *Appl. Phys. Lett.* **2009**, *95*, 053701; (d) Dailey, S.; Feast, W. J.; Peace, R. J.; Sage, I. C.; Till, S.; Wood, E. L. *J. Mater. Chem.* **2001**, *11*, 2238.

[37] (a) Schaffroth, M.; Lindner, B. D.; Vasilenko, V.; Rominger, F.; Bunz, U. H. F. *J. Org. Chem.* **2013**, *78*, 3142. (b) Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *J. Org. Chem.* **1987**, *52*, 1089.

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 KO*t*Bu/TMPLi and KO*t*Bu/*n*BuLi (1.1 equiv, THF, -78 °C, 0.5 h) led to decomposition, whereas the milder Mg-bases, such as TMPMgCl·LiCl (**2**)[9] or $TMP_2Mg{\cdot}2LiCl$ (**3**)[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).



7 **9**

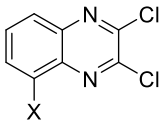
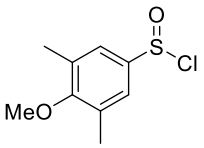
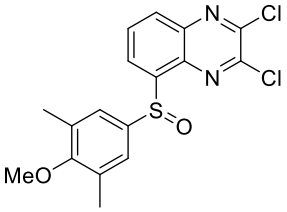
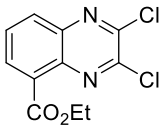
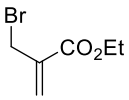
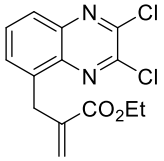
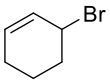
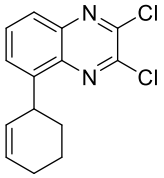
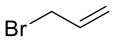
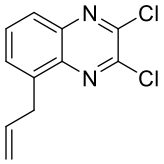
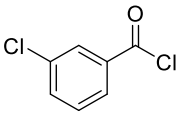
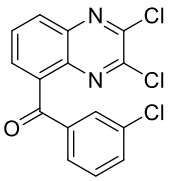
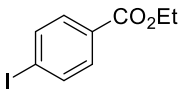
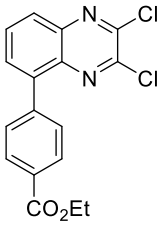
Scheme 24: Selective lithiation of 2,3-dichloroquinoxaline (**7**) with TMPLi (**1**).

The lithiated species was trapped with $(BrCl_2C)_2$ 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,[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[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.

[39] (a) Negishi, E.; Valente, L. F.; Kobayashi, M. *J. Am. Chem. Soc.* **1980**, *102*, 3298. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

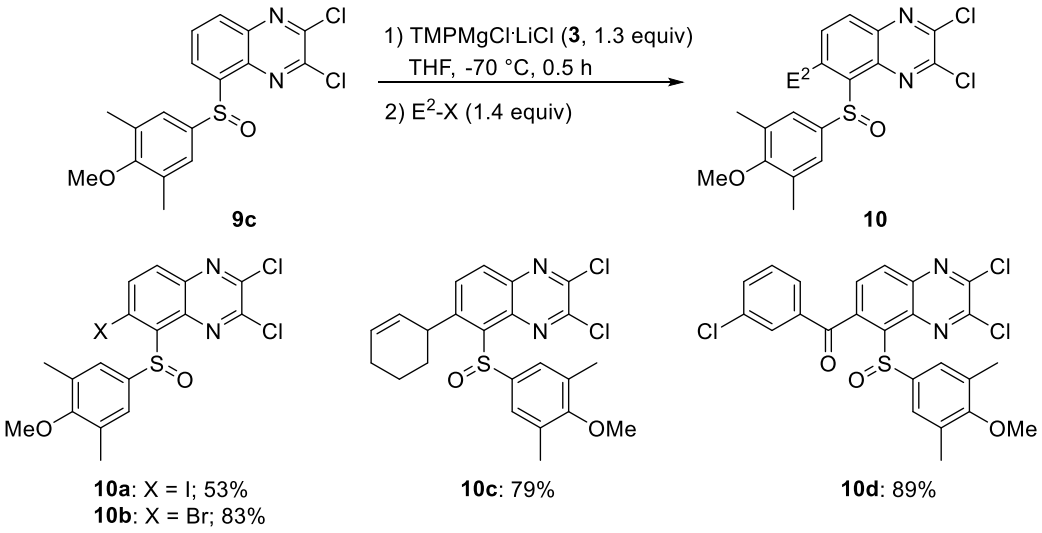
Table 1: Low temperature metalation of **7** leading to various monofunctionalized quinoxalines of type **9**.

Entry	Electrophile	Product	Yield (%)[a]
1	$(BrCl_2C)_2$	 **9a**: X = Br	73[b]
2	I_2	**9b**: X = I	64[b]
3		 **9c**	60[b]
4	EtO_2C-CN	 **9d**	62[b]
5		 **9e**	68[c,d]
6		 **9f**	61[c,d]
7		 **9g**	75[c,d]
8		 **9h**	70[c,e]
9		 **9i**	56[f]

[a]Isolated yield of analytically pure product. [b]$MgCl_2$ solution (1.3 equiv, 1.0 M in THF) was added. [c]$ZnCl_2$ solution (1.3 equiv, 1.0 M in THF) was added. [d]CuCN·2LiCl solution (10 mol%, 1.0 M in THF) was added. [e]CuCN·2LiCl solution (1.3 equiv, 1.0 M in THF) was added. [f]Cross-coupling conditions: $ZnCl_2$ solution (1.3 equiv, 1.0 M in THF), $Pd(PPh_3)_4$ (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.[6a,9b,40] 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 $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (**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.

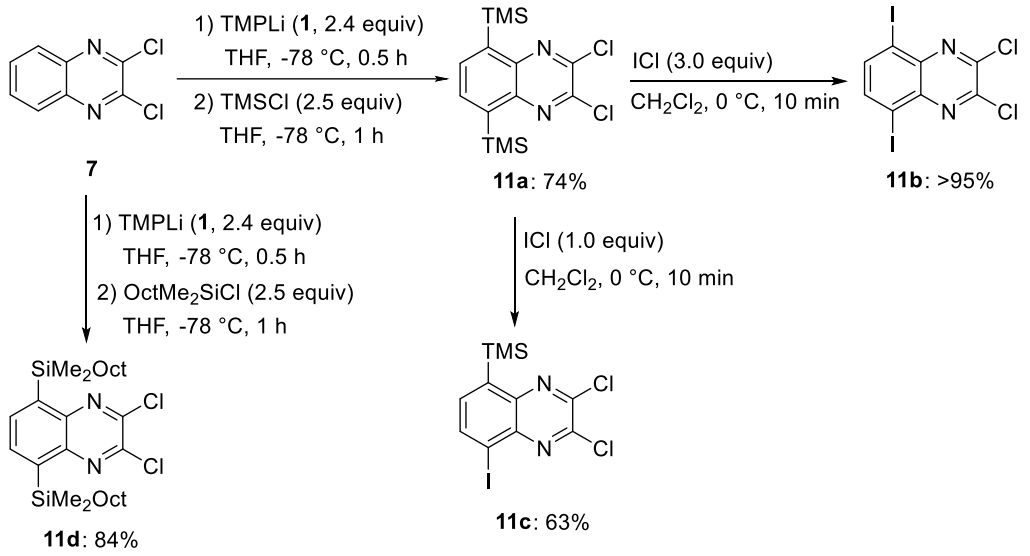
[40] For an overview see: (a) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. (b) Chinchilla, R.; Nájera, C.; Yus, M. *Chem. Rev.* **2004**, *104*, 2667. (c) Whisler, M. C.; MacNeil, S.; Beak, P.; Snieckus, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 2206. (d) Stoll, A. H.; Knochel, P. *Org. Lett.* **2008**, *10*, 113.

In case of the ketone **9h**, similar results were obtained. The addition of TMPMgCl·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 $TMP_2Zn·2MgCl_2·2LiCl$ (**5**; 1.1 equiv) and TMPZnCl·LiCl (**4**; 1.1 equiv) under various conditions, even when the mixture was heated to 50 °C.

Thus, a directed *ortho*-metalation 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[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 metalation of the quinoxaline. Thus, excess TMPLi (**1**) lithiates the intermediate again in position 8 leading to 5,8-disubtituted 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).

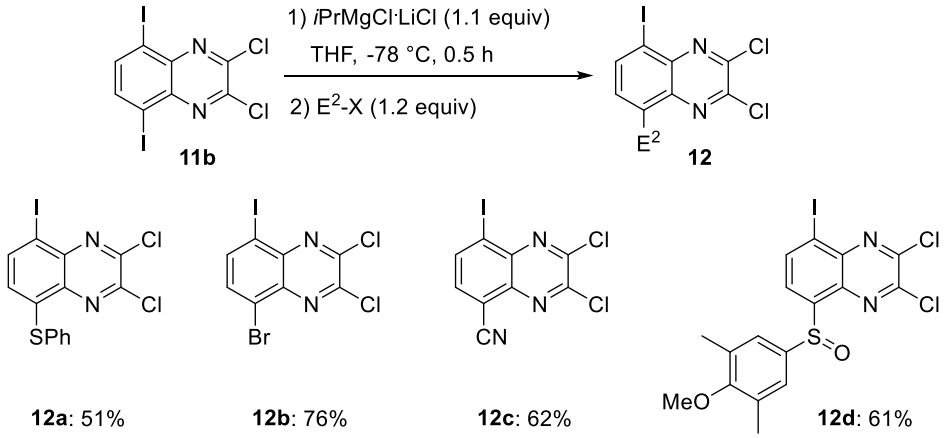
[41] (a) Krizan, T. D., Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155. (b) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156. (c) Guo, L.; Meng, F. S.; Gong, X. D.; Xiao, H. M.; Chen, K. C.; Tian, H. *Dyes and Pigments* **2001**, *49*, 83.



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 *i*PrMgCl·LiCl[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).

[42] (a) Ren, H.; Krasovskiy, A.; Knochel, P. *Org. Lett.* **2004**, *6*, 4215. (b) Ila, H.; Baron, O.; Wagner, A. J.; Knochel, P. *Chem. Commun.* **2006**, 583. (c) Manolikakes, G.; Knochel, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 205.

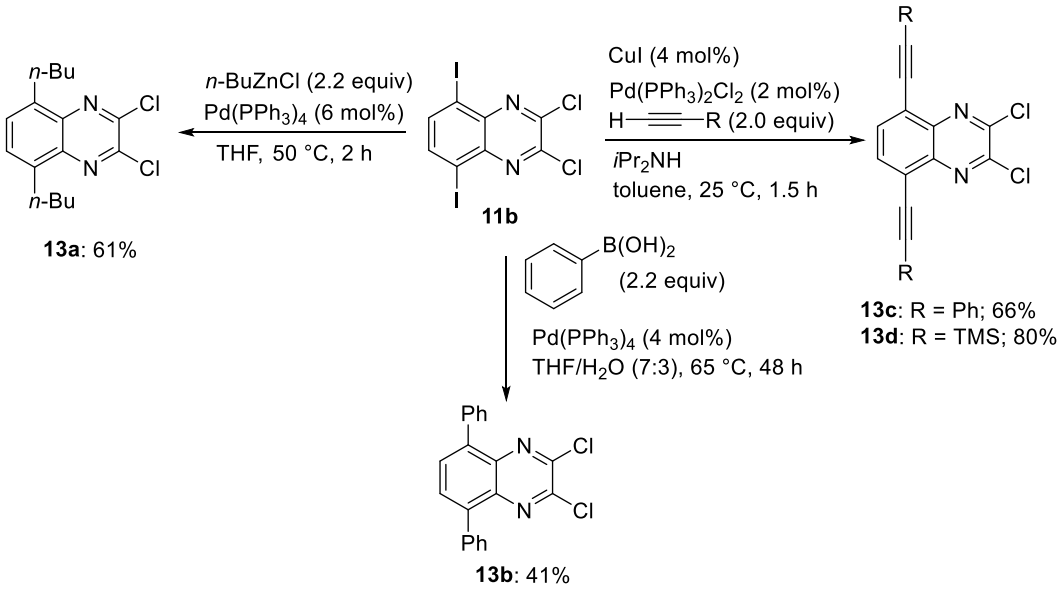


Scheme 27: Synthesis of various 5,8-disubstituted derivatives by I/Mg-exchange.

Since the work of *Satoh*, sulfoxides are known to undergo exchange reactions with organometallic reagents.[43] However, when *n*BuLi (1.1 equiv, THF, -78°C) was added to the iodo-sulfoxide-quinoxaline-derivative **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 *i*PrMgCl·LiCl (1.1 equiv, THF, -78 to -50 °C). Similarly, no exchange was achieved using other organometallic reagents, such as Bu_3MgLi, *n*BuMgCl and PhMgCl (1.1 equiv, THF, -50 to -10 °C).

The diiodide **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 **11b** easily underwent Pd-catalyzed Negishi cross-coupling with *n*BuZnCl (2.2 equiv) leading to the very soluble compound **13a** in 61% yield. Furthermore, **11b** was subjected to Suzuki and Sonogashira cross-coupling reactions leading to the expected products **13b-d**. As anticipated, due to the extended π-system, these compounds were excellent candidates for fluorescent dyes (Scheme 28).

[43] (a) Satoh, T.; Takano, K.; Someya, H.; Matsuda, K. *Tetrahedron Lett.* **1995**, *36*, 7097. (b) Guillaneux, D., Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502. (c) Satoh, T.; Takano, K.; Ota, H.; Someya, H.; Matsuda, K.; Yamakawa, K. *Tetrahedron* **1998**, *54*, 5557. (d) Kagan, H. B.; Luukas, T. O. In *Transition Metals For Organic Synthesis* Beller, M.; Bolm, C.; Eds., Wiley-VCH: Weinheim, **2004**, 479. (e) Kloetzing, R. J.; Knochel, P. *Tetrahedron: Asymm.* **2006**, *17*, 116. (f) Satoh, T. *Chem. Soc. Rev.* **2007**, *36*, 1561.

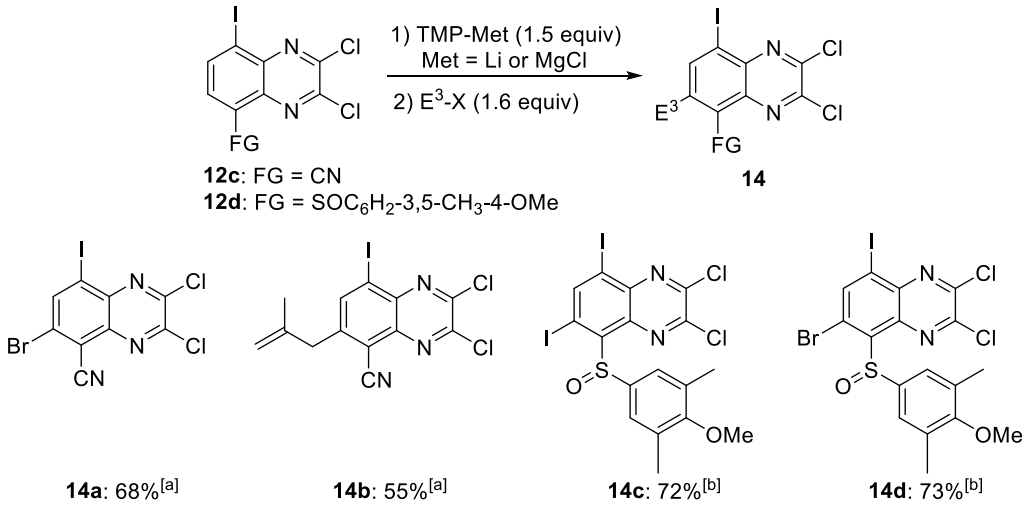


Scheme 28: Cross-coupling reactions of 2,3-dichloro-5,8-diiodoquinoxaline (**11b**).

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 $ZnCl_2$ 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).

[44] Frischmuth, A.; Fernández, M.; Barl, N.M.; Achrainer, F.; Zipse, H.; Berionni, G.; Mayr, H.; Karaghiosoff, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2014**, *53*, 1.

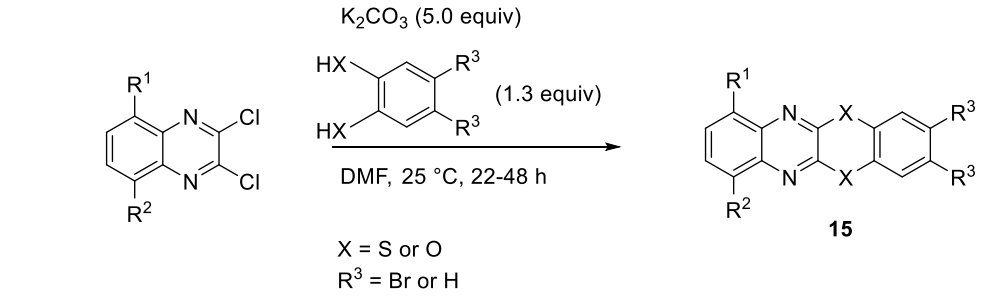


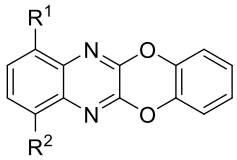
Scheme 29: Preparation of trifunctionalized quinoxalines **14**. [a] $ZnCl_2$ solution (1.1 equiv, 1.0 M in THF), then TMPLi (**1**; 1.5 equiv), THF, -78 °C, 5 min. [b] TMPMgCl·LiCl (**2**; 1.5 equiv), THF, 0 °C, 1.5 h.

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.

1.5 Preparation of Tetracyclic Heterocycles

Polycyclic sulfur and oxygen-heterocycles are of special interest for applications in material science.[45] Thus, several anellation reactions were performed to substitute the electrophilic chlorine atoms by oxygen and sulfur.[37] 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_2CO_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.





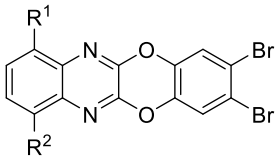
15a: $R^1 = R^2 = H$; 94%

15b: $R^1 = H$, $R^2 = SOC_6H_2Me_2OMe$; 78%

15c: $R^1 = R^2 = I$; 70%

15d: $R^1 = R^2 = Ph$; 62%

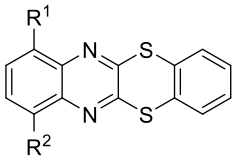
15e: $R^1 = R^2 = C{\equiv}CPh$; 84%



15f: $R^1 = R^2 = H$; 81%

15g: $R^1 = R^2 = nBu$; 52%

15h: $R^1 = R^2 = SiMe_2Oct$; 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%

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

[45] 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[46]

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 trough anellation.

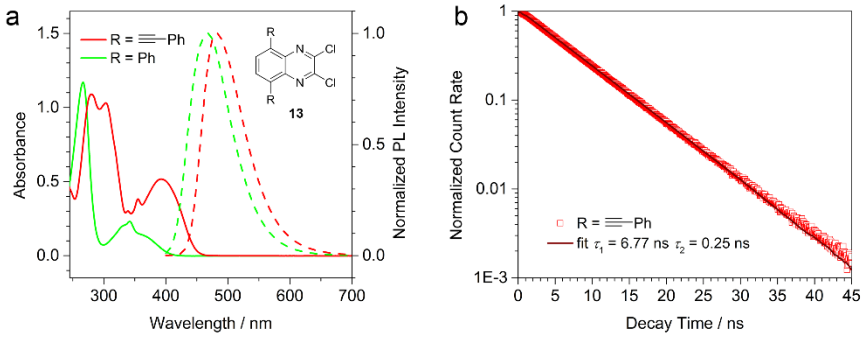


Figure 3: a) UV-Vis absorption (solid line) and normalized PL spectra (dashed line) of compounds **13b** (green) and **13c** (red). b) Time-correlated single photon counting (TCSPC) decay of **13c** recoded after picosecond excitation at 403 nm. The experimental data was corrected for the instrument 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.[47] Due to steric constraints a phenyl substituent on the quinoxaline is likely to be tilted out of plane, whereas the phenylethynyl groups are co-planar 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.

[47] Huang, Y.; Li, L.; Peng, X.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2012**, *22*, 21841.

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

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

[a]Lowest energy maximum of multi-peak fit. [b]λ_{ex} = 365 nm. [c]Relative measurement, using rhodamine 6G as standard (PLQY = 95%). [d]λ_{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.

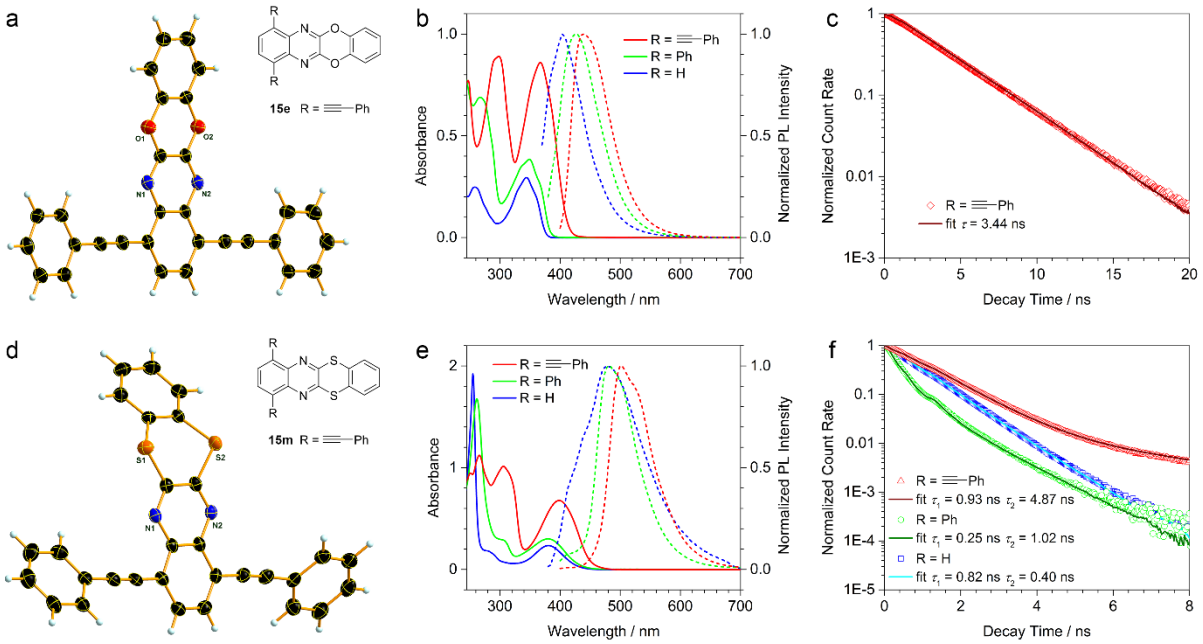


Figure 4: a) Crystal structure fragment showing the planar conformation of **15e**. b) Optical absorption (solid line) and normalized emission spectra (dashed line) of 25 µM dioxane solutions of selected oxygen-bridged tetracyclic heterocycles. c) Time-correlated single photon counting (TCSPC) decays 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 heteroacene 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

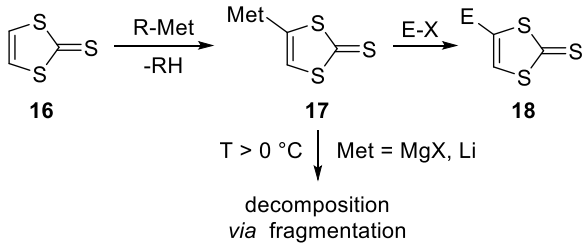
The functionalization of heterocycles is an important synthetic task since many of these ring systems have interesting biological or electronical properties.[42b,48] The directed metalation of heterocycles is one of the most general methods for achieving a broad heterocyclic functionalization.[6a,45,49] TMP-bases of magnesium and zinc, such as TMPMgCl·LiCl (**2**), TMPZnCl·LiCl (**4**) and $TMP_2Zn·2MgCl_2·2LiCl$ (**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[10] 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.[50] 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 *β*-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).[20-22,51]

[48] (a) Katritzky, A. R. In *Handbook of Heterocyclic Chemistry*, 3rd Ed.; Elsevier: Amsterdam, **2010**, 239. (b) Alvarez-Builla, J.; Vaquero, J. J.; Barluenga, J. In *Modern Heterocyclic Chemistry*, Vol. 1; Wiley-VCH: Weinheim, **2011**, 1. (c) Knochel, P.; Schade, M. A.; Bernhardt, S.; Manolikakes, G.; Metzger, A.; Piller, F. M.; Rohbogner, C. J.; Mosrin, M. *Beilstein J. Org. Chem.* **2011**, *7*, 1261.

[49] (a) Chapoulaud, V. G.; Salliot, I.; Plé, N.; Turck, A.; Quéguiner, G. *Tetrahedron* **1999**, *55*, 5389. (b) Turck, A.; Plé, N.; Mongin, F.; Quéguiner, G. *Tetrahedron* **2001**, *57*, 4489. (c) Mulvey, R. E.; Mongin, F.; Uchiyama, M.; Kondo, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3802. (d) Chevallier, F.; Mongin, F. *Chem. Soc. Rev.* **2008**, *37*, 595. (e) Snieckus, V. *Beilstein J. Org. Chem.* **2011**, *7*, 1215. (f) Snieckus, V.; Anctil, E. J.-G. In *The Directed Ortho Metallation (DoM)–Cross-Coupling Nexus. Synthetic Methodology for the Formation of Aryl–Aryl and Aryl–Heteroatom–Aryl Bonds, in Metal-Catalyzed Cross-Coupling Reactions and More*, De Meijere, A.; S. Bräse, S.; Oestreich, M., Eds.; Wiley-VCH: Weinheim, **2014**, 1. (g) Zhao, Y.; Snieckus, V. *Org. Lett.* **2014**, *16*, 3200. (h) Desai, A. A.; Snieckus, V. *Org. Process Res. Dev.* **2014**, *18*, 1191.

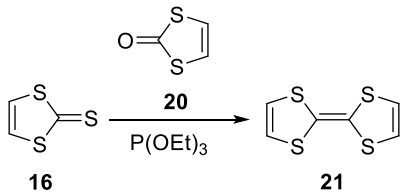
[50] Clayden, J. In *Organolithiums: Selectivity for Synthesis*, Vol. 23; Baldwin, J. E.; Williams, R. M., Eds.; Elsevier: Oxford, **2002**, 9.

[51] (a) Imakobu, T.; Sawa, H.; Kato, R. *Synthetic Metals* **1997**, *86*, 1883. (b) Wright, I. A.; Skabara, P. J.; Forgie, J. C.; Kanibolotsky, A. L.; González, B.; Coles, S. J.; Gambino, S.; Samuel, I. D. W. *J. Mater. Chem.* **2011**, *21*, 1462.



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,[52] carbon nanotubes,[53] covalent organic frameworks[54] and conjugated microporous polymers[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).[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.

[52] (a) Batsanov, A. S.; Bryce, M. R.; Chesney, A.; Howard, J. A. K.; John, D. E.; Moore, A. J.; Wood, C. L.; Gershtenman, H.; Becker, J. Y.; Khodorkovsky, V. Y.; Ellern, A.; Bernstein, J.; Perepichka, I. F.; Rotello, V.; Gray, M.; Cuello, A. O. *J. Mater. Chem.* **2001**, *11*, 2181. (b) Xiong, S.; Pu, D.; Xin, B.; Wang, G. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 1885.

[53] Kowalewska, B.; Kulesza, P. J. *ECS Trans.* **2008**, *13*, 1; *Electroanalysis* **2009**, *21*, 351.

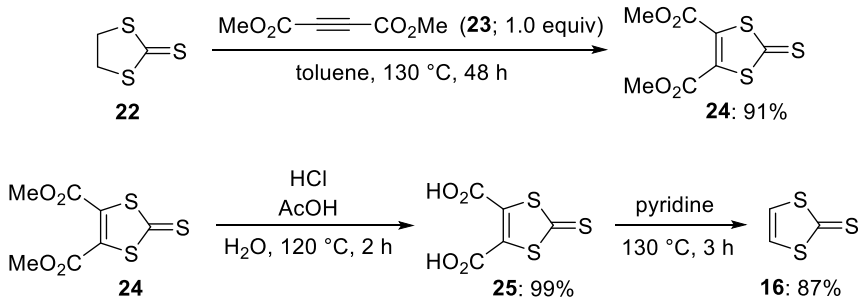
[54] (a) Cai, S.-L.; Zhang, Y.-B.; Pun, A. B.; He, B.; Yang, J.; Toma, F. M.; Sharp, I. D.; Yaghi, O. M.; Fan, J.; Zheng, S.-R.; Thang, W.-G.; Liu, Y. *Chem. Sci.* **2014**, *5*, 4693. (b) Jin, S.; Sakurai, T.; Kowalcyk, T.; Dalapati, S.; Xu, F.; Wei, H.; Chen, X.; Gao, J.; Seki, S.; Irle, S.; Jiang, D. *Chem. Eur. J.* **2014**, *20*, 14608.

[55] Bildirir, H.; Paraknowitsch, J. P.; Thomas, A. *Chem Eur. J.* **2014**, *20*, 9543.

[56] (a) Krief, A. *Tetrahedron* **1986**, *42*, 1209. (b) Garín, J.; Orduna, J.; Savirón, M.; Bryce, M. R.; Moore, A. J.; Morisson, V. *Tetrahedron* **1996**, *52*, 11063. (c) Hasegawa, M.; Takano, J.; Enozawa, H.; Kuwatani, Y.; Iyoda, M. *Tetrahedron Lett.* **2004**, *45*, 4109. (d) Ito, T.; Nakamura, K.; Shirahata, T.; Kawamoto, T.; Mori, T.; Misaki, Y. *Chem. Lett.* **2011**, *40*, 81.

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).

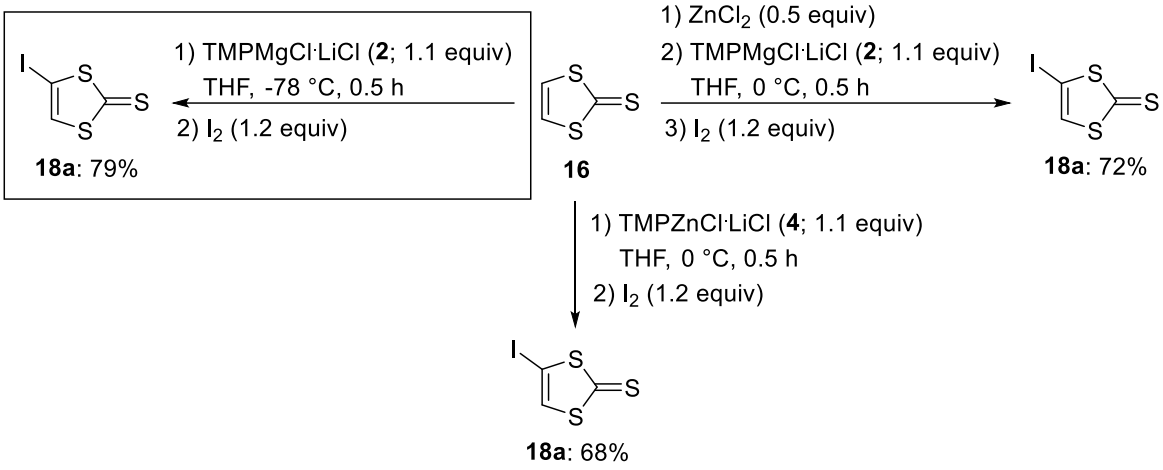


Scheme 33: Preparation of 1,3-dithiole-2-thione (**16**).

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·LiCl (**2**; 1.1 equiv, THF, -78 °C, 0.5 h) or TMPMgCl·LiCl (**2**; 1.1 equiv, THF, 0 °C, 0.5 h) in the presence of $ZnCl_2$ (0.5 equiv) or TMPZnCl·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.

[57] Melby, L. R.; Hartzler, H. D.; Sheppard, W. A. *J. Org. Chem.* **1974**, *39*, 2456.



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

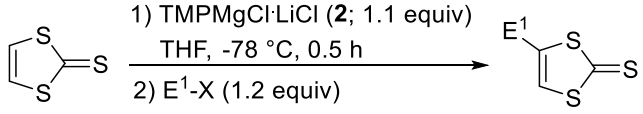
Bromination of the magnesiated DTT-derivative with 1,2-dibromotetrachloroethane produced the corresponding halogenated product **18b** in 84% isolated yield (Table 3, entry 2). Thiolation with *S*-methyl methanethiosulfonate furnished the methyl thioether **18c** in 75% yield (entry 3). Various carbon electrophiles reacted readily. Thus, the acylation with 3-chlorobenzoyl chloride, after domino-transmetalation[58] with $ZnCl_2$ and $CuCN{\cdot}2LiCl$,[59] provided ketone **18d** in 62% yield (entry 4). Copper-mediated allylation with ethyl (2-bromomethyl)acrylate[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 ($Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $Pd(OAc)_2$/SPhos and PEPPSI-*i*Pr) in the coupling with ethyl 4-iodobenzoate. No arylation was observed using $Pd(PPh_3)_2Cl_2$, $Pd(OAc)_2$/SPhos and PEPPSI-*i*Pr (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).

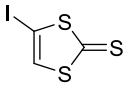
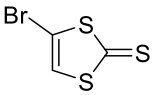
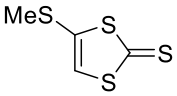
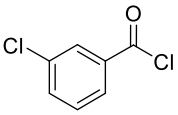
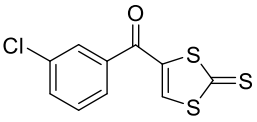
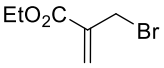
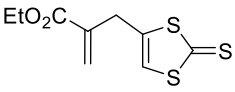
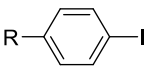
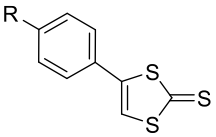
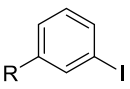
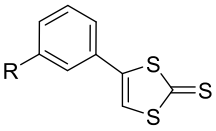
[58] (a) Tietze, L. F. In *Domino Reactions: Concept for Efficient Organic Synthesis*, Wiley-VCH: Weinheim, **2014**, 1. (b) Moriya, K.; Simon, M.; Mose, R.; Karaghiosoff, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2015**, *54*, 10963.

[59] (a) Knochel, P.; Chou, T. S.; Chen, H. G.; Yeh, M. C. P.; Rozema, M. J. *J. Org. Chem.* **1989**, *54*, 5202. (b) Majid, T. N.; Knochel, P. *Tetrahedron Lett.* **1990**, *31*, 4413. (c) Dohle, W.; Lindsay, D. M.; Knochel, P. *Org. Lett.* **2001**, *3*, 2871.

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



16 **18**

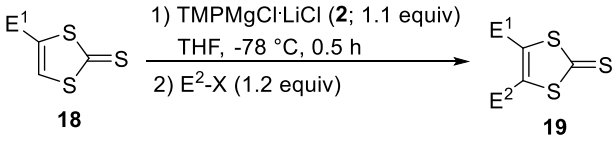
Entry	Electrophile	Product	Yield (%)[a]
1	I_2	 **18a**	79
2	$(BrCl_2C)_2$	 **18b**	84
3	$MeSO_2SMe$	 **18c**	75
4		 **18d**	62[b,c]
5		 **18e**	50[b,c]
			
6	R = CO_2Et	**18f**: R = CO_2Et	84[d]
7	R = CN	**18g**: R = CN	94[d]
8	R = Cl	**18h**: R = Cl	67[d]
9	R = CF_3	**18i**: R = CF_3	66[d]
10	R = CH_3	**18j**: R = CH_3	79[d]
11	R = NO_2	**18k**: R = NO_2	77[d]
12	R = OMe	**18l**: R = OMe	70[d]
			
13	R = NO_2	**18m**: R = NO_2	60[d]
14	R = OMe	**18n**: R = OMe	94[d]

[a]Isolated Yield of analytically pure product. [b]$ZnCl_2$ solution was added. [c]CuCN.2LiCl solution was added. [d]Cross-coupling conditions: $ZnCl_2$ transmetalation, 10 mol% $Pd(PPh_3)_4$, THF/NMP (2:1).

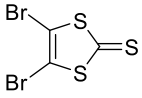
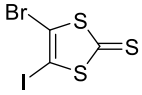
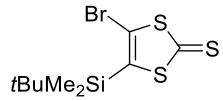
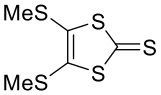
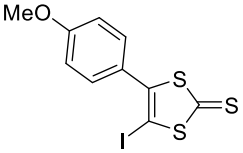
2.4 Preparation of Difunctionalized DTT-Derivatives

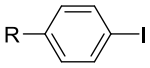
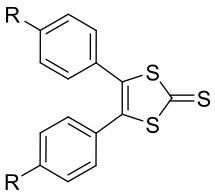
Disubstituted DTT-derivatives of type **19** were obtained by a second magnesiation of various mono-substituted DTTs (**18**) using similar conditions. Subsequent trapping of the magnesiated 4-bromo-DTT **18b** with different electrophiles, such as 1,2-dibromotetrachloroethane, iodine and *tert*-butyldimethylsilyl 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[39] using $Pd(PPh_3)_4$ (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**).



18 **19**

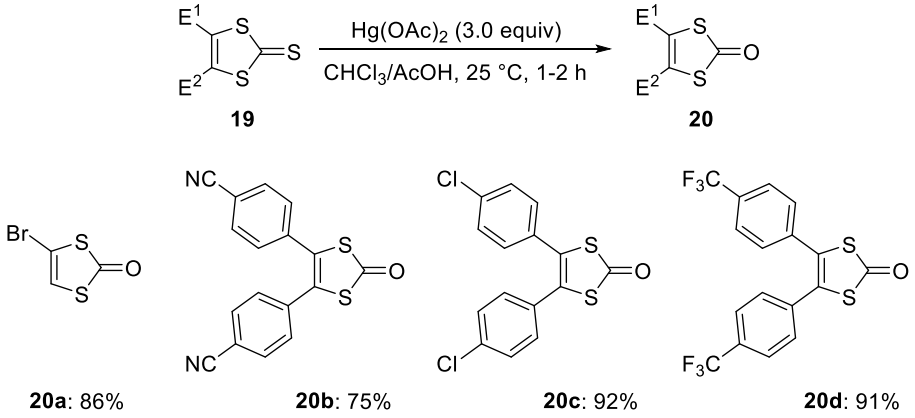
Entry	Substrate	Electrophile	Product	Yield (%)[a]
1	**18b**	$(BrCl_2C)_2$	 **19a**	91
2	**18b**	I_2	 **19b**	70
3	**18b**	*t*$BuMe_2SiOTf$	 **19c**	94
4	**18c**	$MeSO_2SMe$	 **19d**	86
5	**18l**	I_2	 **19e**	96

Entry	Substrate	Electrophile	Product	Yield (%)[a]
				
6	**18g**	R = CN	**19f**: R = CN	83[b]
7	**18h**	R = Cl	**19g**: R = Cl	93[b]
8	**18i**	R = CF_3	**19h**: R = CF_3	89[b]
9	**18j**	R = CH_3	**19i**: R = CH_3	89[b]

[a]Isolated Yield of analytically pure product. [b]Cross-coupling conditions: $ZnCl_2$ transmetalation, 10 mol% $Pd(PPh_3)_4$, THF/NMP (2:1).

2.5 Preparation of Functionalized 1,3-Dithiol-2-one-Derivatives

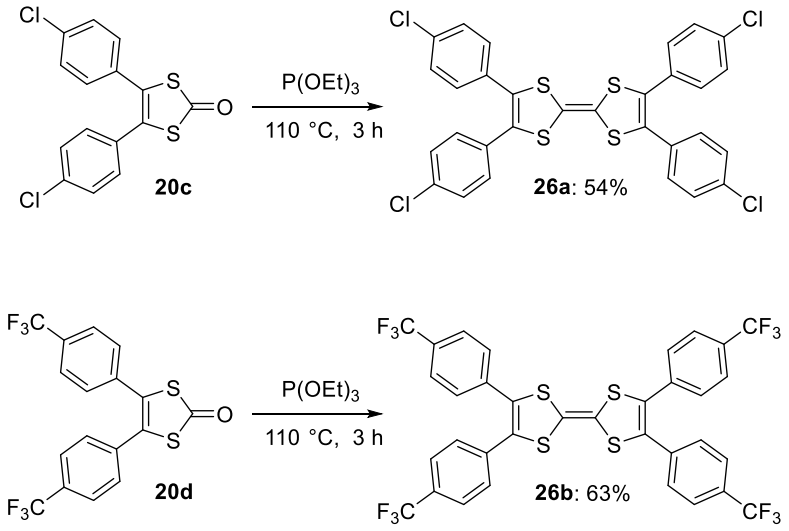
Various 4,5-disubstituted DTTs of type **19** were converted into the corresponding oxygen analogs of type **20** by treatment with $Hg(OAc)_2$ (3.0 equiv) in a mixture of $CHCl_3$ and AcOH (4:1) (25 °C, 1-2 h).[20b] Thus, the monobromo-oxygen analog **20a**, as well as the diarylated compounds **20b-d** were obtained in 75-92% yield (Scheme 35).



Scheme 35: Preparation of oxygen analogs **20a-d**.

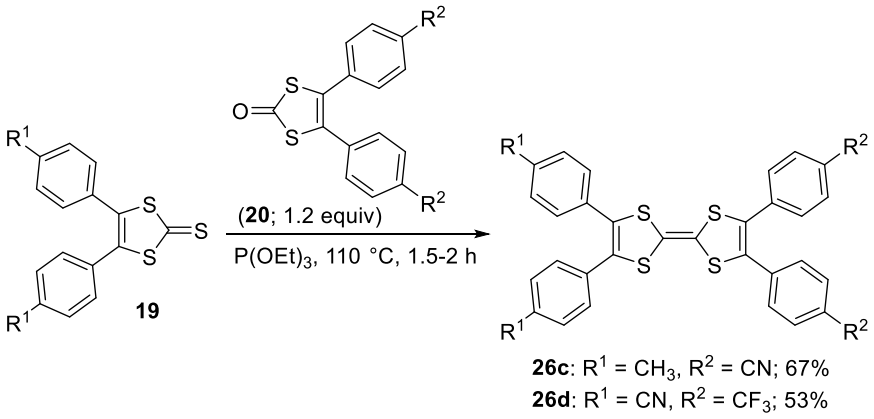
2.6 Preparation of Tetraarylated TTF-Derivatives

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.

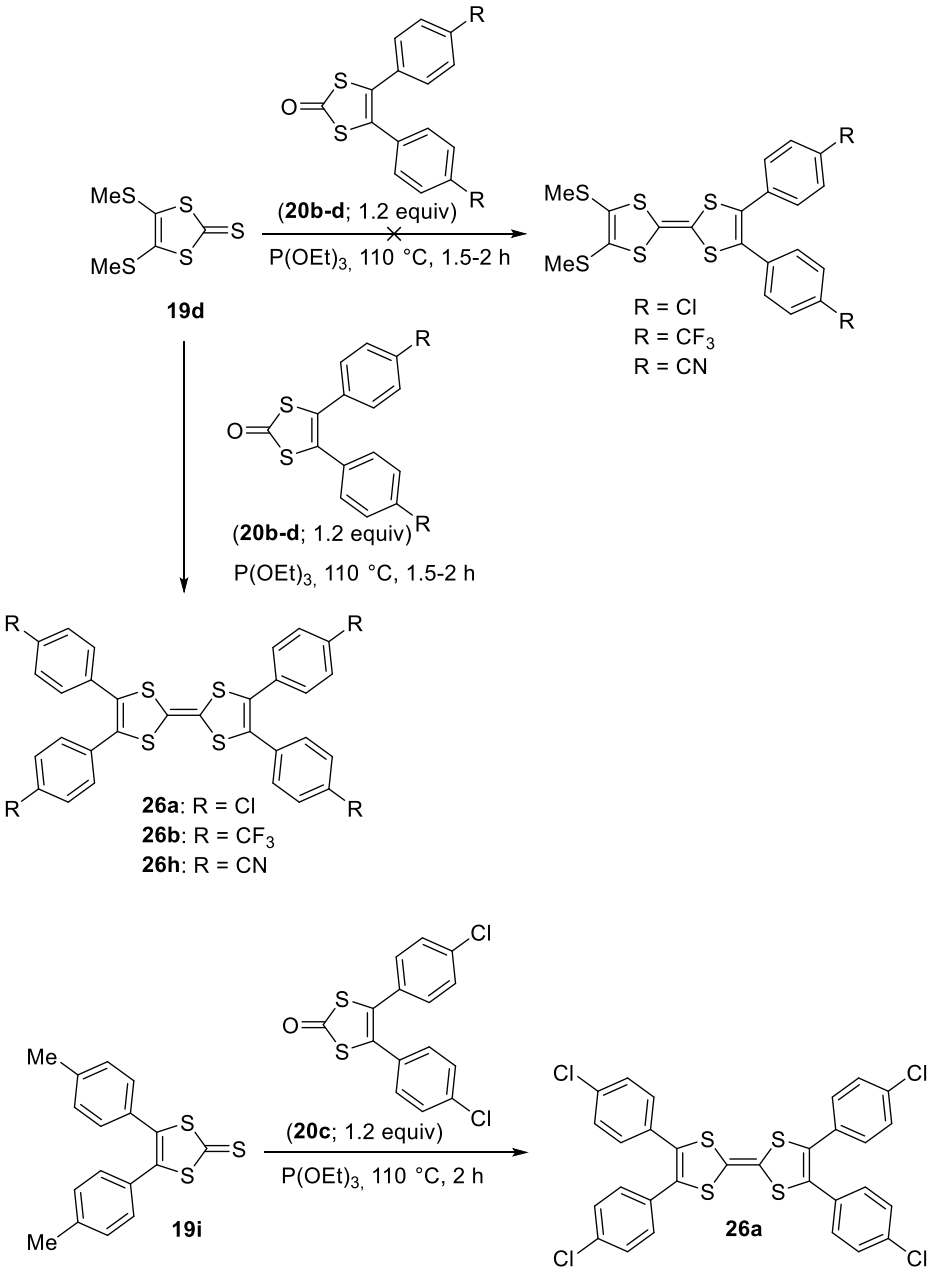


Scheme 37: Preparation of nonsymmetrically substituted TTF-derivatives *via* triethyl phosphite-mediated cross-coupling.

2.7 Donor-Acceptor-TTFs

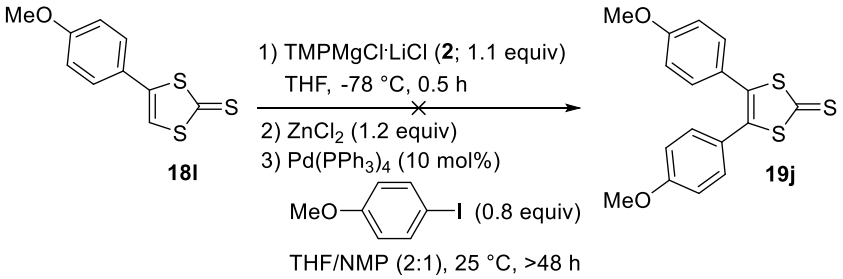
The preparation of donor-acceptor-TTF-derivatives bearing electron-withdrawing groups on one side and electron-donating groups on the other side is of high interest for organic materials. These compounds could exhibit extraordinary charge transfer properties. As shown in Scheme 37, compound **26c** possess both, electron-withdrawing CN-groups, as well as electron-donating CH_3-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).



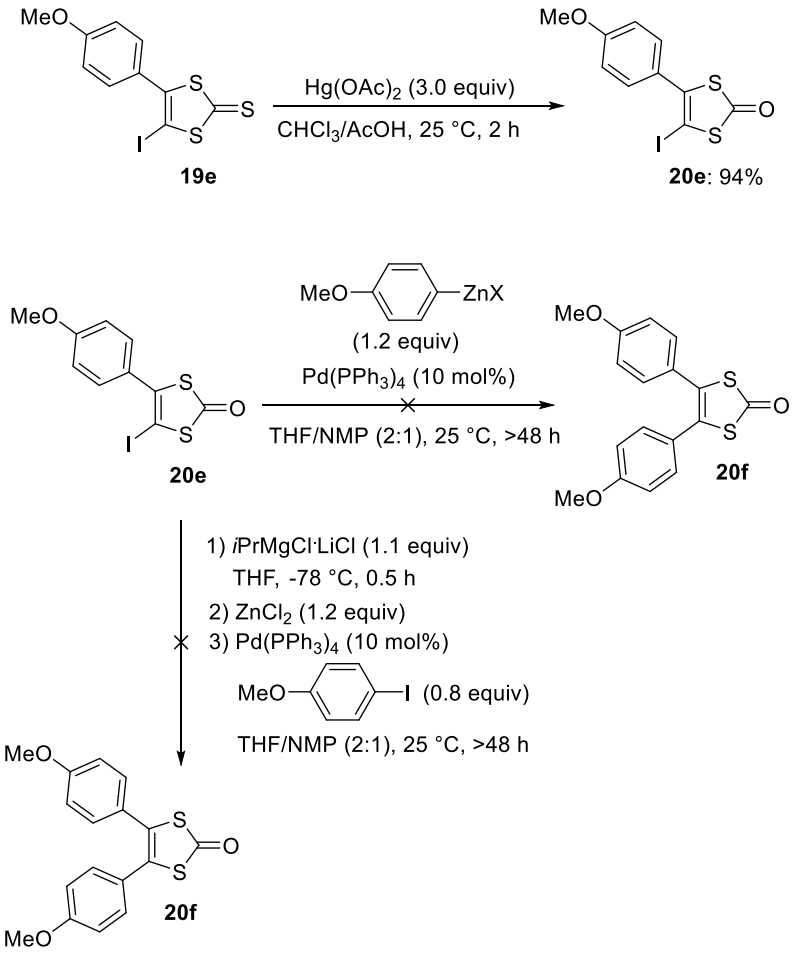
Scheme 38: Attempts to prepare donor-acceptor-TTF-derivatives.

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).



Scheme 39: Attempt to prepare the disubstituted DTT-derivative **19j**.

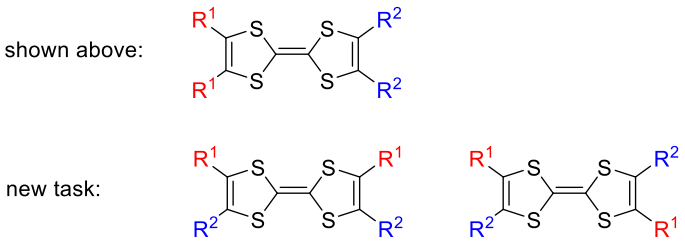
A possible explanation could be that the DTT-derivative **18l** is already very electron-rich so that another strong electron-donating group can not be introduced. In order to remove electron density from the system, the exocyclic sulfur of the iodinated DTT **19e** was converted into the oxygen atom 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*PrMgCl·LiCl (1.1 equiv, THF, -78°C, 0.5 h) (Scheme 40).



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

2.8 Other TTF Isomers

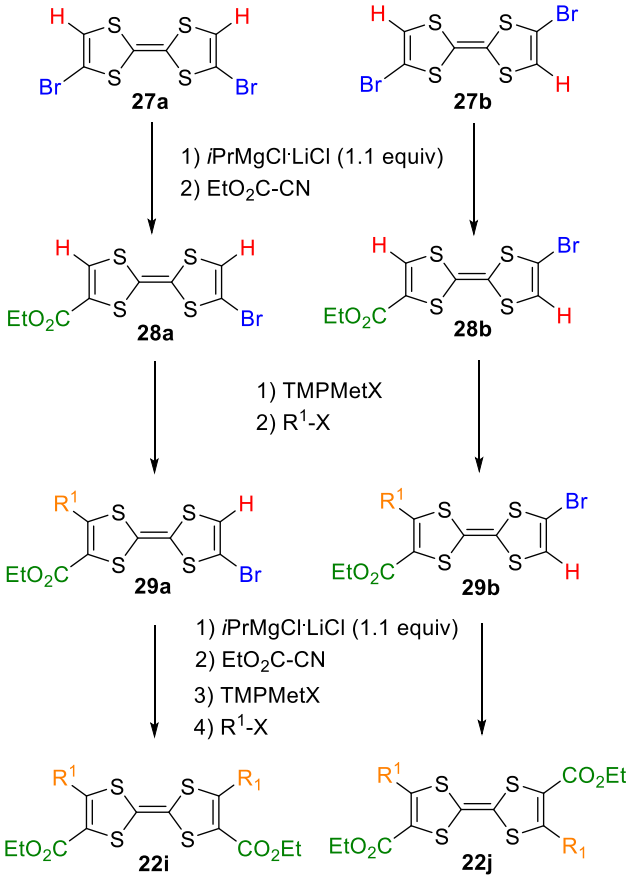
Another synthetically interesting task would be the preparation of other substituted TTF-isomers as shown in Scheme 41.



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

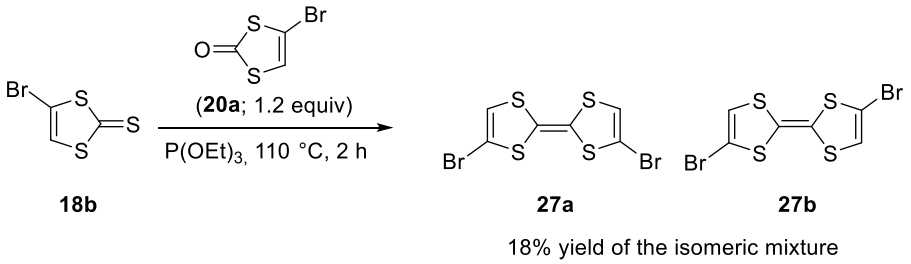
The dibromo-TTF-derivatives **27a** and **27b** should give access to these new isomers. Bromine-magnesium-exchange, followed by subsequent trapping of the Mg-species with ethyl cyanoformate should furnish the ester compounds **28a** and **28b**. Due to the directing effect of

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).



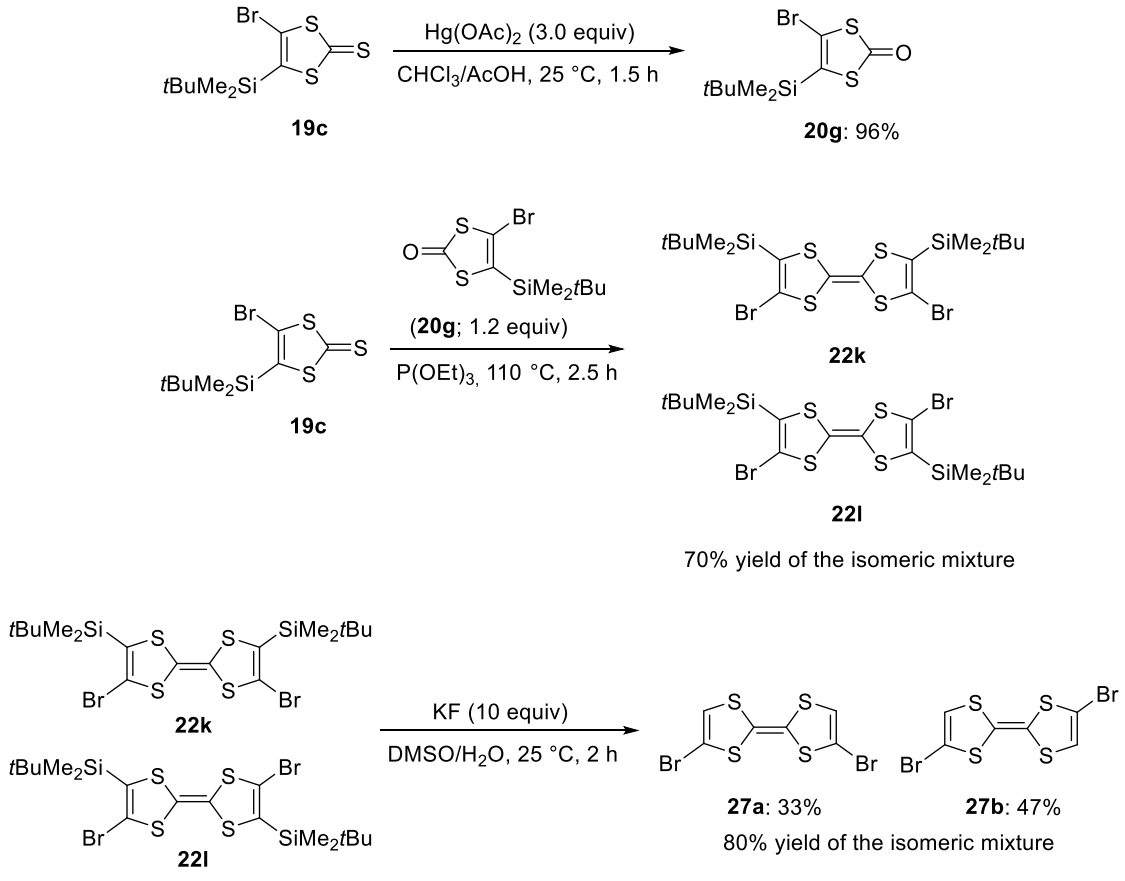
Scheme 42: Synthetical strategy giving access to new TTF-isomers.

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).



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/H_2O, 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 *i*hexane/NEt_3 (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).

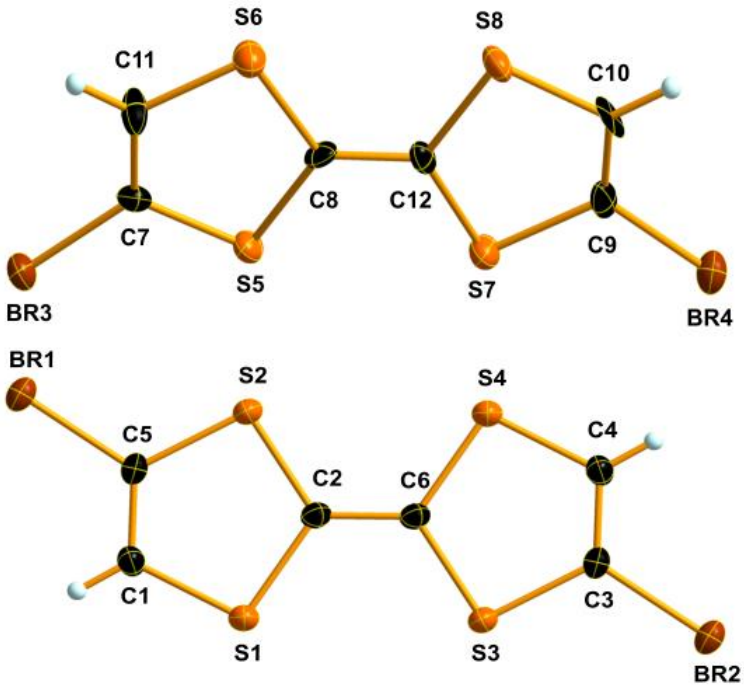


Figure 5: Single crystal X-ray diffraction of the *cis*-isomer **27a** (above) and the *trans*-isomer **27b** (below).

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.

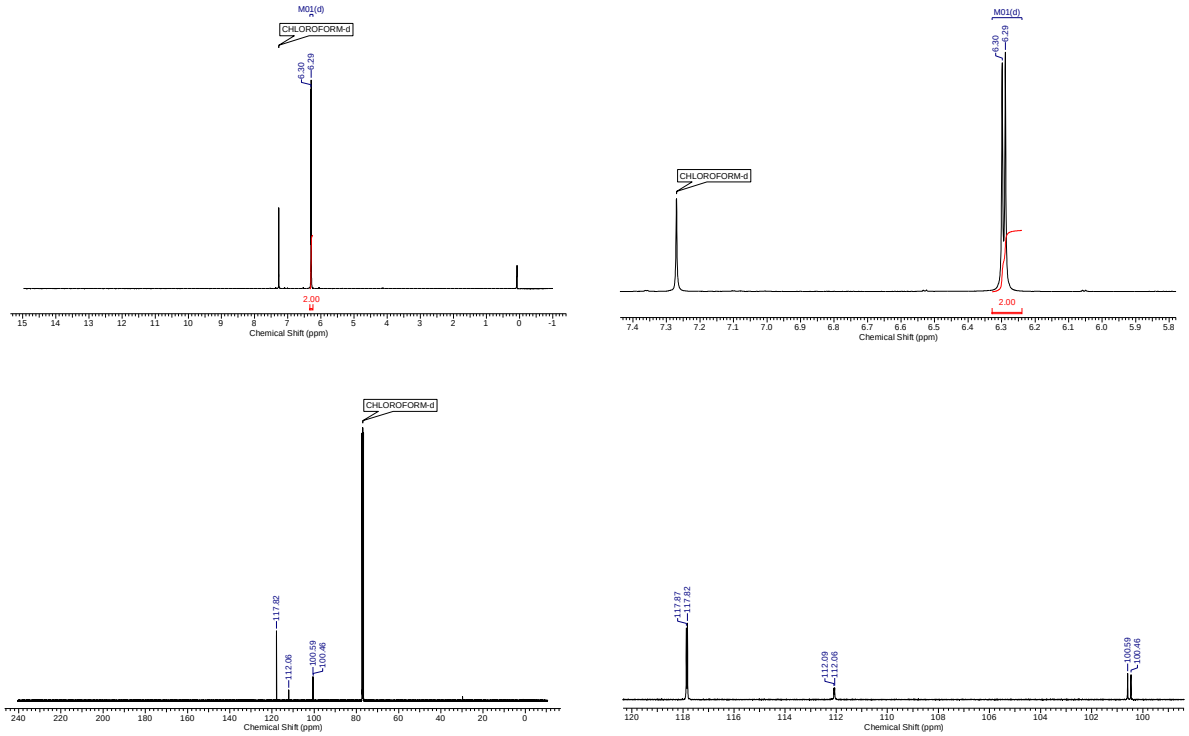


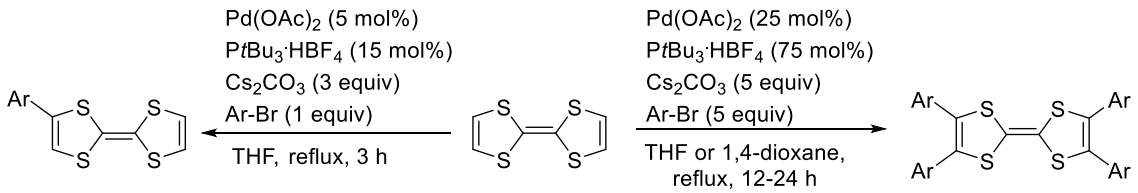
Figure 6: NMR analysis of the *trans*-isomer: ^{1}H-NMR (above) and ^{13}C-NMR (below).

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

3.1 Introduction

Pioneered by the discovery of *Wudl*,[60] tetrathiafulvalenes (TTFs) have emerged into an important class of organic materials[61] owing to their unique optical, electronic and magnetic properties.[23,62] Much effort has been made to functionalize the TTF-scaffold, including C-H arylation[63] and direct metalations.[26-28] Although the C-H arylation enables a fast access to arylated TTF-derivatives, this methodolody 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.

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.

[60] (a) Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* **1972**, *94*, 670. (b) Wudl, F.; Kruger, A. A.; Kaplan, M. L.; Hutton, R. S. *J. Org. Chem.* **1977**, *42*, 768.

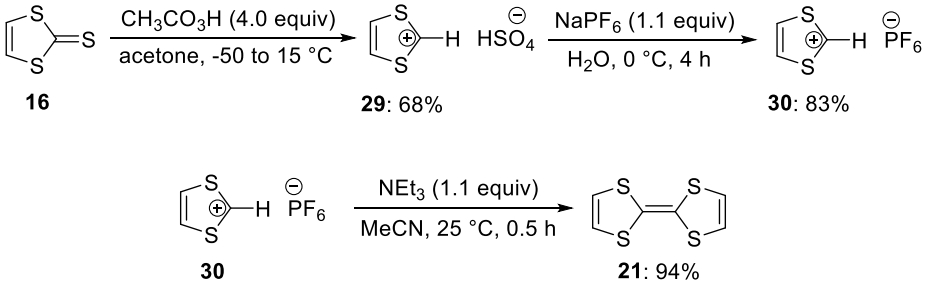
[61] (a) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969. (b) Bunz, U. H. F.; Rotello, V. M. *Angew. Chem., Int. Ed.* **2010**, *49*, 3268.

[62] (a) El-Wareth, A.; Sarhan, A. O. *Tetrahedron* **2005**, *61*, 3889. (b) Lorcy, D.; Bellec, N.; Fourmigué, M.; Avarvari, N. *Coord. Chem. Rev.* **2009**, *253*, 1398.

[63] Mitamura, Y.; Yorimitsu, H.; Oshima, K.; Osuka, A. *Chem. Sci.* **2011**, *2*, 2017.

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).

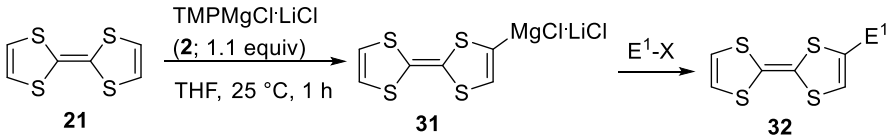


16 **29**: 68% **30**: 83% **30** **21**: 94%

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).



21 **31** **32**

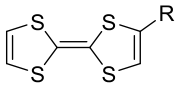
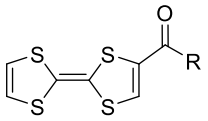
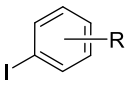
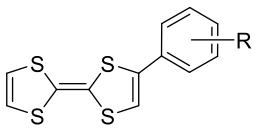
Scheme 47: Preparation of functionalized TTFs (**32**) *via* the magnesiation of TTF (**21**) with TMPMgCl·LiCl (**2**).

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 $MeSO_2SMe$ affording the thioether **32d** in 89% yield (entry 4). An aminomethylation of **31** using the iminium salt $Me_2NCH_2OCOCF_3$[64] provided the amine **32e** in 55% yield (entry 5). The acylation of **31** was directly achieved by the addition

[64] (a) Ahound, A.; Cavé, A.; Kann-Fan, C.; Husson, H.-P.; Rostolan, de J.; Potier, P. *J. Am. Chem. Soc.* **1968**, *90*, 5622. (b) Kinast, G.; Tietze, L.-F. *Angew. Chem., Int. Ed.* **1976**, *15*, 239. (c) Sweeney, J.; Perkins, G. *e*-EROS *Encyclopedia of Reagents in Organic Synthesis*; Wiley: Hoboken, NJ, **2005**; DOI:10.1002/047084289X.rt237.pub.2. (d) Corpet, M.; Gosmini, C. *Synthesis* **2014**, 2258. (e) Werner, V.; Ellwart, M.; Wagner, A. J.; Knochel, P. *Org. Lett.* **2015**, *17*, 2026.

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[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)[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**).

Entry	Electrophile	Product	Yield (%)[a]
			
1	I_2	**32a**: R = I	55
2	$(BrCl_2C)_2$	**32b**: R = Br	67
3	$PhSO_2Cl$	**32c**: R = Cl	65
4	$MeSO_2SMe$	**32d**: R = SMe	89
5	$Me_2N{=}CH_2OCOCF_3$	**32e**: R = CH_2NMe_2	55
			
6	DMF	**32f**: R = H	60
7	NC-CO_2Et	**32g**: R = OEt	72
8	*t*BuCOCl	**32h**: R = *t*Bu	76[b]
9	3-Cl-C_6H_4COCl	**32i**: R = 3-Cl-C_6H_4	83[c]
			
10	R = 4-Cl	**32j**: R = 4-Cl	86[d]
11	R = 4-CO_2Et	**32k**: R = 4-CO_2Et	87[d]
12	R = 4-OMe	**32l**: R = 4-OMe	61[d]
13	R = 3-CF_3	**32m**: R = 3-CF_3	92[d]

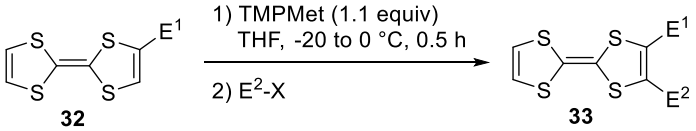
[a]Isolated yield of analytically pure product. [b]CuCN·2LiCl solution was added. [c]Pd-catalyzed acylation reaction using 10 mol% $Pd(PPh_3)_4$. [d]Cross-coupling conditions: $ZnCl_2$ transmetalation, 3 mol% $Pd(dba)_2$, 6 mol% tfp.

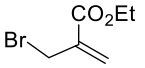
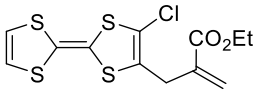
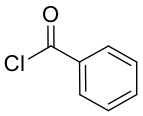
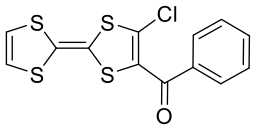
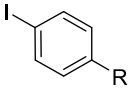
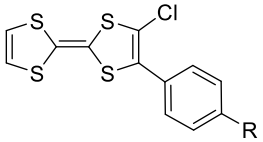
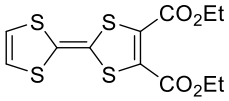
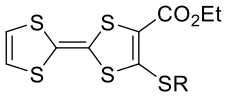
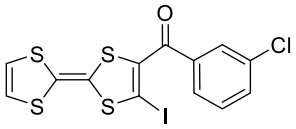
[65] Farina, V.; Krishna, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

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.[40] In case of a chloride (**32c**) or a carboethoxy group (**32g**), the metalation was best performed with TMPMgCl·LiCl (**2**). Thus, the treatment of 4-chloro-TTF (**32c**) with TMPMgCl·LiCl (**2**) at 0 °C (THF, 1.1 equiv, 0.5 h) followed by the copper-catalyzed allylation reaction with ethyl 2-(bromomethyl)acrylate[38] 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 TMPMgCl·LiCl (**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 $PhSO_2SPh$ and $MeSO_2SMe$ (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 $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (**5**; 1.1 equiv, THF, 0 °C, 0.5 h) led to the corresponding zincated-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.

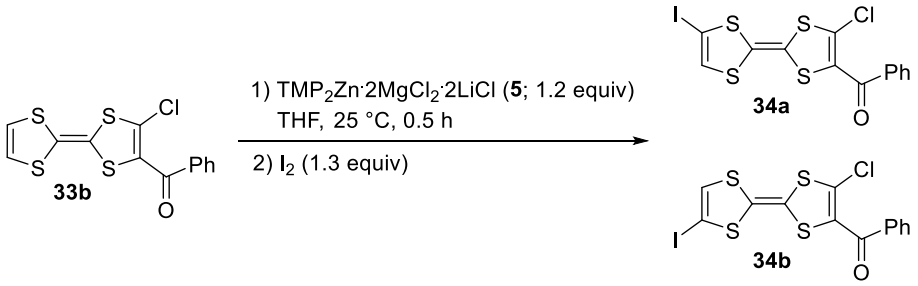


Entry	Substrate	Electrophile	Product	Yield (%)[a]
1	**32c**		 **33a**	85[b,c]
2	**32c**		 **33b**	83[b,d]
				
3	**32c**	R = OMe	**33c**: R = OMe	78[b,e]
4	**32c**	R = CN	**33d**: R = CN	92[b,e]
5	**32g**	NC-CO_2Et	 **33e**	65[f]
6	**32g**	$PhSO_2SPh$	 **33f**: R = Ph	59[f]
7	**32g**	$MeSO_2SMe$	**33g**: R = Me	65[f]
8	**32i**	I_2	 **33h**	83[g]

[a]Isolated yield of analytically pure product. [b]TMPMgCl·LiCl (1.1 equiv, 0 °C) was used. [c]CuCN·2LiCl solution was added. [d]$ZnCl_2$ solution was added. Pd-catalyzed acylation reaction using 10 mol% $Pd(PPh_3)_4$. [e]Cross-coupling conditions: $ZnCl_2$ transmetalation, 3 mol% $Pd(dba)_2$, 6 mol% tfp. [f]TMPMgCl·LiCl (1.1 equiv, -20 °C) was used. [g]$TMP_2Zn·2MgCl_2·2LiCl$ (1.1 equiv, 0 °C) was used.

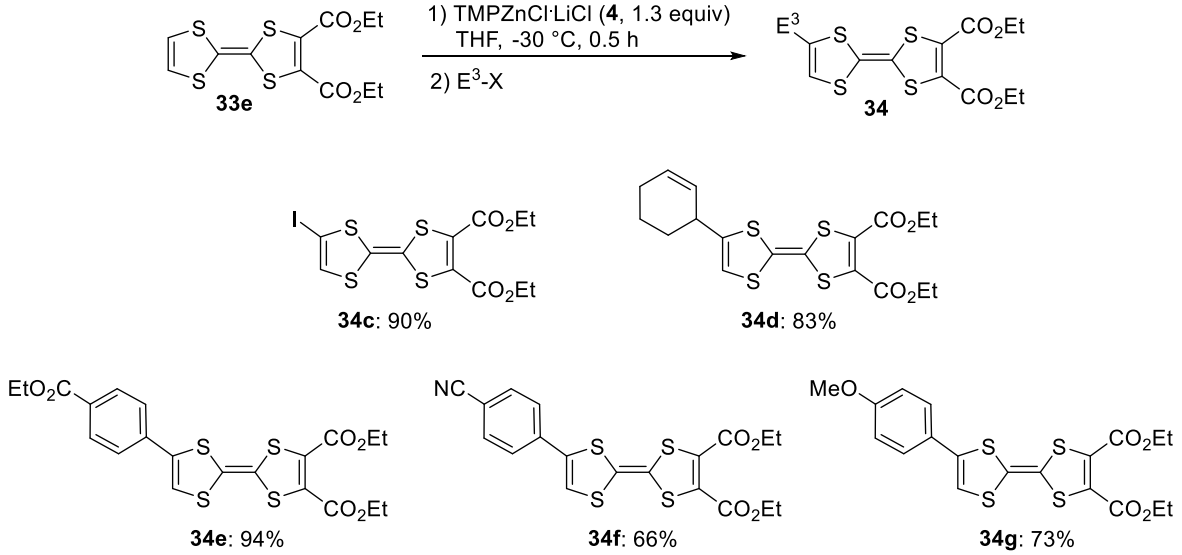
3.5 Preparation of Trifunctionalized TTF-Derivatives

For the preparation of completely nonsymmetrical substituted TTFs, compound **33b** was subjected to further metalation using $TMP_2Zn·2MgCl_2·2LiCl$ (**5**; THF, 1.2 equiv, 25 °C, 0.5 h). After quenching the zincated intermediate with iodine, a mixture of two isomeric compounds (**34a** and **34b**) was obtained in 51% yield and could not be separated (Scheme 48).



Scheme 48: Zincation of disubstituted TTF **33b** leading to an isomeric mixture.

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).



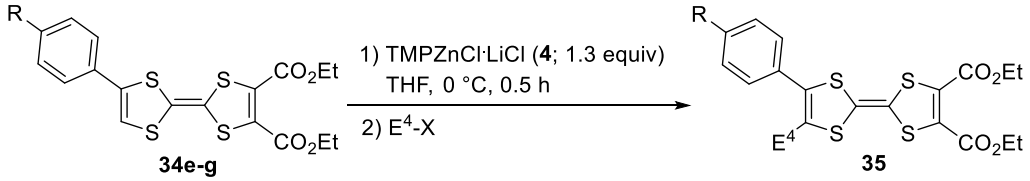
Scheme 49: Preparation of trisubstituted TTF-derivatives of type **34** using TMPZnCl·LiCl (**3**).

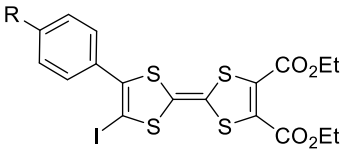
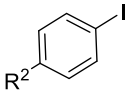
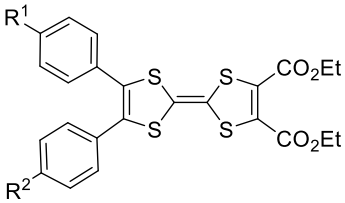
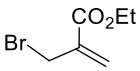
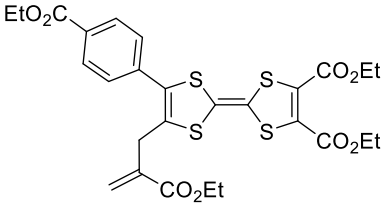
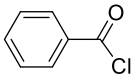
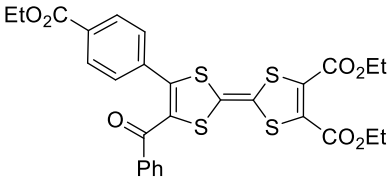
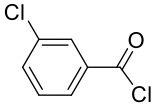
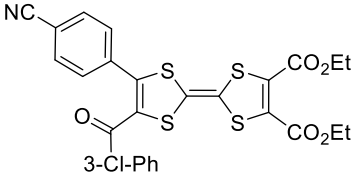
3.6 Preparation of Tetrafunctionalized TTF-Derivatives

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[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 tetrasubsituted 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**).



Entry	Substrate	Electrophile	Product	Yield (%)[a]
				
1	**34e**	I_2	**35a**: R = CO_2Et	88
2	**34f**	I_2	**35b**: R = CN	76
				
3	**34e**	R^2 = CO_2Et	**35c**: R^1 = R^2 = CO_2Et	90[b]
4	**34f**	R^2 = CN	**35d**: R^1 = R^2 = CN	63[b]
5	**34g**	R^2 = OMe	**35e**: R^1 = R^2 = OMe	63[b]
6	**34e**		 **35f**	85[c]
7	**34e**		 **35g**	85[d]
8	**34f**		 **35h**	80[d]

[a]Isolated yield of analytically pure product. [b]Cross-coupling conditions: 3 mol% $Pd(dba)_2$, 6 mol% tfp. [c]CuCN·2LiCl solution was added. [d]Pd-catalyzed acylation reaction using 10 mol% $Pd(PPh_3)_4$.

3.7 UV-VIS and DPV Data of Functionalized TTF-Derivatives[66]

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.

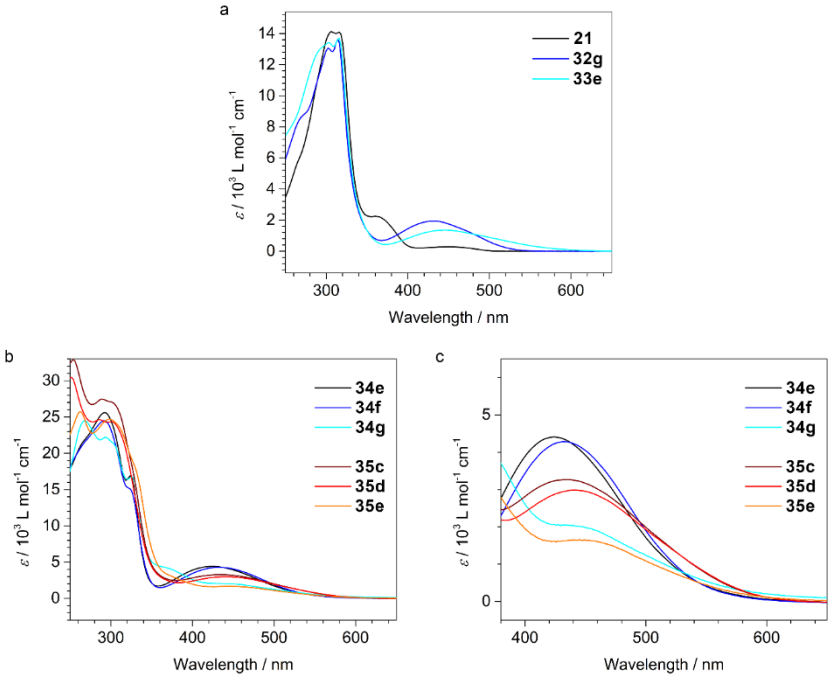


Figure 7: a) UV-VIS absorption spectra of TTF (**21**) and compounds **32g** and **33e**. b) Absorption spectra of the tri- and tetrafunctionalized TTFs **34e-g** and **35c-e**. c) Magnified view on the absorption in the VIS range of these compounds.

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).[67] The highest occupied molecular orbital (HOMO) energies were extracted from scans in oxidation direction (Figure 8) and referenced to the oxidation of ferrocene ($E_{fc/fc+}$ = -4.80 eV *vs.* vacuum).

[66] These measurements were performed by Dr. F. Auras and are given here for the sake of completeness.

[67] (a) Frost, J. M.; Faist, M. A.; Nelson, J. *Adv. Mater.* **2010**, *22*, 4881. (b) Calik, M.; Auras, F.; Salonen, L. M.; Bader, K.; Grill, I.; Handloser, M.; Medina, D. D.; Dogru, M.; Löbermann, F.; Trauner, D.; Hartschuh, A.; Bein, T. *J. Am. Chem. Soc.* **2014**, *136*, 17802. (c) Auras, F.; Li, Y.; Löbermann, F.; Döblinger, M.; Schuster, J.; Peter, L. M.; Trauner, D.; Bein, T. *Chem. Eur. J.* **2014**, *20*, 14971.

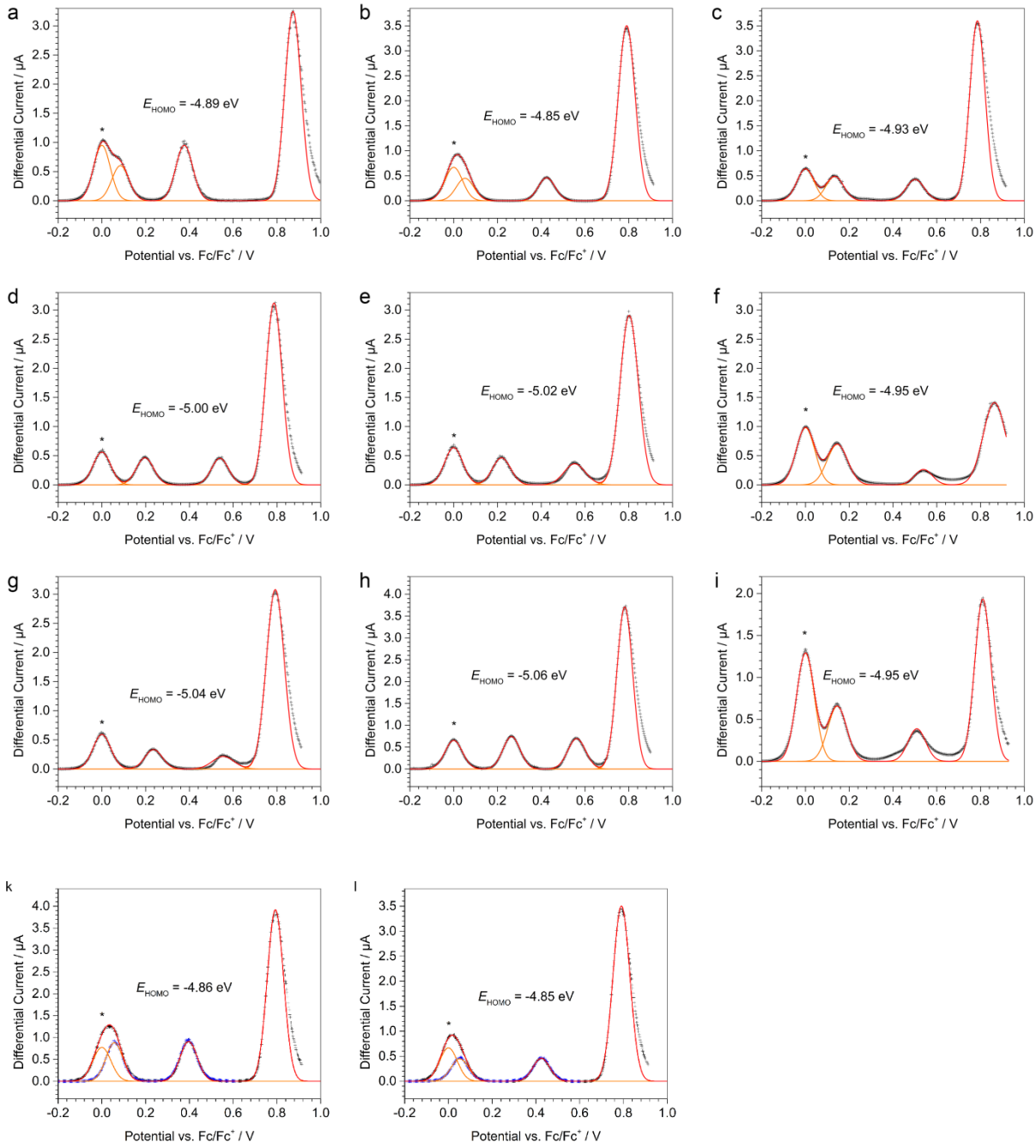


Figure 8: a-i) DPV data of compounds **21**, **32g**, **33e**, **34e-g** and **35c-e**, respectively (black), multi-Gaussian fits to the data (red) and the single Gaussian components (orange). The oxidation signal of the ferrocene internal reference is marked with an asterisk. The potential of the first oxidation, corresponding to the HOMO energy, is converted to vacuum scale assuming $E_{fc/fc+}$ = -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_2Et 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_2Et 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.

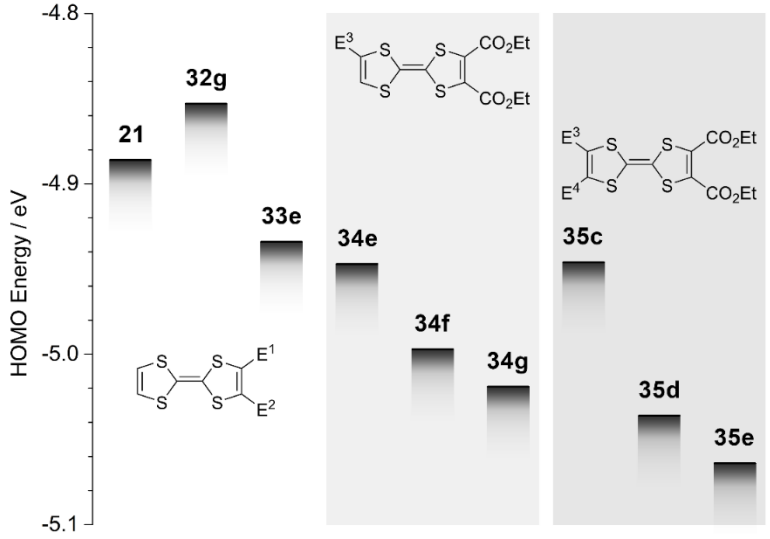
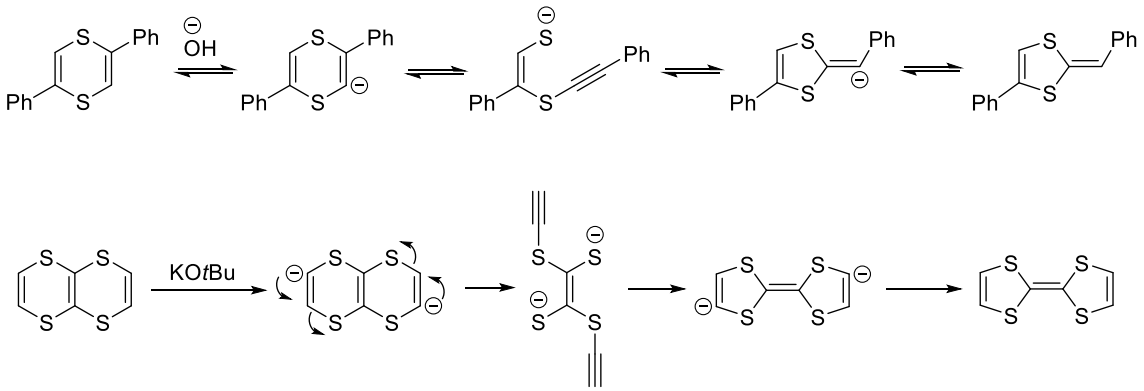


Figure 9: Highest occupied molecular orbital energies of selected substituted TTF-derivatives measured by differential pulse voltammetry.

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.[45,60-62] 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·LiCl (**2**),[9] TMPZnCl·LiCl (**4**),[12] and $TMP_2Zn{\cdot}2MgCl_2$ (**5**).[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.[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_4NOH *via* an open-ring-structure leading to 1,4-dithiafulvalenes.[69] In addition, tetrathianaphthalene is known to isomerize to TTF in the presence of strong bases, such as KO*t*Bu and LDA (Scheme 50).[31,70]



Scheme 50: Side reactions of 1,4-dithiin and 1,4,5,8-tetrathianaphthalene in the presence of strong bases.

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

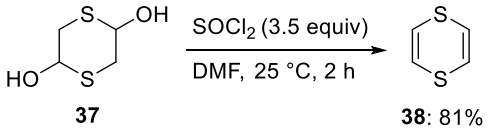
[68] (a) Nakamura, T.; Iwasaka, S.; Nakano, H., Inoue, K., Nogami, T.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 365. (b) Nakano, H.; Nogami, T.; Shirota, Y.; *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2973. (c) Nakano, H.; Miyawaki, K.; Nogami, T.; Shirota, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2604. (d) Ikegawa, S.; Miyawaki, K.; Nogami, T.; Shirota, Y. *Bull. Chem. Soc. Jpn.* **1999**, *66*, 2770. (e) Kanibolotsky, A. L.; Kanibolotskaya, L.; Gordeyev, S.; Skabara, P. J.; McCulloch, I.; Berridge, R.; Lohr, J. E.; Marchioni, F.; Wudl, F. *Org. Lett.* **2007**, *9*, 1601**.**

[69] Anderson, M. L.; Nielsen, M. F.; Hammerich, O. *Acta Chem. Scand.* **1995**, *49*, 503.

[70] (a) Nakatsuji, S.; Amano, Y.; Kawamura, H.; Anzai, H. *J. Chem. Soc., Chem. Commun.* **1994**, 841. (b) Nakatsuji, S.; Amano, Y.; Kawamura, H.; Anzai, H. *Liebigs Ann./Recueil* **1997**, 129. (c) Meline, R. L.; Elsenbaumer, R. L. *Synthesis* **1997**, 617. (d) Meline, R. L.; Elsenbaumer, R. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2467.

4.2 Preparation of 1,4-Dithiin

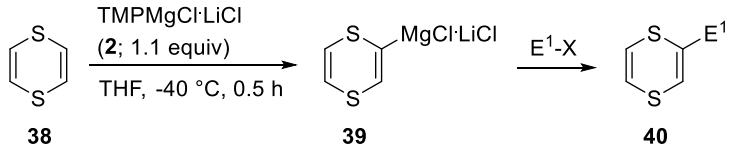
1,4-Dithiin (**38**) was prepared by the reaction of 1,4-dithiane-2,5-diol (**37**; 1.0 equiv) with thionyl chloride (3.5 equiv, DMF, 25 °C, 2 h).[71] Co-destillation of the crude product with DMF, followed by extraction afforded 1,4-dithiin (**38**) in 81% yield (Scheme 51).



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.



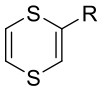
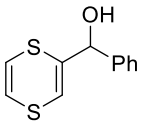
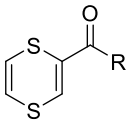
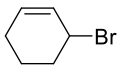
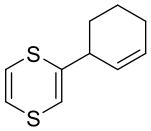
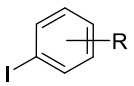
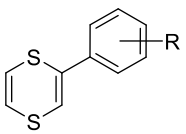
Scheme 52: Magnesiation of 1,4-dithiin (**38**) with TMPMgCl·LiCl (**2**) and subsequent trapping with electrophiles.

Iodination of the magnesiated derivative **39** afforded the expected product **40a** in 83% yield (Table 8, entry 1). Similary, bromination with $(BrCl_2C)_2$ and chlorination with $PhSO_2Cl$ 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 $MeSO_2SMe$ and $PhSO_2SPh$ affording the thioethers **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).

[71] Grant, A. S.; Faraji-Dana, S.; Graham, E. *J. Sulfur Chem.* **2009**, *30*, 135-136.

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 perfomed by a transmetalation with zinc chloride, followed by a Negishi cross-coupling[39] 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 TMPMgCl·LiCl (**2**).

Entry	Electrophile	Product	Yield (%)[a]
			
1	I_2	**40a**: R = I	83
2	$(BrCl_2C)_2$	**40b**: R = Br	78
3	$PhSO_2Cl$	**40c**: R = Cl	56
4	Tos-CN	**40d**: R = CN	60
5	$MeSO_2SMe$	**40e**: R = SMe	75
6	$PhSO_2SPh$	**40f**: R = SPh	77
7	PhCHO	 **40g**	97
			
8	NC-CO_2Et	**40h**: R = OEt	89
9	Cl-$COCO_2Et$	**40i**: R = CO_2Et	56[b,c]
10	*t*BuCOCl	**40j**: R = *t*Bu	89[b,c]
11	3-Cl-C_6H_4COCl	**40k**: R = 3-Cl-C_6H_4	80[b,c]
12	PhCOCl	**40l**: R = Ph	78[b,c]
13	*c*-C_3H_5COCl	**40m**: R = *c*-C_3H_5	65[b,c]
14		 **40n**	73[b,c]
			
15	R = 2-NH_2	**40o**: R = 2-NH_2	94[d]
16	R = 3-Me	**40p**: R = 3-Me	85[d]
17	R = 4-CO_2Et	**40q**: R = 4-CO_2Et	87[d]

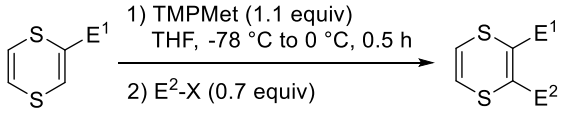
[a]Isolated yield of analytically pure product. [b]$ZnCl_2$ solution was added. [c]CuCN·2LiCl solution was added. [d]Cross-coupling conditions: $ZnCl_2$ transmetalation, 3 mol% $Pd(dba)_2$, 6 mol% tfp.

4.4 Preparation of Difunctionalized 1,4-Dithiin-Derivatives

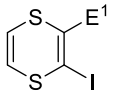
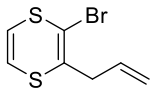
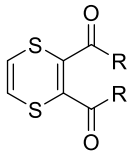
Disubstituted dithiins of type **41** were obtained by a second metalation of various mono-substituted derivatives (**40**). The presence of electron-withdrawing substituents, such as halides, a cyano group, a carboethoxy or an acyl group on the dithiin-core directed the second metalation to the adjacent position.[40] 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**.



40 **41**

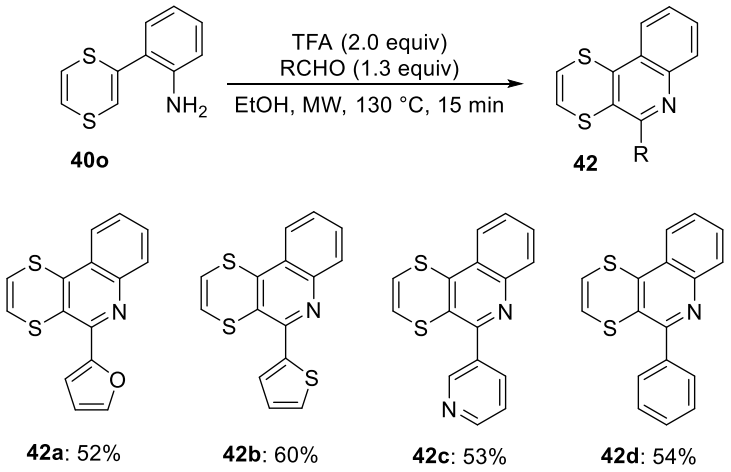
Entry	Substrate	Electrophile	Product	Yield (%)[a]
				
1	**40a**	I_2	**41a**: E^1 = I	68[b]
2	**40c**	I_2	**41b**: E^1 = Cl	71[b]
3	**40d**	I_2	**41c**: E^1 = CN	86[b]
4	**40h**	I_2	**41d**: E^1 = CO_2Et	62[c]
5	**40i**	I_2	**41e**: E^1 = $COCO_2Et$	50[b]
6	**40k**	I_2	**41f**: E^1 = 3-Cl-C_6H_4CO	69[b]
7	**40l**	I_2	**41g**: E^1 = COPh	78[b]
8	**40b**	C_3H_5Br	 **41h**	74[b,d]
				
9	**40k**	3-Cl-C_6H_4COCl	**41i**: R = 3-Cl-C_6H_4	52[b,e]
10	**40l**	PhCOCl	**41j**: R = Ph	59[b,e]

[a]Isolated yield of analytically pure product. [b]TMPZnCl·LiCl (1.1 equiv, THF, -40 °C or 0 °C, 0.5 h). [c]TMPMgCl·LiCl (1.1 equiv, THF, -78 °C, 0.5 h). [d]CuCN·2LiCl solution was added. [d]$Pd(PPh_3)_4$ (10 mol%) was added.

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 fururaI 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).

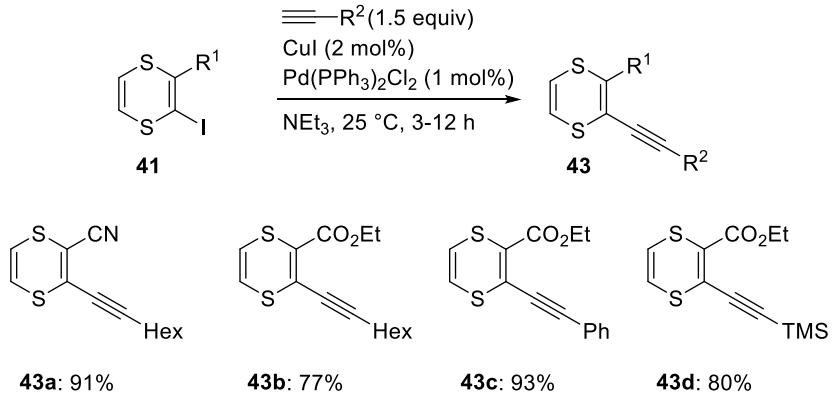
[72] Vavsari, V. F.; Dianati, V.; Ramezanpour, S.; Balalaie, S. *Synlett* **2015**, *26*, 1955.



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

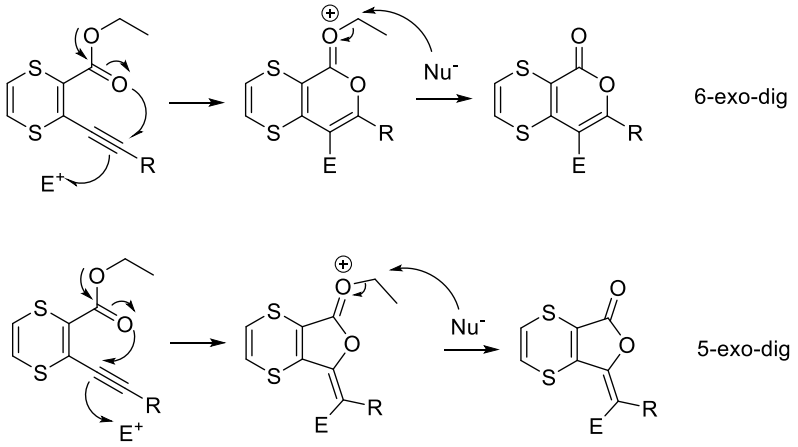
4.6 Iodine-Mediated Electrophilic Cyclizations of Alkynylated 1,4-Dithiin-Derivatives

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% $Pd(PPh_3)_2Cl_2$ (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).



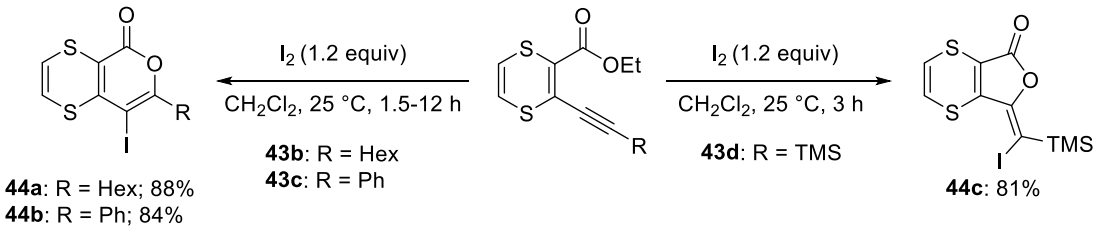
Scheme 54: Preparation of alkynylated 1,4-dithiin-derivatives of type **43** *via* Pd-catalyzed Sonogashira reactions.

The obtained dithiin-derivatives **43b-d** easily underwent electrophilic cyclizations under smooth conditions (CH_2Cl_2, 25 °C, 5-12 h) using iodine (1.2 equiv).[73] 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.

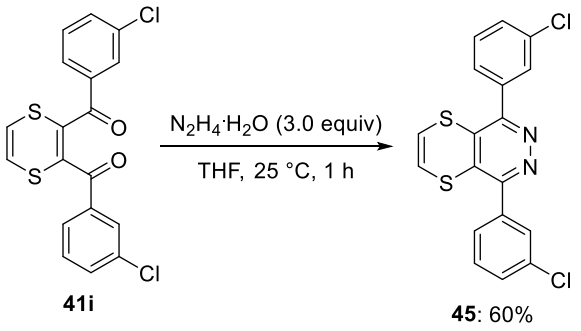


Scheme 56: Electrophilic cyclizations of alkynylated 1,4-dithiin-derivatives.

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).

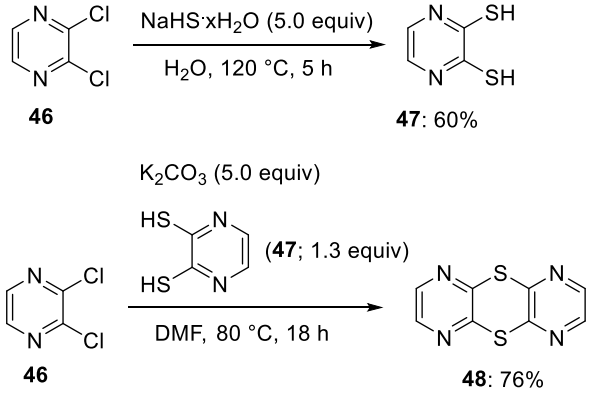
[73] Mehta, S.; Waldo, J. P.; Larock, R. C. *J. Org. Chem.* **2009**, *74*, 1141.



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 (H_2O, 120 °C, 5 h).[74] The following anellation step was best performed in the presence of K_2CO_3 (5.0 equiv) at higher temperatures (DMF, 80 °C, 8 h) leading to the heteroacene **48** in 76% yield (Scheme 58).

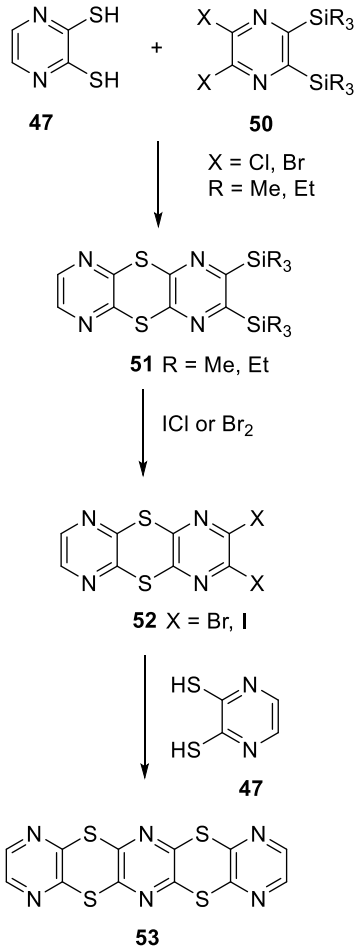


Scheme 58: Preparation of 2,3-dimercaptopyrazine (**47**) followed by anellation with 2,3-dichloropyrazine (**46**).

For the construction of larger *S*-arrays owning interesting electronic properties,[75] 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).

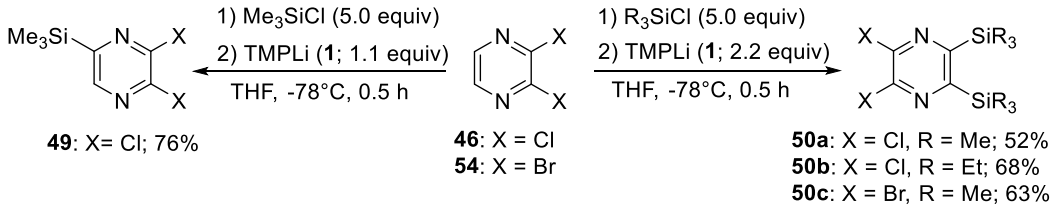
[74] Ribas, X.; Dias, J. C.; Morgado, J.; Wurst, K.; Molins, E.; Ruiz, E.; Almeida, M.; Veciana, J.; Rovira, C. *Chem. Eur. J.* **2004**, *10*, 1691.

[75] (a) Luzio, A.; Musumeci, C.; Newman, C. R.; Facchetti, A.; Marks, T. J.; Pignataro, B. *Chem. Mat.* **2011**, *23*, 1061. (b) Bula, R. P.; Oppel, I. M.; Bettinger, H. F. *J. Org. Chem.* **2012**, *77*, 3538. (c) Aotke, T.; Ikeda, S.; Kuzuhara, D.; Mori, S.; Okujima, T.; Uno, H.; Yamada, H. *Eur. J. Org. Chem.* **2012**, 1723.



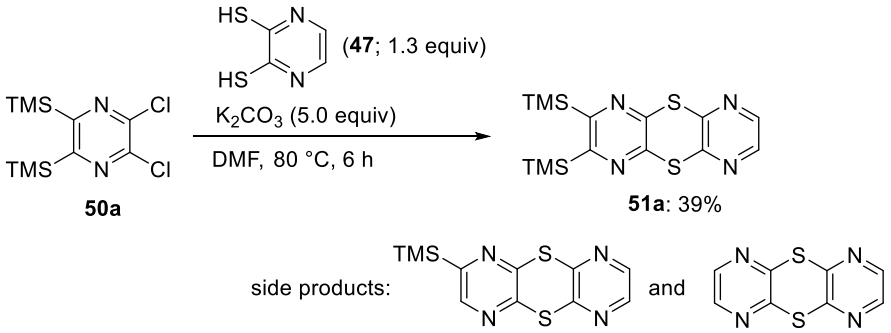
Scheme 59: Iterative synthesis of heteropentacene **53**.

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_3SiCl (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).



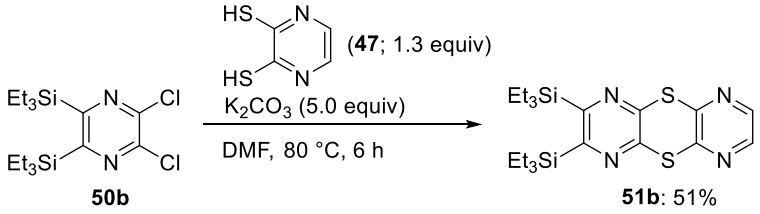
Scheme 60: Preparation of silyl-substituted pyrazines.

The dichloro-di-TMS-subsituted 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).



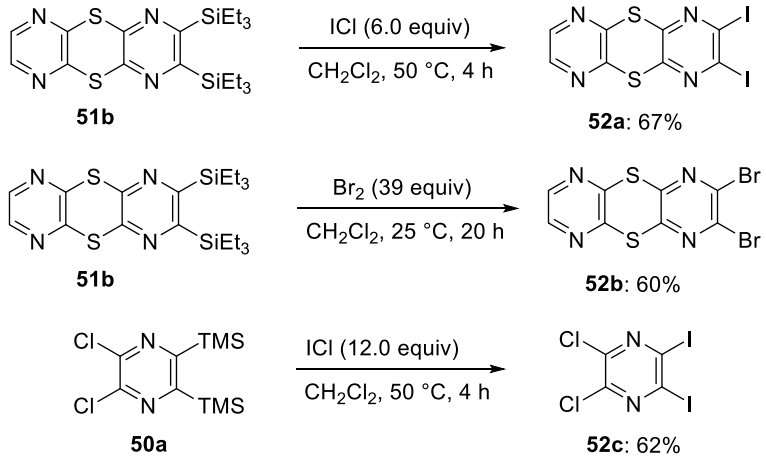
Scheme 61: Anellation of dichloro-di-TMS-substituted pyrazine **50a** with 2,3-dimercaptopyrazine (**47**).

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 K_2CO_3 (5.0 equiv) led to the heteroacene **51b** (DMF, 80 °C, 6 h) in 51% yield (Scheme 62).



Scheme 62: Anellation of bis(triethysilyl)-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, CH_2Cl_2, 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** (CH_2Cl_2, 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).



Scheme 63: Conversion of silyl-groups into halides.

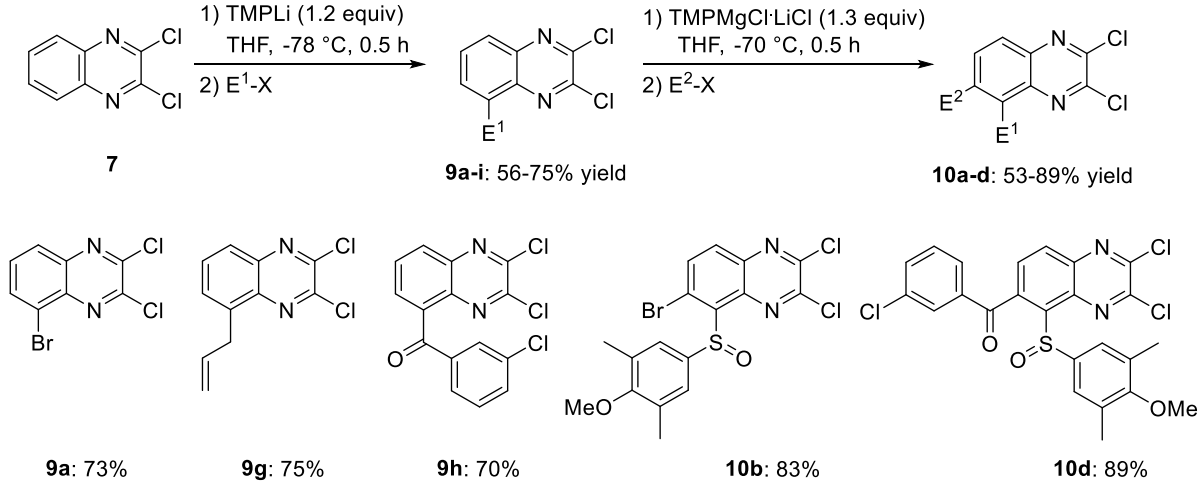
However, another ring enlargement could not be achieved. Neither the iodinated heterocycle **52a**, nor the brominated compound **52b** showed any reaction with dimercaptopyrazine under various conditions.

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.

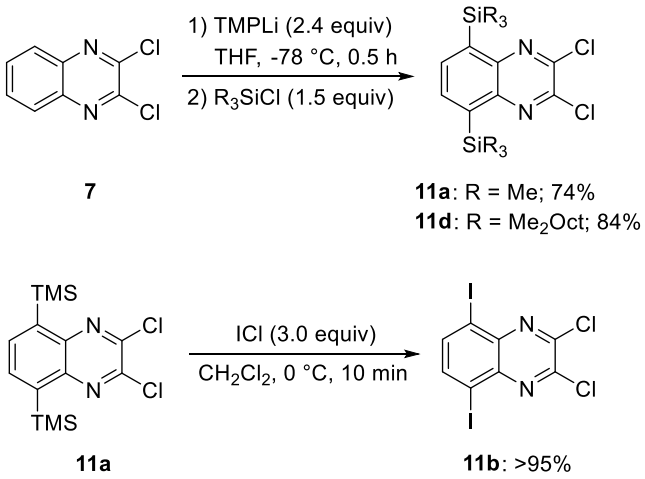
5.1 Functionalization of Quinoxalines Using TMP-Bases: Preparation of Tetracyclic Heterocycles with High Photoluminescence Quantum Yields

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·LiCl. Smooth reaction conditions allowed for the preparation of mono- and difunctionalized quinoxaline-derivatives (Scheme 64).



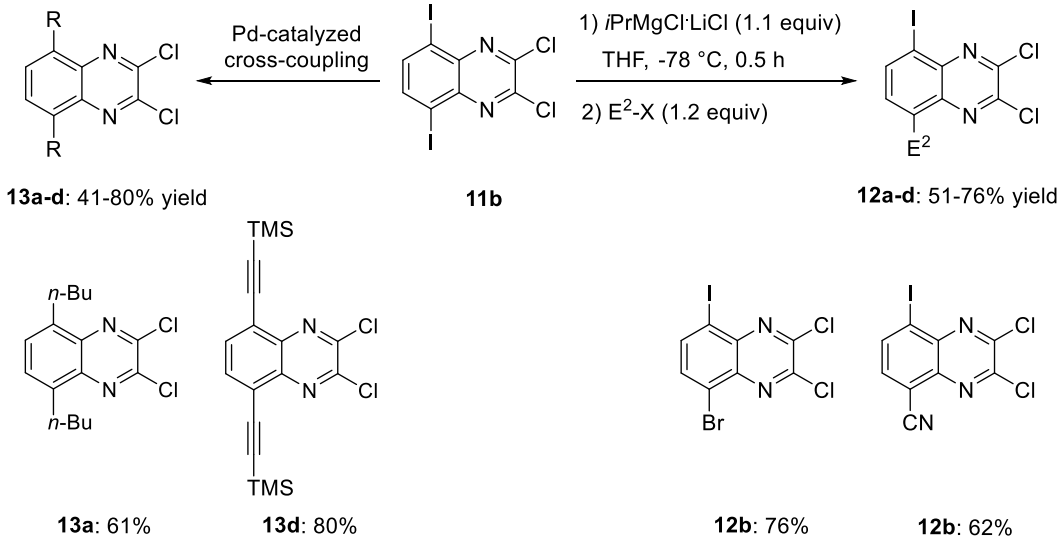
Scheme 64: Preparation of mono- and difunctionalized 2,3-dichloroquinoxalines.

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).



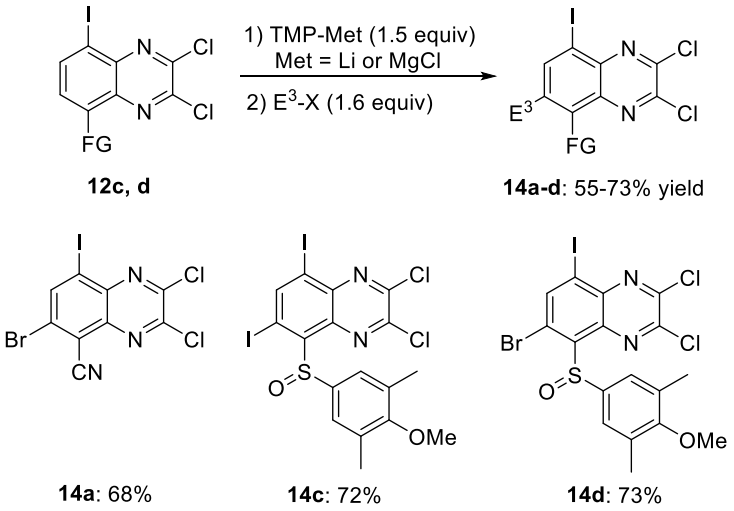
Scheme 65: Direct access to 5,8-difunctionalized quinoxalines.

Diiodoquinoxaline was subjected to I/Mg-exchange reactions using *i*PrMgCl·LiCl, as well as Pd-catalyzed cross-coupling reactions furnishing various 5,8-difunctionalized quinoxalines (Scheme 66).



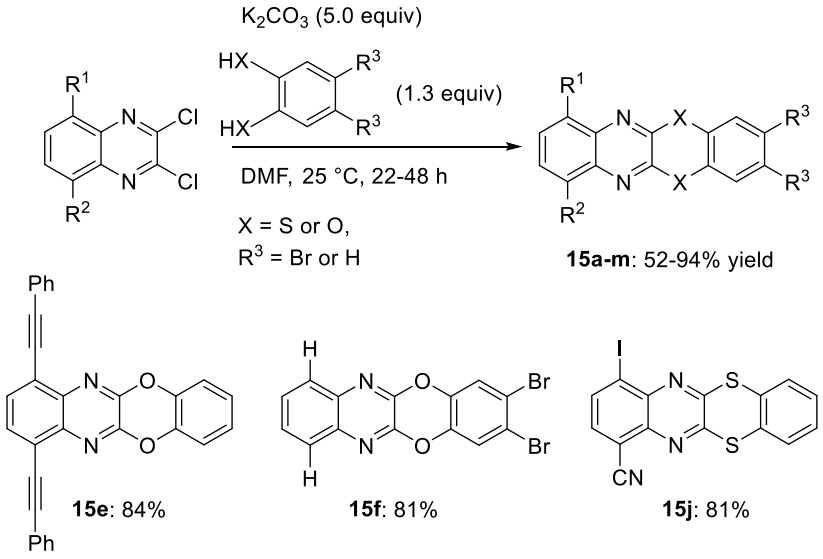
Scheme 66: Preparation of 5,8-disubstituted quinoxalines by I/Mg-exchange and Pd-catalyzed cross-couplings.

Another selective metalation of the corresponding difunctionalized derivatives using TMPLi in the presence of $ZnCl_2$ or using TMPMgCl·LiCl afforded 5,6,8-trifunctionalized quinoxalines in 55-73% yield (Scheme 67).



Scheme 67: Preparation of trifunctionalized quinoxalines.

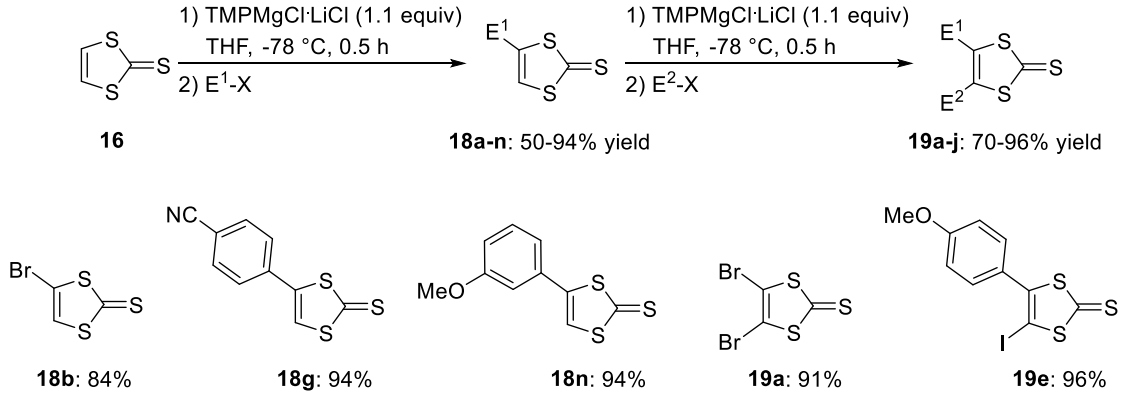
Furthermore, various anellation reactions with 1,2-benzenediol and benzene-1,2-dithiol were performed leading to a series of novel *O*- and *S*-heterocyclic tetracenes owning very high photoluminescence quantum yields (Scheme 68).



Scheme 68: Anellation reactions of functionalized 2,3-dichloroquinoxalines.

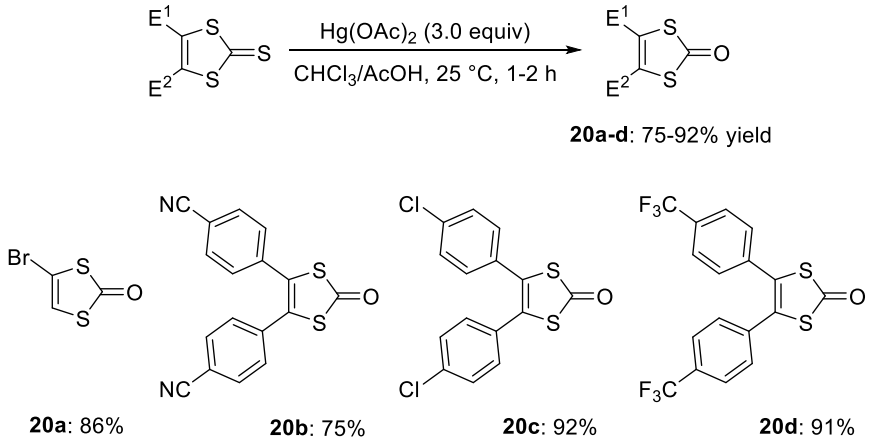
5.2 Selective Metalation of 1,3-Dithiole-2-thiones: An Effective Preparation of New Symmetrically and Nonsymmetrically Tetraarylated Tetrathiafulvalenes

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).



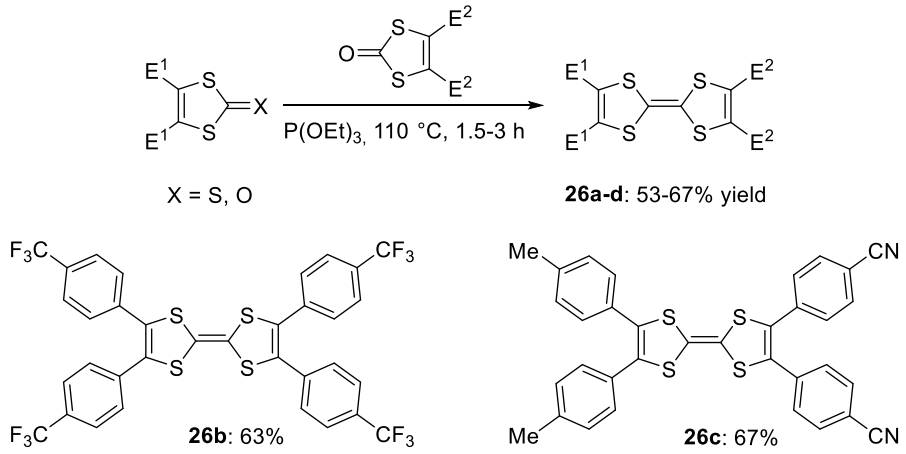
Scheme 69: Preparation of mono- and difunctionalized DTT-derivatives.

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).



Scheme 70: Preparation of oxygen analogs.

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).

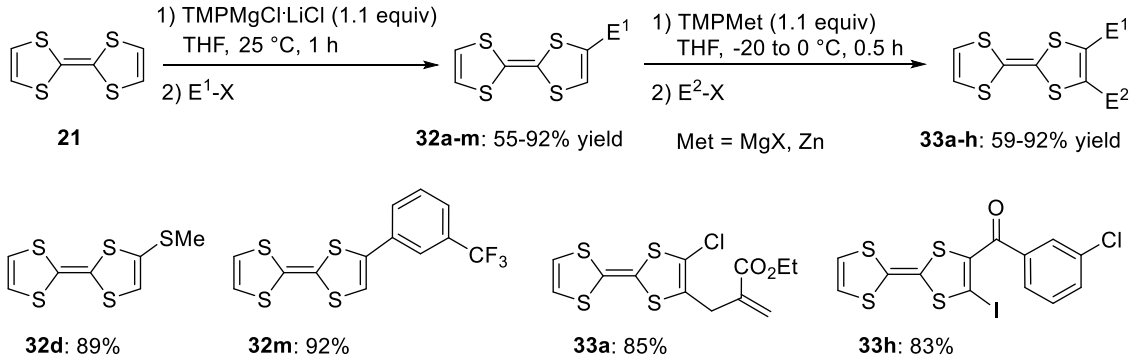


Scheme 71: Preparation of symmetrically and nonsymmetrically tetraarylated TTF-derivatives.

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

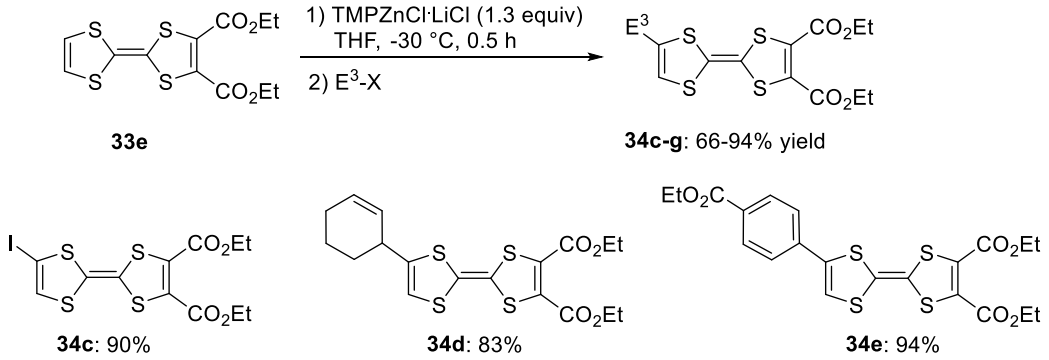
An efficient fully functionalization of TTF was achieved using TMP-bases under smooth reaction conditions.

TTF was magnesiated with TMPMgCl·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).



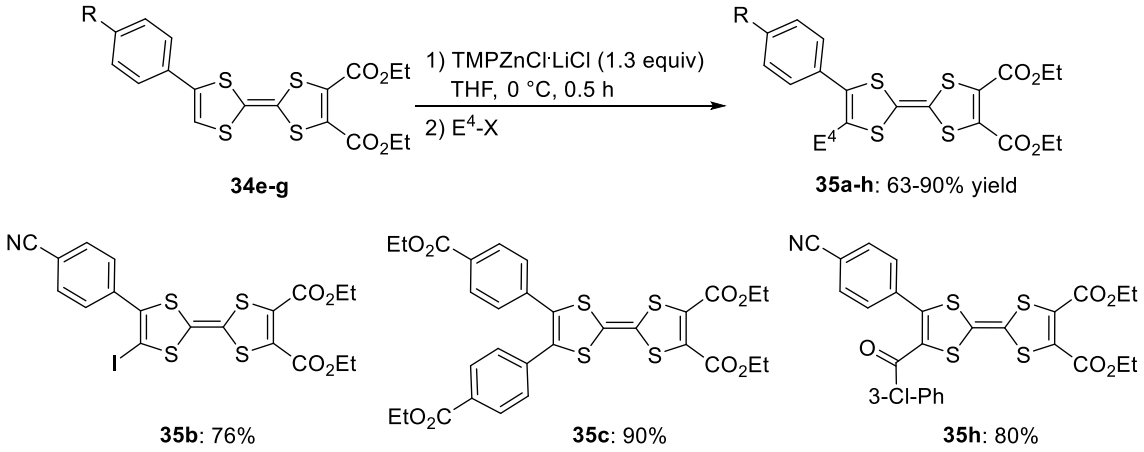
Scheme 72: Preparation of mono- and difunctionalized TTF-derivatives.

The diester-TTF was subjected to further metalation using TMPZnCl·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).



Scheme 73: Preparation of trifunctionalized TTF-derivatives.

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).

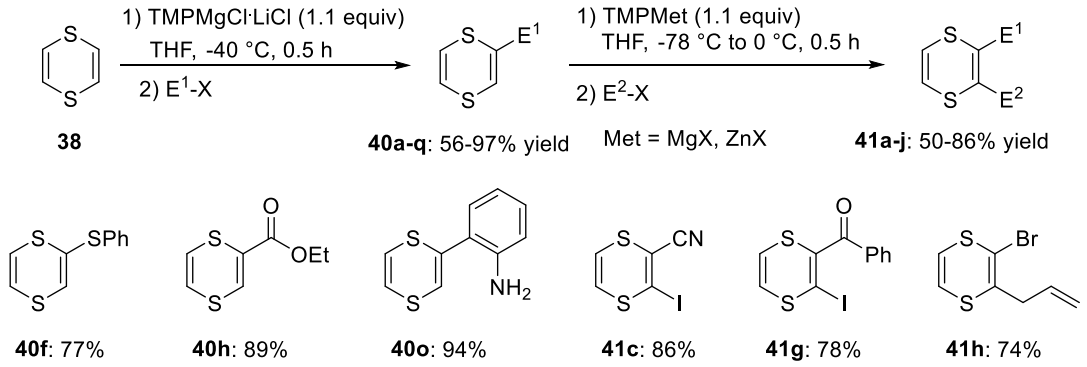


Scheme 74: Preparation of fully functionalized TTF-derivatives.

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.

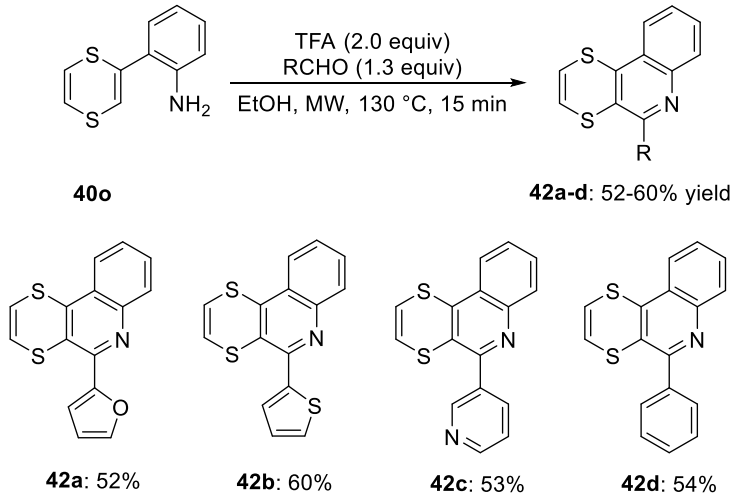
5.4 Selective Functionalization of 1,4-Dithiin Using TMP-Bases: Access to New Heterocycles

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).



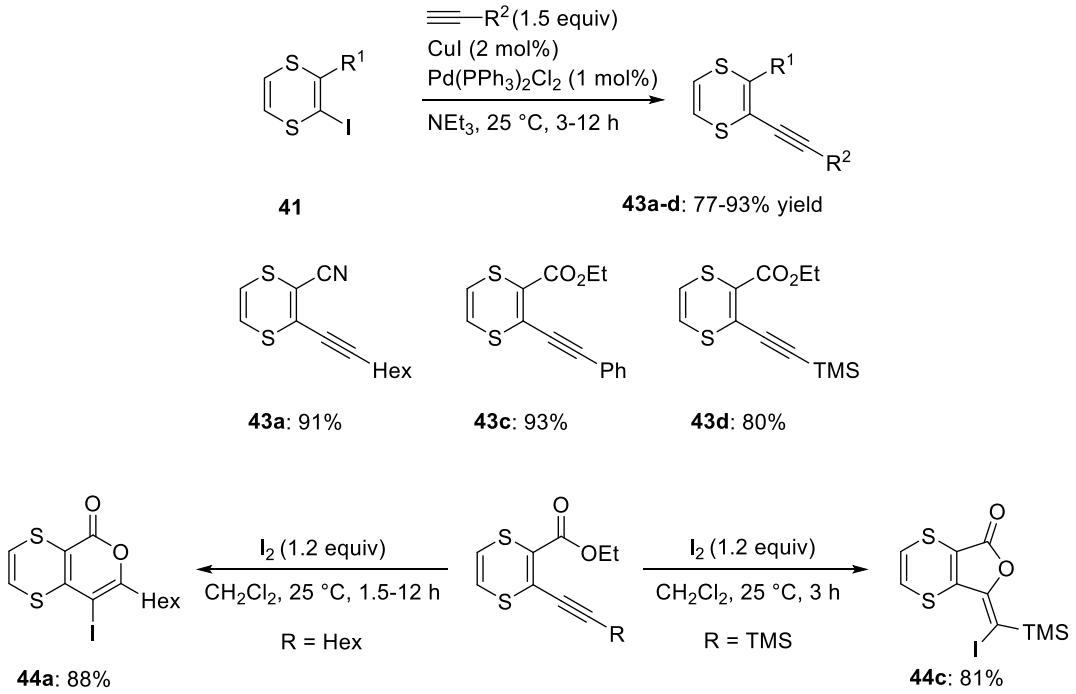
Scheme 75: Preparation of mono- and difunctionalized 1,4-dithiins.

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



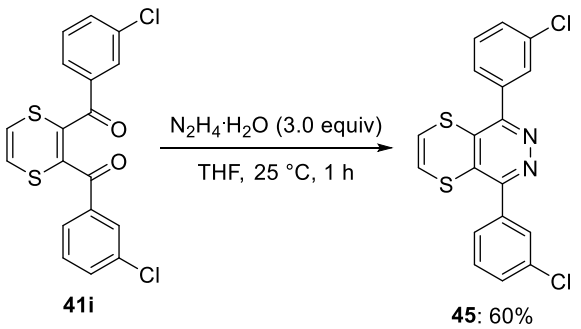
Scheme 76: Preparation of 1,4-dithiin-fused quinolines.

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).



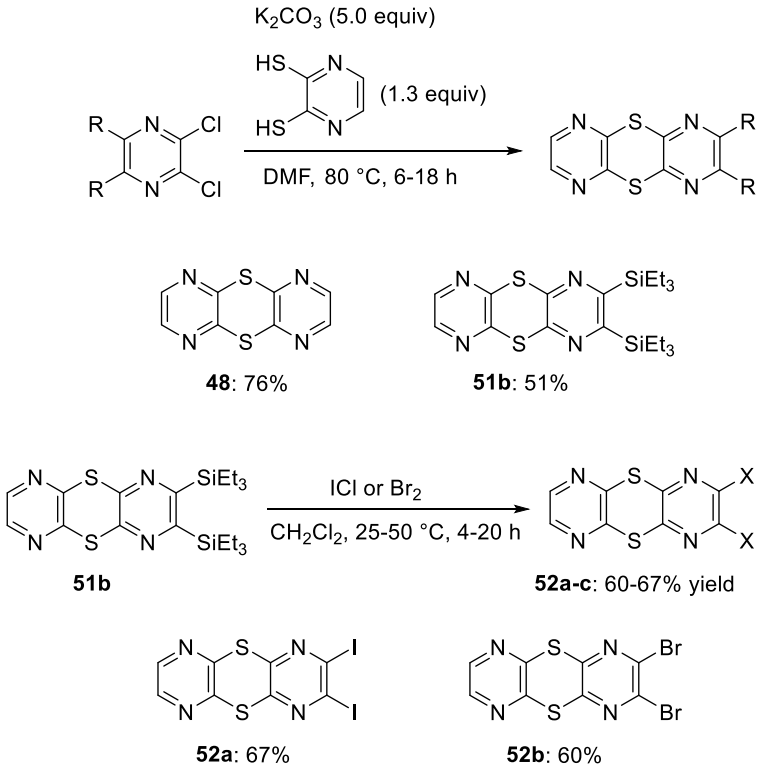
Scheme 77: Preparation of alkynylated 1,4-dithiin-derivatives followed by electrophilic cyclization.

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



Scheme 78: Preparation of a 1,4-dithiin-fused pyridazine.

The anellation of dichloropyrazines with dimercaptopyrazine 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_2Cl_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_2O 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.

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).

$MgCl_2$·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.

$ZnCl_2$ solution (1.0 M in THF) was prepared by drying $ZnCl_2$ (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).

***i*PrMgCl·LiCl** solution was purchased from Rockwood Lithium GmbH.

***n*BuLi** solution in hexane was purchased from Rockwood Lithium.

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

TMP_2Mg·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]

TMP_2Zn·2$MgCl_2$·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 I_2 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.

TMPMgCl·LiCl, **TMP_2Mg·2LiCl**, **TMPZnCl·LiCl** and **TMP_2Zn·2$MgCl_2$·2LiCl** 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 SiO_2 (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.
- $KMnO_4$ (3.0 g), 5 drops of conc. H_2SO_4 in water (300 mL)

Flash column chromatography was performed using SiO_2 (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 chromathography/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 4.9×10^{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 spectromenter at an incident photon flux of 1.6×10^{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 *i*PrMgCl·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). *i*PrMgCl·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. NH_4Cl solution.

Typical Procedure 4 for the metalation of 2,3-dichloro-8-iodoquinoxaline-5-carbonitrile (12c) with TMPLi (1) in the presence of $ZnCl_2$ (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). $ZnCl_2$ 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):

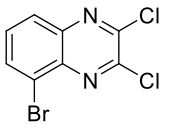
A dry and argon flushed *Schlenk*-flask was charged with a solution of 2,3-dichloro-5-iodo-8-((4-methoxy-3,5-dimethylphenyl)sulfinyl)quinoxaline (**12d**; 1.0 equiv) in dry THF (0.2 M). TMPMgCl·LiCl (**2**; 1.5 equiv, 1.12 M in THF) was added dropwise at 0 °C and the reaction mixture was stirred at this 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), K_2CO_3 (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. NH_4Cl solution using undecane as internal standard.

2.2 Preparation of Monofunctionalized 2,3-Dichloroquinoxalines

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



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. $MgCl_2$ 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. 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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column

chromatography on silica gel (*i*hexane/CH_2Cl_2, 5:1) yielding **9a** as colorless solid (203 mg, 73%).

m.p.: 134.7 – 136.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 8.10 (d, *J* = 7.4 Hz, 1H), 8.04 – 7.90 (m, 1H), 7.73 – 7.57 (m, 1H).

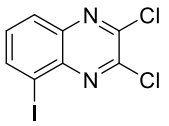
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 146.5, 146.4, 141.3, 138.7, 134.7, 131.4, 127.9, 122.6.

IR (cm^{-1}): $\tilde{\nu}$ = 3064, 3035, 1967, 1904, 1841, 1600, 1542, 1534, 1463, 1440, 1363, 1330, 1302, 1267, 1204, 1183, 1170, 1127, 1066, 1051, 1011, 984, 920, 903, 839, 811, 765, 695, 660, 640, 593, 554.

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 $C_8H_3BrCl_2N_2$ (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. $MgCl_2$ 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. 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. $Na_2S_2O_3$ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **9b** as yellow solid (208 mg, 64%).

m.p.: 129.8 – 131.7 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

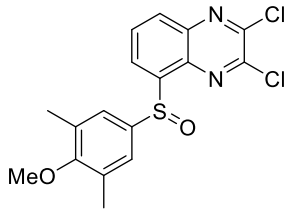
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 146.5, 141.5 (2C), 141.0, 140.6, 132.1, 128.9, 99.6.

IR (cm^{-1}): $\tilde{\nu}$ = 2948, 2896, 2847, 1586, 1538, 1458, 1436, 1289, 1265, 1200, 1166, 1121, 999, 977, 915, 894, 828, 807, 775, 692, 692, 654.

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).

HRMS for $C_8H_3Cl_2IN_2$ (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_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 2:1) yielding **9c** as colorless solid (229 mg, 60%).

m.p.: 169.9 – 175.0 °C (decomp.).

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/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).

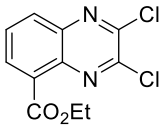
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 159.5, 146.4, 145.1, 143.7, 140.4, 138.7, 136.3, 132.2, 131.3, 130.0, 126.3, 126.2, 59.6, 16.2.

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.

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 $C_{17}H_{14}Cl_2N_2O_2S$ (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. $MgCl_2$ 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, 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **9d** as colorless solid (168 mg, 62%).

m.p.: 163.3 – 165.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

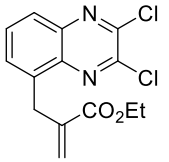
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 165.4, 146.3, 146.1, 140.4, 138.1, 132.3, 131.6, 130.6, 130.3, 61.9, 14.3.

IR (cm^{-1}): $\tilde{\nu}$ = 2990, 1984, 1716, 1598, 1569, 1463, 1449, 1368, 1333, 1291, 1267, 1196, 1173, 1123, 1076, 1037, 944, 871, 856, 833, 811, 778, 753, 702, 659, 642, 614, 607, 599, 581, 572, 567, 556.

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 $C_{11}H_8Cl_2N_2O_2$ (269.9963): found: 269.9964.

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. $ZnCl_2$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:2) yielding **9e** as colorless solid (212 mg, 68%).

m.p.: 43.9 – 47.5 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

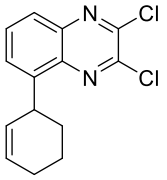
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 166.7, 145.2, 144.3, 140.9, 139.4, 138.9, 137.8, 131.2, 131.0, 127.4, 126.6, 60.8, 32.5, 14.1.

IR (cm^{-1}): $\tilde{\nu}$ = 3045, 2981, 2958, 2939, 2907, 1965, 1913, 1712, 1628, 1602, 1568, 1527, 1478, 1470, 1452, 1440, 1414, 1379, 1364, 1325, 1309, 1292, 1267, 1206, 1173, 1161, 1146, 1126, 1113, 1075, 1064, 1042, 1028, 998, 984, 968, 951, 922, 893, 882, 858, 835, 8820, 809, 775, 764, 755, 715, 699, 689, 681.

MS (70 eV, EI) *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 $C_{14}H_{12}Cl_2N_2O_2$ (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. $ZnCl_2$ 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. $CuCN{\cdot}2LiCl$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

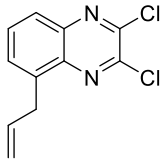
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 144.9, 144.1, 140.9, 138.9 (2C), 131.0, 129.6, 129.5, 129.2, 126.0, 35.0, 31.4, 25.1, 20.8.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{14}H_{12}N_2Cl_2$ (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. $ZnCl_2$ 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. $CuCN{\cdot}2LiCl$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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 **9g** as colorless solid (179 mg, 75%).

m.p.: 74.3 – 76.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

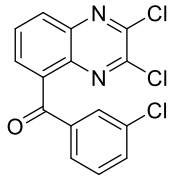
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 145.2, 144.3, 140.9, 139.2, 139.0, 136.2, 131.1, 130.6, 126.4, 116.8, 34.7.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 241 (8), 238 (45) [M^+], 225 (65), 223 (100), 140 (15), 115 (13), 85 (9), 43 (10).

HRMS for $C_{11}H_8Cl_2N_2$ (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. $ZnCl_2$ 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. $CuCN{\cdot}2LiCl$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 92:8) yielding **9h** as colorless solid (236 mg, 70%).

m.p.: 127.9 – 132.9 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

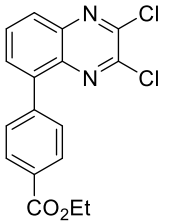
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 193.6, 146.5, 146.1, 140.2, 138.9, 138.2, 137.5, 134.9, 133.6, 130.6, 130.6, 130.4, 129.8, 129.8, 128.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{15}H_7Cl_3N_2O$ (335.9624): found: 335.9613.

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. $ZnCl_2$ 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. $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **9i** as colorless solid (229 mg, 66%).

m.p.: 156.1 – 158.4 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

^{13}C-NMR (75 MHz, $CDCl_3$) *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.

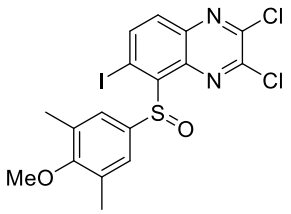
IR (cm^{-1}): $\tilde{\nu}$ = 2983, 1702, 1608, 1595, 1566, 1538, 1470, 1450, 1404, 1363, 1312, 1269, 1182, 1157, 1182, 1157, 1128, 1104, 1026, 996, 863, 822, 768, 707, 699, 654.

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 $C_{17}H_{12}Cl_2N_2O_2$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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.).

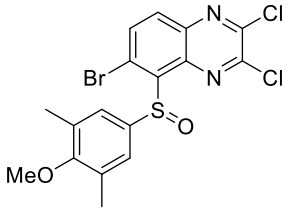
^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 8.21 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.60 (s, 2H), 3.68 (s, 3H), 2.27 (s, 6H).

^{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 $C_{17}H_{14}Cl_2IN_2O_2S$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **10b** as yellow solid (381 mg, 83%).

m.p.: 270.9 – 275.9 °C (decomp.).

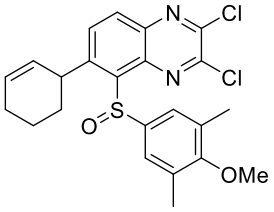
^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 7.99 – 7.94 (m, 1H), 7.94 – 7.89 (m, 1H), 7.59 (s, 2H), 3.72 (s, 3H), 2.30 (s, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) *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}): $\tilde{\nu}$ = 2923, 1706, 1595, 1468, 1376, 1307, 1271, 1216, 1133, 1097, 1006, 967, 915, 819, 783, 735.

HRMS (ESI) for $C_{17}H_{14}BrCl_2N_2O_2S$ (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. $ZnCl_2$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **10c** as yellow solid (381 mg, 83%).

m.p.: 186.5 – 191.6 °C.

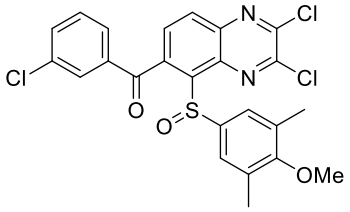
^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 8.00 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.38 (s, 2H), 6.06 – 5.91 (m, 1H), 5.43 (d, *J* = 9.8 Hz, 1H), 5.08 – 4.89 (m, 1H), 3.69 (s, 3H), 2.53 – 1.55 (m, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) *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}): $\tilde{\nu}$ = 2930, 1693, 1595, 1475, 1378, 1273, 1219, 1178, 1131, 1095, 1006, 822, 720, 662.

HRMS (ESI) for $C_{23}H_{23}Cl_2N_2O_2S$ (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. $ZnCl_2$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 6:1) yielding **10d** as yellow solid (465 mg, 89%).

m.p.: 189.5 – 192.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

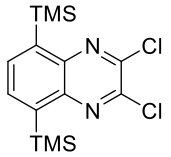
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 193.6, 159.7, 147.4, 146.0, 142.5, 140.5, 140.3, 139.0, 137.5, 136.5, 134.9, 133.2, 132.2, 130.5, 130.1, 129.9, 129.3, 127.4, 127.3, 59.6, 16.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{24}H_{17}Cl_3N_2O_3S$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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%).

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.89 (s, 2H), 0.44 (s, 18H).

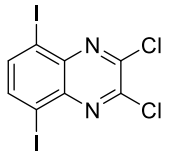
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 144.6, 143.0, 142.5, 136.6, -0.5.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 342 (1) [M^+], 331 (14), 330 (14), 329 (71), 328 (22), 327 (100).

HRMS for $C_{14}H_{20}Cl_2N_2Si_2$ (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 CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was stirred for 10 min and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_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 **11b** as yellow solid (450 mg, quantitative).

m.p.: 178.0 – 183.5 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 8.05 (s, 2H).

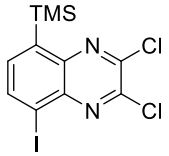
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 147.7, 142.0, 140.9, 100.3.

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

HRMS for $C_8H_2Cl_2I_2N_2$ (449.7684): found: 449.7678.

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



ICl (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_2Cl_2 (2 mL) at 0 °C. The reaction mixture was stirred for 10 min and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_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, $CDCl_3$) *δ*/ppm = 8.31 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 0.43 (s, 9H).

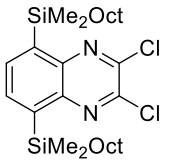
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 145.8, 144.8, 144.5, 142.7, 141.0, 140.9, 138.0, 101.0, -0.6.

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, EI) *m/z* (%) = 396 (7) [M^+], 385 (12), 384 (10), 383 (67), 382 (16), 381 (100).

HRMS for $C_{11}H_{11}Cl_2IN_2Si$ (395.9113): found: 395.9101.

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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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%).

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.87 (s, 2H), 1.41 – 1.14 (m, 24H), 1.02 – 0.82 (m, 10H), 0.40 (s, 12H).

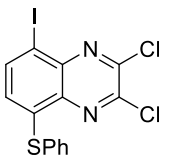
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 145.0, 143.3, 142.4, 137.4, 77.9, 34.0, 32.3, 29.7, 24.4, 23.1, 16.3, 14.5, -1.8.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{28}H_{48}Cl_2N_2Si_2$ (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). *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. *S*-Phenyl benzenethiosulfonate (300 mg,

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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 9:1) yielding **12a** as yellow solid (219 mg, 51%).

m.p.: 142.6 – 146.5 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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, 1 H).

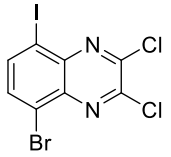
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 147.1, 145.4, 141.7, 141.0, 140.9, 137.3, 135.7, 130.1, 129.9, 129.8, 127.8, 93.8.

IR (cm^{-1}): $\tilde{\nu}$ = 1560, 1526, 1474, 1440, 1359, 1268, 1259, 1192, 1169, 1099, 1014, 1000, 915, 838, 826, 822, 747, 705, 688, 673.

MS (70 eV, EI) *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 $C_{14}H_7Cl_2IN_2S$ (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). *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. 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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 95:5) yielding **12b** as yellowish solid (305 mg, 76%).

m.p.: 172.4 – 175.9 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 8.21 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H).

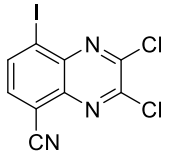
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 147.7, 147.6, 141.6, 141.3, 138.7, 135.3, 123.5, 98.8.

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 $C_8H_2BrCl_2IN_2$ (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_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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, $CDCl_3$) *δ*/ppm = 8.47 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H).

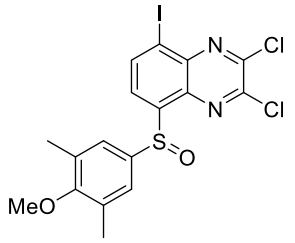
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 149.3, 148.9, 140.9, 140.9, 139.5, 136.5, 114.7, 112.6, 107.1.

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 $C_9H_2Cl_2IN_3$ (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). *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. 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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 5:1) yielding **12d** as yellow solid (309 mg, 61%).

m.p.: 234.1 – 238.1 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

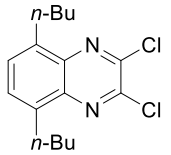
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 159.6, 147.5, 146.3, 144.6, 141.4, 140.8, 138.3, 135.9, 132.3, 127.1, 126.2, 102.3, 59.6, 16.2.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 506 (60) [M^+], 460 (69), 458 (100), 443 (49), 183 (61), 167 (55), 151 (51).

HRMS for $C_{17}H_{13}Cl_2IN_2O_2S$ (505.9119): found: 505.9116.

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



$ZnCl_2$ solution (2.2 mL, 2.2 mmol, 1.0 M in THF) was added dropwise to *n*BuMgCl (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 *n*BuZnCl solution was added dropwise to a solution of 2,3-dichloro-5,8-diiodoquinoxaline (**11b**; 451 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (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 Na_2SO_4. 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.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

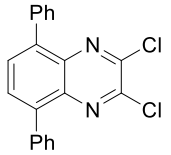
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 143.5, 139.8, 138.9, 130.1, 32.9, 30.3, 22.6, 14.0.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{16}H_{20}Cl_2N_2$ (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_2CO_3 (420 mg, 3.0 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) in degassed THF (10 mL) and H_2O (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_2Cl_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, $CDCl_3$) *δ*/ppm = 7.93 (s, 2H), 7.75 – 7.69 (m, 4H), 7.59 – 7.45 (m, 6H).

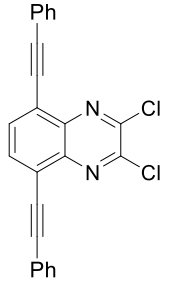
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 144.6, 139.2, 138.8, 137.2, 131.3, 130.5, 128.2, 128.1.

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 $C_{20}H_{12}Cl_2N_2$ (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 CuI (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.

NH_4Cl (100 mL) and extracted with Et_2O (2 x 100 mL). The organic layer was dried over anhydrous $MgSO_4$, and after filtration, the solvents were removed *in vacuo*. Purification by crystallisation from a mixture of CH_2Cl_2 and Et_2O yielded **13c** as pale yellow crystals (792 mg, 66%).

m.p.: 176.1 – 179.2 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.97 (s, 2H), 7.71 – 7.66 (m, 4H), 7.44 – 7.39 (m, 6H).

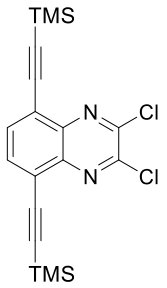
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 146.5, 140.9, 134.0, 132.0, 129.1, 128.4, 122.9, 122.7, 98.5, 85.3.

IR (cm^{-1}): $\tilde{\nu}$ = 3056, 2209, 1556, 1534, 1492, 1270, 1260, 1170, 1123, 1102, 1058, 999, 938, 915, 843, 720, 684.

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

HRMS for $C_{24}H_{12}Cl_2N_2$ (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), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) and CuI (100 mg, 0.5 mmol) in degassed NEt_3 (20 mL) and benzene (40 mL) was stirred at 25 °C for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl (100 mL) and extracted with Et_2O (2 x 100 mL). The organic fraction was dried over anhydrous $MgSO_4$, and after filtration, the solvents were removed *in vacuo*. Purification by flash column chromatography on silica gel (*i*hexane/EtOAc 99:1) yielded **13d** as pale solid (1.77 g, 80%).

m.p.: 156.4 – 159.7 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.86 (s, 2H), 0.34 (s, 18H).

^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 146.6, 140.8, 134.6, 122.9, 104.8, 99.8, -0.2.

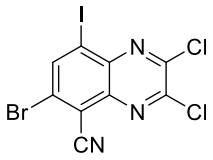
IR (cm^{-1}): $\tilde{\nu}$ = 3075, 2953, 2918, 2850, 1591, 1477, 1467, 1455, 1410, 1371, 1314, 1279, 1242, 1238, 1209, 1172, 1099, 973, 869, 834, 808, 768, 719.

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 $C_{18}H_{20}Cl_2N_2Si_2$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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).

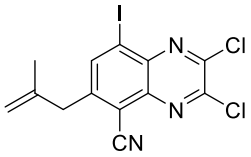
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 149.9, 148.8, 144.3, 140.1, 139.8, 130.8, 115.2, 113.7, 107.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_9HBrCl_2IN_3$ (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). $ZnCl_2$ 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. $CuCN{\cdot}2LiCl$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **14b** as yellow solid (224 mg, 55%).

m.p.: 143.6 – 148.3 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 8.34 (s, 1H), 5.01 (s, 1H), 4.80 (s, 1H), 3.77 (s, 2H), 1.77 (s, 3H).

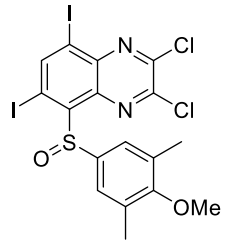
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 149.9, 149.0, 148.0, 142.6, 141.4, 139.7, 139.6, 115.0, 114.0, 112.2, 106.2, 42.8, 22.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 403 (13) [M^+], 280 (14), 179 (11), 278 (73), 277 (18), 276 (100), 127 (24), 41 (26).

HRMS for $C_{13}H_8Cl_2IN_3$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **14c** as yellow solid (456 mg, 72%).

m.p.: 200.0 – 203.7 °C.

^{1}H-NMR (400 MHz, benzene-d_6) δ/ppm = 8.39 (s, 1H), 7.88 (s, 2H), 3.21 (s, 3H), 2.13 (s, 6H).

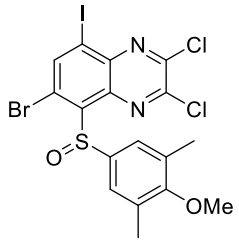
^{13}C-NMR (101 MHz, benzene-d_6) δ/ppm = 159.9, 151.9, 147.2, 145.9, 144.8, 141.9, 139.6, 137.4, 132.4, 126.7, 105.6, 99.8, 59.6, 16.6.

IR (cm^{-1}): $\tilde{\nu}$ = 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).

HRMS for $C_{17}H_{12}Cl_2I_2N_2O_2S$ (631.8086): found: 631.8076.

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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 5:1) yielding **14d** as yellow solid (428 mg, 73%).

m.p.: 113.8 – 116.0 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 8.56 (s, 1H), 7.56 (s, 2H), 3.71 (s, 3H), 2.30 (s, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 159.2, 147.4, 146.8, 145.7, 140.8, 140.6, 137.6, 136.8, 132.0, 126.9, 125.5, 104.8, 59.7, 16.3.

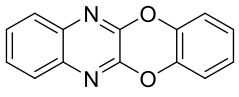
IR (cm^{-1}): $\tilde{\nu}$ = 2922, 1692, 1552, 1514, 1471, 1428, 1412, 1359, 1268, 1216, 1175, 1122, 1094, 1069, 1012, 874, 759, 723, 667.

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 $C_{17}H_{12}BrCl_2IN_2O_2S$ (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), 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 22 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:1) yielding **15a** as colorless solid (221 mg, 94%).

m.p.: 264.8 – 268.2 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.89 – 7.71 (m, 2H), 7.66 – 7.47 (m, 2H), 7.22 – 6.95 (m, 4H).

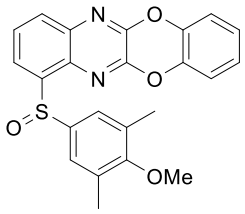
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 144.7, 140.4, 139.1, 128.9, 127.3, 125.2, 117.2.

IR (cm^{-1}): $\tilde{\nu}$ = 3056, 3025, 2923, 2852, 2149, 2091, 2046, 1986, 1965, 1938, 1907, 1827, 1790, 1746, 1610, 1575, 1520, 1467, 1457, 1450, 1424, 1374, 1341, 1331, 1321, 1286, 1270, 1219, 1192, 1170, 1151, 1145, 1140, 1120, 1107, 1029, 1016, 955, 938, 925, 871, 864, 854, 779, 760, 749, 714.

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

HRMS for $C_{14}H_8N_2O_2$ (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_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 48 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (CH_2Cl_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).

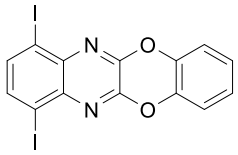
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 159.3, 145.2, 144.4, 142.1, 140.1, 140.1, 139.4, 139.0, 135.2, 132.1, 129.3, 128.9, 126.1, 125.6, 125.5, 124.2, 117.2, 117.2, 59.6, 16.2.

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 $C_{23}H_{18}N_2O_4S$ (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_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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:2) yielding **15c** as colorless solid (344 mg, 70%).

m.p.: 299.4 – 301.4 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.84 (s, 2H), 7.23 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H).

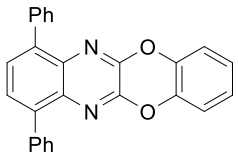
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 146.3, 140.1, 139.8, 139.5, 125.7, 117.4, 98.9.

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, EI) *m/z* (%) = 489 (25), 488 (100) [M^+], 244 (13), 235 (11), 234 (78).

HRMS for $C_{14}H_6I_2N_2O_2$ (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_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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by crystallisation from CH_2Cl_2 yielding **15d** as colorless solid (241 mg, 62%).

m.p.: > 300 °C.

^{1}H-NMR (400 MHz, 80 °C, DMSO-d_6) δ/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).

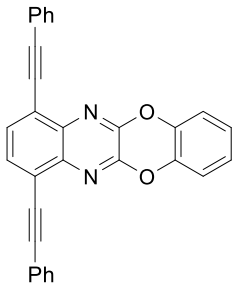
^{13}C-NMR: The low solubility and rapid precipitation of this compound frustrated attempts at collecting a ^{13}C spectrum.

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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by crystallisation from CH_2Cl_2 yielding **15e** as pale yellow solid (367 mg, 84%).

m.p.: 279.0 – 281.4 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ/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).

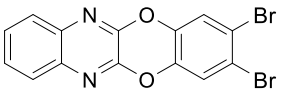
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 145.3, 140.4, 139.6, 132.3, 131.9, 128.7, 128.3, 125.4, 123.0, 121.9, 117.3, 97.1, 85.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{30}H_{16}N_2O_2$ (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_2CO_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 °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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:1) yielding **15f** as colorless solid (318 mg, 81%).

m.p.: 274.5 – 276.2 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 7.84 (dd, *J* = 6.2, 3.4 Hz, 2H), 7.64 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.40 (s, 2H).

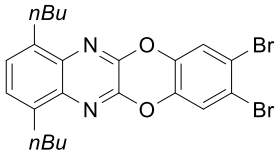
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 143.5, 140.0, 139.1, 129.5, 127.5, 121.6, 119.8.

IR (cm^{-1}): $\tilde{\nu}$ = 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).

HRMS for $C_{14}H_6Br_2N_2O_2$ (391.8796): found: 391.8797.

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), K_2CO_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 °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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 6:1) yielding **15g** as colorless solid (264 mg, 52%).

m.p.: 195.3 – 198.4 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

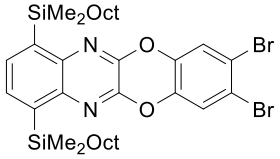
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 142.0, 140.3, 138.1, 138.0, 128.6, 121.5, 119.4, 32.8, 30.5, 22.6, 14.1.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{22}H_{22}Br_2N_2O_2$ (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), K_2CO_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 °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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 6:1) yielding **15h** as colorless oil (557 mg, 73%).

^{1}H-NMR (300 MHz, $CDCl_3$) *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, *J* = 7.0 Hz, 6H), 0.40 (s, 12H).

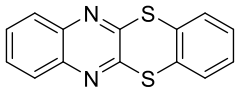
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 143.5, 141.8, 140.9, 140.7, 135.4, 121.8, 119.3, 33.8, 32.2, 29.5, 29.5, 24.2, 22.9, 16.1, 14.3, -1.9.

IR (cm^{-1}): $\tilde{\nu}$ = 3074, 2953, 2918, 2850, 1591, 1477, 1455, 1464, 1415, 1370, 1314, 1278, 1268, 1237, 1226, 1209, 1172, 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 $C_{34}H_{50}Br_2N_2O_2Si_2$ (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), K_2CO_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 22 h. The reaction mixture was quenched with water (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:2) yielding **15i** as yellow solid (144 mg, 54%).

m.p.: 165.8 – 170.2 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

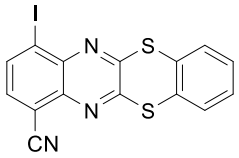
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 152.3 (2C), 140.7 (2C), 131.5 (2C), 130.1 (2C), 128.8 (2C), 128.3 (4C).

IR (cm^{-1}): $\tilde{\nu}$ = 2923, 2852, 1739, 1563, 1553, 1508, 1475, 1466, 1453, 1419, 1334, 1257, 1182, 1132, 1112, 1049, 1010, 935, 887, 859, 787, 758, 736, 708, 660.

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

HRMS for $C_{14}H_8N_2S_2$ (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), K_2CO_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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:1) yielding **15j** as orange solid (340 mg, 81%).

m.p.: 273.8 – 280.2 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

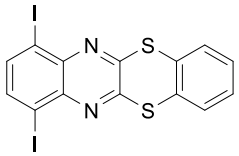
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 156.8, 156.3, 140.8, 140.1, 139.4, 135.2, 130.0, 130.0, 128.8, 128.8, 128.7, 128.7, 115.4, 112.4, 108.0.

IR (cm^{-1}): $\tilde{\nu}$ = 3050, 2226, 1908, 1567, 1545, 1505, 1453, 1423, 1354, 1259, 1173, 1110, 1063, 973, 889, 837, 798, 740, 711, 701, 658.

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

HRMS for $C_{15}H_6IN_3S_2$ (418.9048): found: 418.9043.

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



According to **TP 6**, a suspension of 2,3-dichloro-5,8-diiodoquinoxaline (**11b**; 451 mg, 1.0 mmol), K_2CO_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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 5:1) yielding **15k** as yellow solid (453 mg, 87%).

m.p.: 248.6 – 253.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

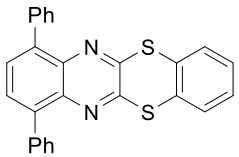
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 155.1, 141.0, 140.8, 130.7, 128.7, 128.6, 101.5.

IR (cm^{-1}): $\tilde{\nu}$ = 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.

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

HRMS for $C_{14}H_6I_2N_2S_2$ (519.8062): found: 519.8061.

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



According to **TP 6**, a suspension of 2,3-dichloro-5,8-diphenylquinoxaline (**13b**; 351 mg, 1.0 mmol), K_2CO_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_2SO_4. After filtration, the

solvents were evaporated *in vacuo*. The crude product was purified by crystallisation from CH_2Cl_2 yielding **15l** 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).

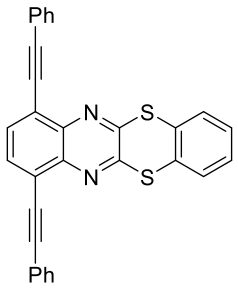
^{13}C-NMR: The low solubility and rapid precipitation of this compound frustrated attempts at collecting a ^{13}C spectrum.

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, EI) *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 $C_{26}H_{16}N_2S_2$ (420.0755): found: 420.0751.

Synthesis of 7,10-bis(phenylethynyl)benzo[5,6][1,4]dithiino[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_2CO_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_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by crystallisation from CH_2Cl_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).

^{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 $C_{30}H_{16}N_2S_2$ (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):

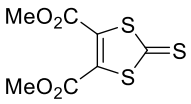
According to the literature,[20b] the corresponding DTT-derivative (1.0 equiv) was dissolved in $CHCl_3$ (0.05 M) and conc. AcOH (0.16 M). $Hg(OAc)_2$ (3.0 equiv) was added portion wise at 25 °C and the reaction mixture was stirred at this temperature for the indicated time. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq. NH_4Cl solution.

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

According to the literature,[20b] the corresponding thioketone (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. NH_4Cl solution.

3.2 Preparation of Starting Material

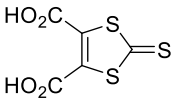
Synthesis of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (24)



According to the literature,[57] 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 (*i*hexane/EtOAc, 7:1) yielding **24** as yellow solid (34.2 g, 91%).

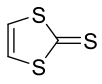
^{1}H-NMR (200 MHz, $CDCl_3$) *δ*/ppm = 3.91 (s, 6H).

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



According to the literature,[57] 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 $MgSO_4$ 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)



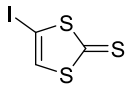
According to the literature,[57] a solution of 2-thioxo-1,3-dithiole-4,5-dicarboxylic acid (**25**; 8.45 g, 38.0 mmol) in pyridine (55 mL) was refluxed for 3 h and was then allowed to cool to 25 °C. After removing the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **16** as yellow solid (4.44 g, 87%).

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.11 (s, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 213.3, 129.2.

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. $Na_2S_2O_3$ solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **18a** as brownish solid (1.65 g, 79%).

m.p.: 105.7 – 108.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 7.21 (s, 1H).

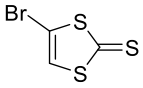
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 215.1, 133.8, 69.9.

IR (cm^{-1}): $\tilde{\nu}$ = 3066, 2922, 2852, 2358, 2064, 1746, 1519, 1485, 1463, 1378, 1184, 1045, 1015, 919, 885, 758, 645, 566, 555.

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

HRMS for C_3HIS_3 (259.8285): found: 259.8275.

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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **18b** as yellow solid (90 mg, 84%).

m.p.: 61.8 – 63.5 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.01 (s, 1H).

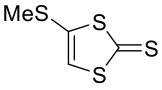
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 211.8, 127.4, 106.2.

IR (cm^{-1}): $\tilde{\nu}$ = 3071, 1503, 1182, 1047, 1012, 904, 881, 806, 765, 650.

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

HRMS for C_3HBrS_3 (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. NH_4Cl solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product

was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **18c** as brownish solid (1.08 g, 75%).

m.p.: 73.3 – 75.1 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 6.91 (s, 1H), 2.51 (s, 3H).

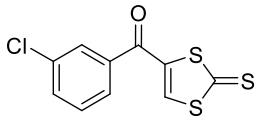
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 213.5, 138.5, 127.2, 19.8.

IR (cm^{-1}): $\tilde{\nu}$ = 3058, 2976, 2909, 1772, 1630, 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 $C_4H_4S_4$ (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. $ZnCl_2$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 9:1) yielding **18d** as brown oil (84 mg, 62%).

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

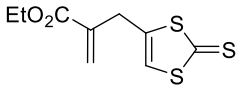
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 210.6, 182.5, 145.3, 139.6, 137.2, 135.3, 133.4, 130.3, 128.8, 126.9.

IR (cm^{-1}): $\tilde{\nu}$ = 3061, 2920, 2852, 1628, 1591, 1568, 1511, 1422, 1291, 1280, 1266, 1210, 1119, 1075, 1053, 1023, 998, 987, 898, 881, 837, 825, 805, 799, 727, 707, 696, 678, 649, 563.

MS (70 eV, EI) *m/z* (%) = 274 (26), 272 (58) [M^+], 196 (21), 141 (30), 139 (100), 111 (53), 75 (29).

HRMS for $C_{10}H_5OClS_3$ (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. $ZnCl_2$ 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. 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)acrylate[38] (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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:1) yielding **18e** as yellow oil (124 mg, 50%).

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

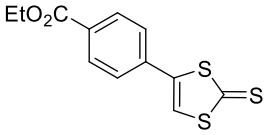
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 213.5, 165.6, 144.2, 136.5, 128.1, 124.3, 61.4, 33.5, 14.1.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_9H_{10}O_2S_3$ (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_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

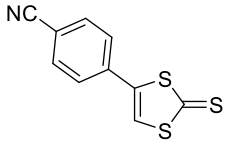
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 211.6, 165.5, 144.8, 134.8, 131.3, 130.6, 126.3, 123.7, 61.4, 14.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 283 (13), 282 (100) [M^+], 237 (10), 178 (18), 161 (56), 89 (20).

HRMS for $C_{12}H_{10}O_2S_3$ (281.9843): found: 281.9836.

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. $ZnCl_2$ 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-iodobenzonitrile (1.83 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 18 h and was then quenched with sat. aq. NH_4Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:2) yielding **18g** as yellow solid (1.77 g, 94%).

m.p.: 195.8 – 198.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.74 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.28 (s, 1H).

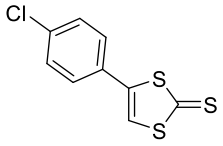
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 210.9, 143.4, 134.9, 133.2, 127.0, 124.8, 117.9, 113.2.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 237 (16), 236 (18) [$M+H^+$], 160 (12), 159 (100), 146 (11), 115 (12), 76 (22).

HRMS for $C_{10}H_6NS_3$ (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. $ZnCl_2$ 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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **18h** as yellow solid (263 mg, 67%).

m.p.: 91.4 – 97.9 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.46 – 7.30 (m, 4H), 7.11 (s, 1H).

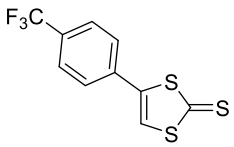
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 211.7, 144.7, 135.7, 129.6, 129.5, 127.7, 122.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 245 (49), 245 (14), 244 (100) [M^+], 170 (40), 155 (13), 136 (16), 89 (31), 75 (10).

HRMS for $C_9H_5ClS_3$ (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. $ZnCl_2$ 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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **18i** as yellow solid (287 mg, 66%).

m.p.: 121.5 – 123.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm = 7.71 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.24 (s, 1H).

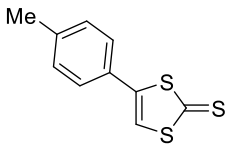
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 211.4, 144.1, 134.2, 131.5 (q, J = 32.8 Hz), 126.8, 126.4 (q, J = 3.9 Hz), 123.9, 123.6 (q, J = 272.4 Hz).

IR (cm^{-1}): $\tilde{\nu}$ = 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, 729, 692, 650, 628, 594.

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

HRMS for $C_{10}H_5F_3S_3$ (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. $ZnCl_2$ 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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in*

vacuo. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **18j** as yellow solid (284 mg, 79%).

m.p.: 91.4 – 97.9 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.36 – 7.28 (m, 2H), 7.28 – 7.19 (m, 2H), 7.06 (s, 1H), 2.40 (s, 3H).

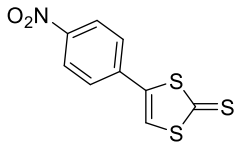
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 212.4, 146.5, 140.0, 130.0, 128.3, 126.3, 121.0, 21.3.

IR (cm^{-1}): $\tilde{\nu}$ = 3043, 3020, 2912, 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 $C_{10}H_8S_3$ (223.9788): found: 223.9766.

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



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. $ZnCl_2$ 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 1-iodo-4-nitrobenzene (1.99 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_4Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:1) yielding **18k** as brownish solid (1.57 g, 77%).

m.p.: 209.0 – 210.6 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 8.32 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.33 (s, 1H).

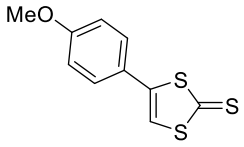
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 210.7, 148.0, 142.9, 136.6, 127.2, 125.4, 124.8.

IR (cm^{-1}): $\tilde{\nu}$ = 3118, 3079, 3062, 3034, 3004, 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, 1010, 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 $C_9H_5O_2NS_3$ (254.9482): found: 254.9479.

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



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. $ZnCl_2$ 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_4Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **18l** as yellow solid (1.34 g, 70%).

m.p.: 104.2 – 106.9 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.35 (d, *J* = 8.7 Hz, 2H), 7.00 – 6.90 (m, 3H), 3.85 (s, 3H).

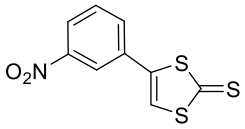
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 212.3, 160.7, 146.2, 127.9, 123.7, 120.0, 114.7, 55.4.

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.

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

HRMS for $C_{10}H_8OS_3$ (239.9737): found: 239.9724.

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



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 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_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:2) yielding **18m** as yellow solid (122 mg, 60%).

m.p.: 183.4 – 186.3 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

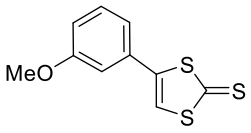
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 210.8, 148.8, 142.7, 132.5, 132.1, 130.6, 124.5, 124.1, 121.2.

IR (cm^{-1}): $\tilde{\nu}$ = 3082, 3051, 3028, 2847, 2360, 2335, 2087, 1982, 1925, 1815, 1747, 1577, 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, EI) *m/z* (%) = 257 (11), 255 (100) [M^+], 225 (19), 166 (11), 149 (12), 89 (31), 76 (12), 43 (23).

HRMS for $C_9H_5O_2NS_3$ (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. $ZnCl_2$ 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 3-iodoanisole (187 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 18 h and was then quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **18n** as yellow solid (181 mg, 94%).

m.p.: 94.3 – 97.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 212.1, 160.1, 146.0, 132.1, 130.4, 122.1, 118.9, 115.0, 112.3, 55.4.

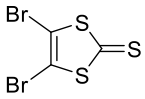
IR (cm^{-1}): $\tilde{\nu}$ = 3067, 3039, 2991, 2959, 2928, 2828, 2360, 2331, 2088, 1937, 1732, 1600, 1575, 1531, 1489, 1462, 1450, 1423, 1326, 1290, 1272, 1261, 1223, 1199, 1165, 1092, 1054, 1034, 960, 888, 853, 788, 774, 757, 686, 677, 622, 610, 563.

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

HRMS for $C_{10}H_8OS_3$ (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. NH_4Cl solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **19a** as yellow solid (2.07 g, 91%).

m.p.: 96.3 – 97.7 °C.

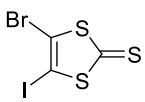
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 208.7, 107.2.

IR (cm^{-1}): $\tilde{\nu}$ = 2952, 2921, 2852, 2102, 1928, 1501, 1463, 1455, 1377, 1137, 1077, 978, 876, 867, 825, 746, 730.

MS (70 eV, EI) *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 $C_3Br_2S_3$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_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.

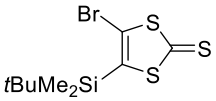
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 213.1, 112.8, 76.1.

IR (cm^{-1}): $\tilde{\nu}$ = 2920, 2359, 2338, 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_3BrIS_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_4Cl solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_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, $CDCl_3$) *δ*/ppm = 1.01 (s, 9H), 0.41 (s, 6H).

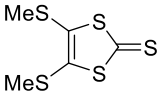
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 215.4, 143.7, 110.6, 26.6, 18.5, -4.1.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_9H_{15}BrS_3Si$ (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. NH_4Cl solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **19d** as green-brownish solid (1.13 g, 86%).

m.p.: 87.5 – 95.6 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 2.50 (s, 6H).

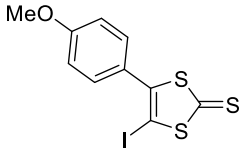
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 210.8, 135.9, 19.2.

IR (cm^{-1}): $\tilde{\nu}$ = 3057, 2980, 2911, 2841, 2817, 2270, 2103, 1998, 1666, 1613, 1482, 1468, 1417, 1312, 1251, 1191, 1054, 1028, 978, 965, 939, 900, 885, 819, 737, 711, 694, 659.

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 $C_5H_6S_5$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

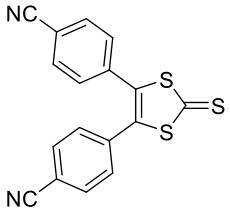
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 214.6, 160.9, 146.4, 130.5, 123.5, 114.4, 68.5, 55.4.

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

HRMS for $C_{10}H_7OIS_3$ (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. $ZnCl_2$ 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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:2) yielding **19f** as yellow solid (1.12 g, 83%).

m.p.: 184.3 – 189.2 °C (decomp.).

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.63 (d, *J* = 8.3 Hz, 4H), 7.31 (d, *J* = 8.3 Hz, 4H).

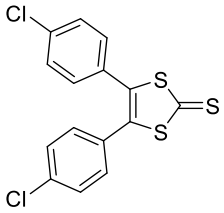
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 208.3, 138.5, 134.1, 133.0, 129.8, 117.5, 113.7.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 351 (19), 338 (14), 337 (18), 336 (79) [M^+], 324 (12), 320 (100), 266 (20), 246 (26).

HRMS for $C_{17}H_8N_2S_3$ (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. $ZnCl_2$ 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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **19g** as yellow solid (1.62 g, 93%).

m.p.: 154.9 – 158.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 7.34 – 7.27 (m, 4H), 7.18 – 7.11 (m, 4H).

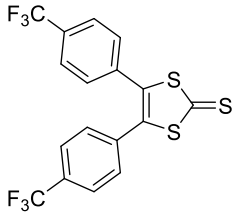
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 209.7, 138.3, 135.7, 130.4, 129.4, 128.5.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{15}H_8Cl_2S_3$ (353.9165): found: 353.9161.

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. $ZnCl_2$ 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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **19h** as yellow solid (1.50 g, 89%).

m.p.: 162.0 – 166.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 7.60 (d, *J* = 8.2 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 4H).

^{13}C-NMR (101 MHz, $CDCl_3$) *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).

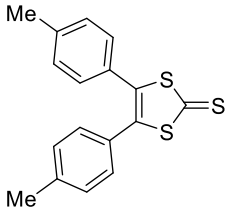
^{19}F-NMR (376 MHz, $CDCl_3$) *δ*/ppm = -63.0.

IR (cm^{-1}): $\tilde{\nu}$ = 3048, 2927, 2360, 2336, 1920, 1796, 1676, 1615, 1577, 1476, 1434, 1409, 1316, 1235, 1166, 1122, 1112, 1065, 1016, 955, 899, 881, 845, 838, 812, 768, 760, 742, 732, 696, 673, 654, 633, 614, 596.

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

HRMS for $C_{17}H_8F_6S_3$ (421.9692): found: 421.9687.

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



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. $ZnCl_2$ 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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (50 mL), extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **19i** as yellow solid (1.09 g, 89%).

m.p.: 155.3 – 157.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.10 (s, 8H), 2.34 (s, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 211.0, 139.4, 139.1, 129.6, 129.0, 127.5, 21.3.

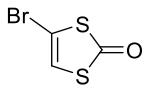
IR (cm^{-1}): $\tilde{\nu}$ = 3023, 2916, 2849, 2364, 2087, 1906, 1803, 1605, 1568, 1555, 1510, 1496, 1443, 1409, 1379, 1318, 1212, 1193, 1186, 1116, 1108, 1064, 1047, 1024, 964, 942, 904, 880, 834, 818, 799, 760, 714, 648, 638, 610.

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

HRMS for $C_{17}H_{14}S_3$ (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_2CO_3 (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and after filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **20a** as colorless solid (337 mg, 86%).

m.p.: 60.0 – 64.9 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 6.83 (s, 1H).

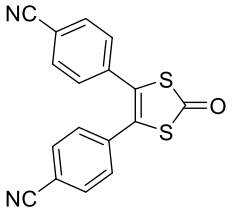
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 191.4, 117.0, 99.5.

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_3HOBrS_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_2CO_3 (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and after filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

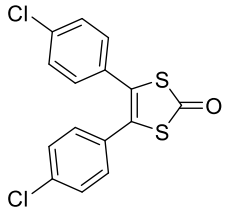
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 188.0, 135.5, 132.8, 130.1, 128.8, 117.7, 113.2.

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, 943, 889, 840, 830, 804, 762, 730, 712, 653, 609, 592, 582, 571.

MS (70 eV, EI) *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 $C_{17}H_8ON_2S_2$ (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_2CO_3 (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and after filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **20c** as yellowish solid (624 mg, 92%).

m.p.: 141.2 – 145.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 7.31 – 7.23 (m, 4H), 7.19 – 7.09 (m, 4H).

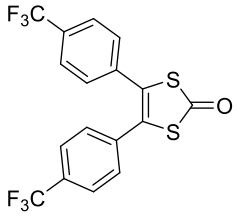
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 189.5, 135.1, 130.7, 129.8, 129.2, 128.0.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{15}H_8OCl_2S_2$ (337.9394): found: 337.9388.

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_2CO_3 (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and after filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

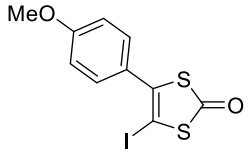
^{19}F-NMR (376 MHz, $CDCl_3$) *δ*/ppm = -63.0.

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, EI) *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 $C_{17}H_8OF_6S_2$ (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_2CO_3 (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and after filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

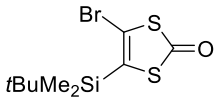
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 194.1, 160.6, 135.1, 130.6, 125.1, 114.2, 61.9, 55.4.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 352 (10), 351 (11), 350 (80) [M^+], 163 (35), 151 (100), 108 (20).

HRMS for $C_{10}H_7O_2IS_2$ (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-dithiol-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_2CO_3 (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_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.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 1.01 (s, 9H), 0.40 (s, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 194.2, 131.5, 104.0, 26.7, 18.6, -3.6.

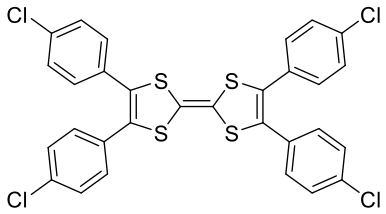
IR (cm^{-1}): $\tilde{\nu}$ = 3304, 2950, 2927, 2894, 2881, 2856, 1758, 1716, 1656, 1586, 1492, 1470, 1461, 1443, 1410, 1400, 1362, 1253, 1006, 956, 880, 835, 820, 803, 775, 709, 690, 674, 578.

MS (70 eV, EI) *m/z* (%) = 312 (37), 310 (34) [M^+], 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 $C_9H_{15}OSiS_2$ (309.9517): found: 309.9512.

3.6 Preparation of Tetraarylated TTF-Derivatives

Synthesis of 4,4',5,5'-tetrakis(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 $P(OEt)_3$ (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_2Cl_2, 9:1) yielding **26a** as red solid (87 mg, 54%).

m.p.: 260.3 – 262.1 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 7.24 (d, *J* = 8.2 Hz, 8H), 7.14 (d, *J* = 8.5 Hz, 8H).

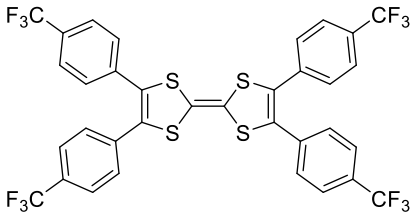
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 134.6, 130.7, 130.3, 129.1, 128.5, 108.4.

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

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 $C_{30}H_{16}Cl_4S_4$ (643.8889): found: 643.8885.

Synthesis of 4,4',5,5'-tetrakis(4-(trifluoromethyl)phenyl)-2,2'-bi(1,3-dithiolylidene) (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 (*i*hexane/EtOAc, 98:2) yielding **26b** as red solid (127 mg, 63%).

m.p.: 229.5 – 233.1 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 7.57 – 7.49 (m, 8H), 7.38 – 7.29 (m, 8H).

^{13}C-NMR (151 MHz, $CDCl_3$) *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.

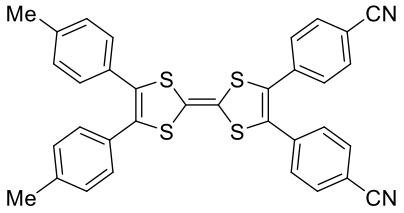
^{19}F-NMR (376 MHz, $CDCl_3$) *δ*/ppm = -62.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{34}H_{16}F_{12}S_4$ (779.9943): found: 779.9945.

Synthesis of 4,4'-(4',5'-di-*p*-tolyl-TTF-4,5-diyl)dibenzonitrile (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)dibenzonitrile (**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 (*i*hexane/CH_2Cl_2, 1:1) yielding **26c** as brown solid (393 mg, 67%).

m.p.: 263.1 – 265.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/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).

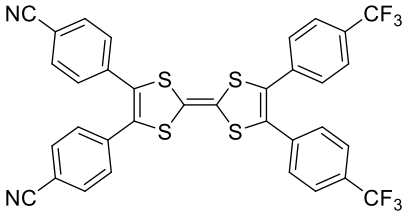
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 138.5, 136.7, 132.6, 130.0, 129.7, 129.5, 129.3, 128.9, 128.4, 118.0, 112.5, 104.2, 21.3. (One signal not observed; possible coincidental isochronicity).

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{34}H_{22}N_2S_4$ (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 $P(OEt)_3$ (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_2Cl_2, 1:1) yielding **26d** as dark red solid (132 mg, 53%).

m.p.: 241.2 – 246.6 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 7.61 – 7.51 (m, 8H), 7.37 – 7.26 (m, 8H).

^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 136.3, 135.4, 132.7, 130.9 (q, *J* = 32.8 Hz), 129.9, 129.7, 129.4, 125.9 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 272.4 Hz), 117.9, 112.8, 110.0, 107.4. (One signal not observed; possible coincidental isochronicity).

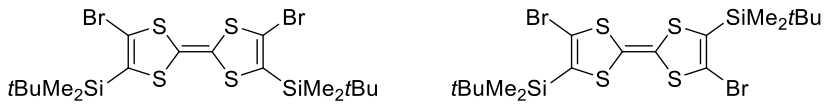
^{19}F-NMR (376 MHz, $CDCl_3$) *δ*/ppm = -62.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 696 (27), 695 (38), 694 (100) [M^+], 505 (11), 347 (17), 314 (39), 228 (32).

HRMS for $C_{34}H_{16}N_2F_6S_4$ (694.0101): found: 694.0095.

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



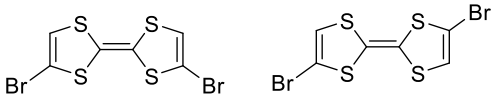
According to **TP 4**, 4-bromo-5-(*tert*-butyldimethylsilyl)-1,3-dithiole-2-thione (**19c**; 2.07 g, 6.32 mmol) was dissolved in freshly distilled $P(OEt)_3$ (60 mL). 4-Bromo-5-(*tert*-butyldimethylsilyl)-1,3-dithiole-2-one (**20f**; 2.36 g, 7.58 mmol) was added at 25 °C and the reaction mixture was

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, EI) *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 $C_{18}H_{30}Br_2Si_2S_4$ (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_2O (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_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 6.30 (s, 2H), 6.29 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 117.9, 117.8, 112.1, 112.1, 100.6, 100.5.

IR (cm^{-1}): $\tilde{\nu}$ = 1474, 1185, 894, 785, 7643, 734.

MS (70 eV, EI) *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 $C_6H_2Br_2S_4$ (359.7406): found: 359.7403.

E-isomer (**27b**):

m.p.: 136.3 – 141.9 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 6.29 (s, 2H), 6.29 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 117.9, 117.8, 112.1, 112.1, 100.6, 100.5.

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

MS (70 eV, EI) *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).

HRMS for $C_6H_2Br_2S_4$ (359.7406): found: 359.7392.

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

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 $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (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). $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (**5**;

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):

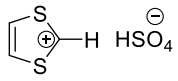
A dry and argon flushed *Schlenk*-flask was charged with a solution of diethyl TTF-4,5-dicarboxylate (**33e**; 1.0 equiv) in dry THF (0.25 M). TMPZnCl·LiCl (**4**; 1.3 equiv, 1.25 M in THF) was added dropwise at -30 °C and the reaction mixture was stirred at this temperature for 0.5 h. The completion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

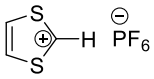
4.2 Preparation of Starting Material

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



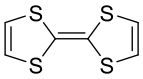
According to the literature,[57] a precooled solution (-50 °C) of peracetic acid (9.22 g, 121 mmol, 21 mL, 39% in acetic acid) in acetone (50 mL) was added dropwise to a solution of DTT (**16**; 4.07 g, 30 mmol) in acetone (80 mL) at -50 °C with a rate that the temperature did not rise above -40 °C. 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 vaccum. 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-ylium hexafluorophosphate (30)



According to the literature,[57] a solution of 1,3-dithiol-2-ylium hydrogen sulfate (**29**; 8.81 g, 44 mmol) in H_2O (40 mL) was added dropwise to a solution of sodium hexafluorophosphate (8.06 g, 48 mmol) in H_2O (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_2O (50 mL) and dried under high vacum. The title compound (**30**) was obtained as colorless solid (9.06 g, 83%) and was used without further purification.

Synthesis of tetrathiafulvalene (TTF) (21)



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-ylium 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_2O (600 mL) was added and the resulting precipitate was filtered, washed with H_2O (50 mL) and dried under high vacum. TTF (**21**) was obtained as yellow solid (3.58 g, 98%).

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 6.32 (s, 4H).

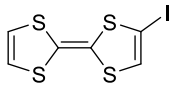
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 119.1, 110.1.

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).

HRMS for $C_6H_4S_4$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 98:2) yielding **32a** as yellow solid (182 mg, 55%).

m.p.: 61.8 – 63.5 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 6.42 (s, 1H), 6.34 (s, 2H).

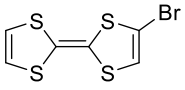
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 124.3, 119.0, 119.0, 112.8, 111.0, 63.7.

IR (cm^{-1}): $\tilde{\nu}$ = 3063, 2355, 2115, 1842, 1594, 1548, 1522, 1488, 1293, 1252, 1192, 1086, 868, 794, 770, 746, 735.

MS (70 eV, EI) *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 $C_6H_3IS_4$ (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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **32b** as yellow solid (189 mg, 67%).

m.p.: 52.8 – 53.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 6.34 (br. s, 2H), 6.27 (br. s, 1H).

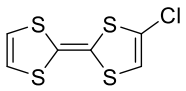
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 127.6, 119.0, 118.0, 114.0, 100.4. (One quaternary carbon not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_6H_3BrS_4$ (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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 99:1) yielding **32c** as orange solid (155 mg, 65%).

m.p.: 66.5 – 68.3 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 6.33 (br. s, 2H), 6.15 (s, 1H).

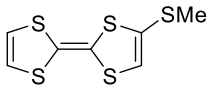
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 118.9 (2C), 117.6, 115.1, 114.5. (One quaternary carbon not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 3064, 2922, 1732, 1564, 1536, 1516, 1470, 1252, 1188, 1169, 1075, 945, 867, 811, 796, 775, 737.

MS (70 eV, EI) *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 $C_6H_3ClS_4$ (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·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_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 9:1) yielding **32d** as yellow oil (222 mg, 89%).

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 6.32 (br. s, 2H), 6.29 (br. s, 1H), 2.41 (s, 3H).

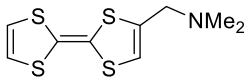
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 128.8, 119.7, 119.0, 118.9, 113.0, 109.6, 19.4.

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, EI) *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 $C_7H_6S_5$ (249.9073): found: 249.9072.

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_2Cl_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_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_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, $CDCl_3$) *δ*/ppm = 6.30 (br. s, 2H), 6.10 (s, 1H), 3.21 (s, 2H), 2.27 (s, 6H).

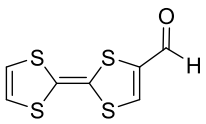
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 136.4, 119.2, 118.8, 114.2, 110.2, 110.1, 59.5, 45.0.

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 $C_9H_{11}NS_4$ (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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **32f** as dark red solid (139 mg, 60%).

m.p.: 111.2 – 113.0 °C (decomp.).

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 9.48 (s, 1H), 7.43 (s, 1H), 6.39 – 6.30 (m, 2H).

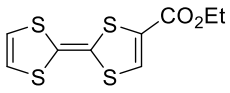
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 179.6, 141.5, 139.9, 119.3, 118.7, 115.9, 105.5.

IR (cm^{-1}): $\tilde{\nu}$ = 3068, 2921, 1712, 1644, 1550, 1532, 1367, 1252, 1228, 1143, 1074, 865, 829, 796, 776, 736, 696.

MS (70 eV, EI) *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 $C_7H_4OS_4$ (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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **32g** as red solid (199 mg, 72%).

m.p.: 83.8 – 85.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

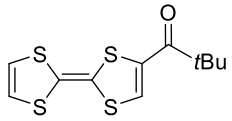
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 159.4, 131.8, 128.7, 119.2, 118.7, 113.5, 107.8, 61.9, 14.2.

IR (cm^{-1}): $\tilde{\nu}$ = 3069, 3057, 2976, 2924, 2901, 1693, 1567, 1537, 1472, 1438, 1392, 1366, 1286, 1198, 1154, 1112, 1066, 1004, 865, 841, 814, 793, 780, 770, 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 $C_9H_8O_2S_4$ (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_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **32h** as dark red solid (219 mg, 76%).

m.p.: 155.9 – 157.4 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.33 (br. s, 1H), 6.31 (br. s, 2H), 1.31 (s, 9H).

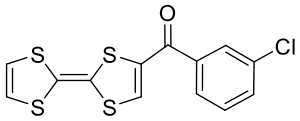
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 196.0, 138.2, 130.4, 119.4, 118.6, 43.8, 27.8. (Quaternary carbons not observed).

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).

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_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

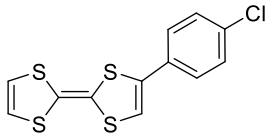
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 183.7, 139.6, 138.5, 136.6, 134.9, 132.4, 130.0, 128.5, 126.6, 119.4, 118.7, 115.4, 105.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{13}H_7OClS_4$ (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. $ZnCl_2$ 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 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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **32j** as orange solid (271 mg, 86%).

m.p.: 105.5 – 107.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 7.33 (s, 4H), 6.50 (s, 1H), 6.36 – 6.31 (m, 2H).

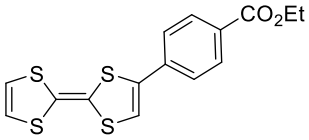
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 134.8, 134.1, 130.9, 129.0, 127.4, 119.1, 119.0, 114.2, 112.2, 108.5.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{12}H_7ClS_4$ (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. $ZnCl_2$ 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 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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **32k** as red solid (307 mg, 87%).

m.p.: 126.8 – 128.3 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

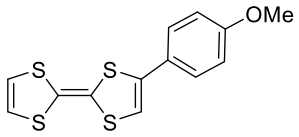
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 165.9, 137.3, 137.1, 136.2, 135.1, 130.1, 125.9, 119.0, 116.2, 61.1, 14.3. (Quaternary carbons not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{15}H_{12}O_2S_4$ (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. $ZnCl_2$ 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 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_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in*

vacuo. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **32l** as yellow solid (189 mg, 61%).

m.p.: 159.9 – 161.5 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

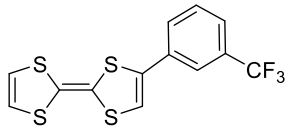
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.7, 135.8, 127.6, 119.0, 114.2 (2C), 111.3, 55.4. (Quaternary carbons not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{13}H_{10}OS_4$ (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. $ZnCl_2$ 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 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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 10:1) yielding **32m** as red solid (321 mg, 92%).

m.p.: 73.2 – 75.1 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.70 – 7.62 (m, 1H), 7.62 – 7.43 (m, 3H), 6.64 (s, 1H), 6.34 (br. s, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/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.

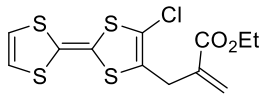
IR (cm^{-1}): $\tilde{\nu}$ = 3065, 1889, 1712, 1608, 1586, 1556, 1537, 1482, 1440, 1326, 1290, 1225, 1212, 1162, 1106, 1090, 1074, 997, 959, 908, 890, 838, 808, 794, 779, 767, 756, 734, 690, 682, 654.

MS (70 eV, EI) *m/z* (%) = 350 (16), 349 (14), 348 (100) [M^+], 303 (16), 170 (18), 102 (20).

HRMS for $C_{13}H_7F_3S_4$ (347.9383): found: 347.9362.

4.4 Preparation of Difunctionalized TTF-Derivatives

Synthesis of ethyl 2-((5-chloro-TTF-4-yl)methyl)acrylate (33a)



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_4Cl/NH_3 solution (8:1, 5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **33a** as orange solid (298 mg, 85%).

m.p.: 44.5 – 46.3 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

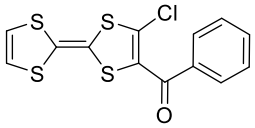
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 165.9, 135.6, 127.4 (2C), 127.2, 119.0, 118.9, 114.2, 112.6, 61.1, 31.1, 14.2.

IR (cm^{-1}): $\tilde{\nu}$ = 3409, 3067, 2976, 2931, 2870, 2361, 2190, 1911, 1716, 1630, 1604, 1594, 1545, 1521, 1492, 1468, 1445, 1418, 1402, 1367, 1334, 1292, 1255, 1219, 1156, 1110, 1027, 974, 952, 938, 931, 882, 858, 815, 798, 776, 765, 736, 720.

MS (70 eV, EI) *m/z* (%) = 352 (47), 351 (16), 350 (100) [M^+], 324 (14), 322 (26), 277 (12), 146 (66), 102 (23), 76 (10).

HRMS for $C_{12}H_{11}O_2ClS_4$ (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. $ZnCl_2$ 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 benzoyl chloride (169 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 at 25 °C for 1 h and was then quenched with sat. aq. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **33b** as dark red solid (285 mg, 83%).

m.p.: 100.9 – 103.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

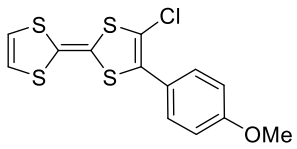
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 186.1, 136.4, 133.6, 129.6, 129.3, 128.6, 125.9, 119.3, 118.7, 118.3. (One quaternary carbon not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 344 (39), 343 (13), 342 (80) [M^+], 146 (42), 105 (100), 102 (16), 77 (63), 51 (15).

HRMS for $C_{13}H_7OClS_4$ (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·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_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **33c** as orange solid (269 mg, 78%).

m.p.: 109.2 – 111.2 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

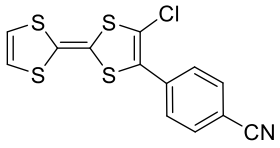
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 160.1, 148.9, 148.8, 130.3, 123.5, 123.4, 119.0, 114.0, 111.1, 111.0, 55.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 346 (48), 345 (17), 344 (100) [M^+], 299 (44), 166 (10), 151 (12), 146 (29), 123 (10), 102 (40), 76 (12).

HRMS for $C_{13}H_9OClS_4$ (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. $ZnCl_2$ 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-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. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **33d** as dark red solid (313 mg, 92%).

m.p.: 208.7 – 209.9 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 7.75 – 7.61 (m, 4H), 6.38 (br. s, 2H).

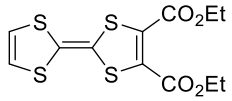
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 135.1, 132.4, 129.4, 126.8, 119.1, 119.0, 118.2, 117.1, 114.6, 112.6. (One quaternary carbon not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{13}H_6NClS_4$ (338.9072): found: 338.9074.

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. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **33e** as dark red solid (226 mg, 65%).

m.p.: 65.5 – 67.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 6.43 (br. s, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.3 Hz, 6H).

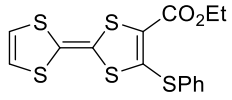
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.6, 132.2, 119.0, 116.4, 110.0, 62.7, 13.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{12}H_{12}O_4S_4$ (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)

at -40 °C. The reaction mixture was allowed to warm up to -20 °C within 6 h and was then quenched with sat. aq. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **33f** as red solid (226 mg, 59%).

m.p.: 108.7 – 109.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

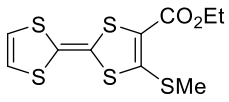
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 160.3, 148.4, 135.5, 130.9, 130.6, 129.2, 119.1, 118.6, 114.8, 113.8, 105.0, 61.8, 14.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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).

HRMS for $C_{15}H_{12}O_2S_5$ (383.9441): found: 383.9435.

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. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **33g** as red solid (209 mg, 65%).

m.p.: 102.5 – 103.4 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

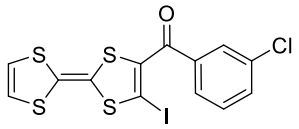
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 160.2, 148.0, 119.3, 118.6, 115.3, 113.6, 61.6, 18.2, 14.3. (One quaternary carbon not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 3057, 2982, 2932, 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 $C_{10}H_{10}O_2S_5$ (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). $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (**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. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:1) yielding **33h** as dark purple solid (389 mg, 83%).

m.p.: 135.9 – 136.8 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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, $CDCl_3$) *δ*/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.

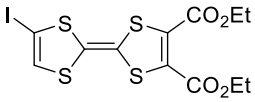
IR (cm^{-1}): $\tilde{\nu}$ = 3084, 3064, 2921, 2852, 1886, 1633, 1589, 1566, 1520, 1457, 1420, 1377, 1278, 1243, 1227, 1168, 1101, 1083, 997, 966, 916, 890, 858, 795, 766, 738, 675.

MS (70 eV, EI) *m/z* (%) = 468 (32) [M^+], 146 (100), 139 (35), 111 (42), 102 (31), 88 (21), 76 (31), 75 (33), 70 (24), 57 (21).

HRMS for $C_{13}H_6OClIS_4$ (467.8035): found: 467.8034.

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. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:1) yielding **34c** as red solid (427 mg, 90%).

m.p.: 58.8 – 60.6 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 6.44 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.0 Hz, 6H).

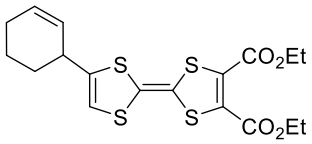
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.4, 159.4, 132.1, 132.1, 124.0, 117.2, 106.0, 63.5, 62.8 (2C), 13.9 (2C).

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, EI) *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 $C_{12}H_{11}O_4IS_4$ (473.8585): found: 473.8582.

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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **34d** as dark red oil (356 mg, 83%).

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

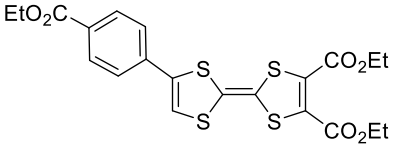
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.7 (2C), 141.8, 132.2 (2C), 130.1, 127.1, 117.2, 112.2, 103.0, 62.6 (2C), 37.8, 29.5, 24.8, 20.1, 13.9 (2C).

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{18}H_{20}O_4S_4$ (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_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

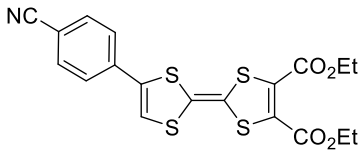
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 165.8, 159.5 (2C), 135.9, 135.2, 132.2, 132.2, 130.2 (2C), 130.1, 126.0 (2C), 115.8, 114.3, 105.9, 62.7 (2C), 61.2, 14.3, 13.9 (2C).

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, EI) *m/z* (%) = 498 (21), 497 (25), 496 (100) [M^+], 424 (13), 396 (21), 368 (19), 294 (13), 266 (11).

HRMS for $C_{21}H_{20}O_6S_4$ (496.0143): found: 496.0138.

Synthesis of diethyl 4'-(4-cyanophenyl)-TTF-4,5-dicarboxylate (34f)



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_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:7) yielding **34f** as dark red solid (297 mg, 66%).

m.p.: 175.8 – 177.7 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

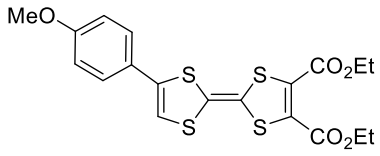
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.4 (2C), 136.0, 134.2, 132.7 (2C), 132.1 (2C), 126.6 (2C), 118.3, 117.3, 113.3, 111.8, 62.8 (2C), 13.9 (2C). (One quaternary carbon not observed).

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, 1014, 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 $C_{19}H_{16}O_4NS_4$ ($M+H^+$; 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_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 3:2) yielding **34g** as red solid (332 mg, 73%).

m.p.: 96.5 – 101.9 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/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).

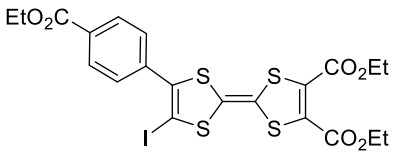
IR (cm^{-1}): $\tilde{\nu}$ = 3056, 2981, 2964, 2934, 2841, 2360, 2342, 1730, 1719, 1650, 1626, 1608, 1577, 1561, 1505, 1472, 1462, 1442, 1418, 1392, 1362, 1343, 1302, 1252, 1178, 1094, 1029, 1020, 928, 922, 884, 859, 850, 831, 304, 782, 773, 746, 708, 694, 671.

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 $C_{19}H_{18}O_5S_4$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:2) yielding **35a** as red solid (548 mg, 88%).

m.p.: 138.2 – 140.1 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

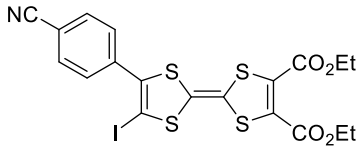
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 165.7, 159.4 (2C), 136.9, 134.0, 132.2, 132.1, 131.3, 129.9 (2C), 129.2 (2C), 115.7, 107.4, 64.3, 62.8 (2C), 61.3, 14.3, 13.9 (2C).

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 $C_{21}H_{19}O_6IS_4$ (621.9109): found: 621.9120.

Synthesis of diethyl 4'-(4-cyanophenyl)-5'-iodo-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. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

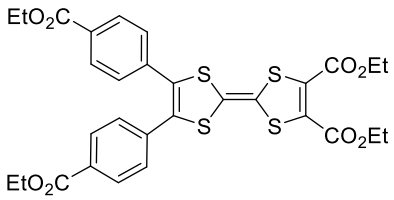
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.3 (2C), 137.2, 132.9, 132.5 (2C), 132.1 (2C), 129.9 (2C), 118.0, 114.8, 113.1, 108.3, 65.7, 62.8 (2C), 13.9 (2C).

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 $C_{19}H_{14}O_4NIS_4$ (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. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:4) yielding **35c** as red solid (580 mg, 90%).

m.p.: 131.7 – 133.9 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

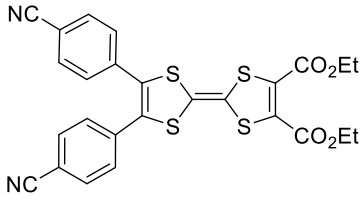
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 165.7, 159.5, 136.3, 132.3, 130.6, 130.0, 129.6, 129.0, 111.9, 106.3, 62.8, 61.2, 14.3, 13.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{30}H_{28}O_8S_4$ (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_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

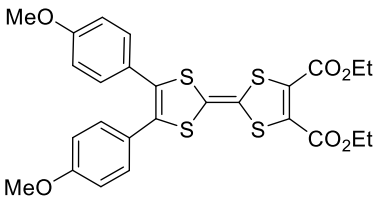
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.3, 136.1, 132.7, 132.2, 129.7, 117.9, 112.8, 110.0, 108.3, 62.9, 13.9. (One quaternary carbon not observed).

IR (cm^{-1}): $\tilde{\nu}$ = 2360, 2340, 2226, 1743, 1570, 1243, 1091, 1026, 850, 814, 758, 668.

MS (70 eV, EI) *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 $C_{26}H_{18}O_4N_2S_4$ (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_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:3) yielding **35e** as red solid (353 mg, 63%).

m.p.: 117.1 – 125.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/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).

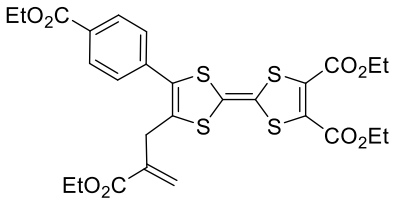
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 159.5, 143.3, 132.3, 130.5, 130.4, 129.0, 128.4, 125.4, 114.0, 62.7, 55.2, 14.0.

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, EI) *m/z* (%) = 562 (22), 561 (32), 560 (100) [M^+], 371 (11), 270 (16), 238 (21), 223 (24).

HRMS for $C_{26}H_{24}O_6S_4$ (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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:4) yielding **35f** as red oil (323 mg, 53%).

^{1}H-NMR (600 MHz, $CDCl_3$) 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).

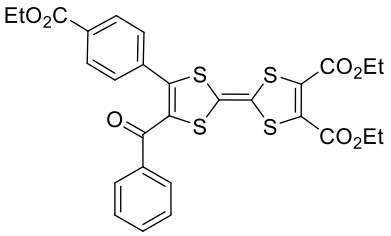
^{13}C-NMR (151 MHz, $CDCl_3$) δ/ppm = 165.8, 165.8, 159.6, 159.6, 136.9, 136.2, 132.3, 132.2, 130.8, 130.0 (2C), 129.2, 128.7 (2C), 128.5, 127.4, 113.2, 104.8, 62.7 (2C), 61.2, 61.2, 31.8, 14.3, 14.1, 13.9 (2C).

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_{27}H_{28}O_8S_4$ (608.0667): found: 608.0664.

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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:4) yielding **35g** as red solid (511 mg, 85%).

m.p.: 69.9 – 72.8 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

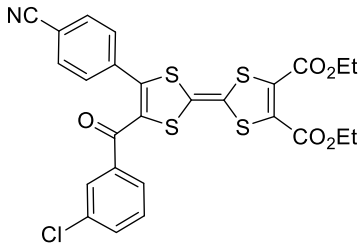
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 187.9, 165.4, 159.3 (2C), 142.2, 135.7, 135.3, 133.3, 132.5, 131.8 (2C), 129.5 (2C), 129.3 (2C), 129.2 (2C), 128.2 (2C), 128.0, 110.4, 109.1, 62.8 (2C), 61.2, 14.2, 13.9 (2C).

IR (cm^{-1}): $\tilde{\nu}$ = 2985, 2360, 2341, 1715, 1632, 1579, 1446, 1366, 1274, 1252, 1173, 1094, 1016, 916, 863, 810, 768, 758, 718, 693, 657.

MS (70 eV, EI) *m/z* (%) = 602 (25), 601 (36), 600 (100) [M^+], 528 (15), 500 (13), 262 (12), 190 (13), 105 (82), 77 (37).

HRMS for $C_{28}H_{24}O_7S_4$ (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 $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 1:4) yielding **35h** as red solid (470 mg, 80%).

m.p.: 47.4 – 49.3 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *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).

^{13}C-NMR (151 MHz, $CDCl_3$) *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}): $\tilde{\nu}$ = 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 $C_{26}H_{20}O_5NS_4$ (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,[72] 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. NH_4Cl 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), CuI (2 mol%) and $Pd(PPh_3)_2Cl_2$ (1 mol%) in NEt_3 (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. NH_4Cl solution.

Typical Procedure 5 for electrophilic cyclizations with iodine (TP 5):

According to the literature,[73] a solution of iodine (1.2 equiv) in dry CH_2Cl_2 (0.15 M) was added dropwise to a solution of the corresponding alkynylated ethyl 1,4-dithiine-2-carboxylate (1.0 equiv) in dry CH_2Cl_2 (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. $Na_2S_2O_3$ solution.

5.2 Preparation of 1,4-Dithiin

According to the literature,[71] 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 Et_2O (400 mL). The organic layer was washed with water (3 x 150 mL), sat. aq. $NaHCO_3$ solution (2 x 100 mL) and sat. aq. NaCl solution (100 mL). The organic layer was dried over anhydrous $MgSO_4$ 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.

^{1}H-NMR (200 MHz, $CDCl_3$) *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

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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **40a** as yellow liquid (114 mg, 67%).

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 6.52 – 6.46 (m, 2H), 6.24 (d, *J* = 6.6 Hz, 1H).

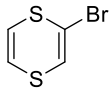
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 125.9, 122.7, 121.7, 72.9.

IR (cm^{-1}): $\tilde{\nu}$ = 3025, 2921, 1678, 1598, 1554, 1534, 1513, 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 $C_4H_3IS_2$ (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. NH_4Cl solution (10 mL), extracted with Et_2O (3 x 80 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **40b** as yellow liquid (529 mg, 77%).

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 6.52 – 6.46 (m, 2H), 6.23 (d, *J* = 6.5 Hz, 1H).

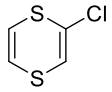
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 126.0, 122.8, 121.9, 73.0.

IR (cm^{-1}): $\tilde{\nu}$ = 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).

HRMS for $C_4H_3BrS_2$ (193.8860): found: 193.8840.

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. NH_4Cl solution (10 mL), extracted with Et_2O (3 x 80 mL) and dried over anhydrous Na_2SO_4. 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%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm = 6.35 (d, *J* = 6.7, 1H), 6.32 (d, *J* = 6.7 Hz, 1H), 6.14 (s, 1H).

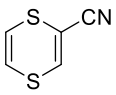
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 123.0, 122.6, 122.3, 117.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_4H_3ClS_2$ (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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **40d** as orange liquid (59 mg, 60%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 7.13 (s, 1H), 6.37 – 6.21 (m, 2H).

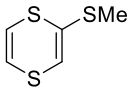
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 140.0, 122.0, 121.1, 114.4, 105.3.

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 $C_5H_3NS_2$ (140.9707): found: 140.9694.

Synthesis of ethyl 2-(methylthio)-1,4-dithiin (40e)



According to **TP 1**, 1,4-dithiin (**38**; 349 mg, 3.0 mmol) was dissolved in dry THF (6 mL). TMPMgCl·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_4Cl solution (10 mL), extracted with Et_2O (3 x 70 mL) and dried over anhydrous Na_2SO_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%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm = 6.46 – 6.39 (m, 1H), 6.36 (d, *J* = 6.6 Hz, 1H), 5.97 (s, 1H), 2.40 (s, 3H).

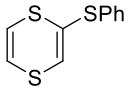
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 132.9, 124.6, 122.7, 114.5, 18.0.

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 $C_5H_6S_3$ (161.9632): found: 161.9630.

Synthesis of 2-(phenylthio)-1,4-dithiin (40f)



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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **40f** as yellow liquid (121 mg, 77%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 7.47 – 7.28 (m, 5H), 6.39 – 6.25 (m, 3H).

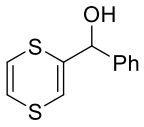
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 133.5, 130.6, 129.23, 128.7, 127.8, 123.1, 122.7, 122.6.

IR (cm^{-1}): $\tilde{\nu}$ = 3029, 1947, 1881, 1580, 1515, 1474, 1438, 1326, 1299, 1278, 1217, 1177, 1156, 1137, 1082, 1068, 1023, 1000, 896, 814, 773, 737, 670.

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 $C_{10}H_8S_3$ (223.9788): found: 223.9765.

Synthesis of (1,4-dithiin-2-yl)(phenyl)methanol (40g)



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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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 **40g** as yellowish solid (75 mg, 97%).

m.p.: 64.9 – 68.3 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ/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).

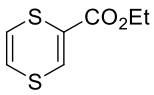
^{13}C-NMR (101 MHz, $CDCl_3$) *δ*/ppm = 140.3, 139.6, 128.5, 128.3, 126.6, 123.7, 121.9, 118.3, 75.7.

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, EI) 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_4Cl solution (10 mL), extracted with Et_2O (3 x 70 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **40h** as red liquid (704 mg, 89%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ/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).

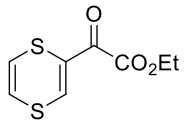
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 161.1, 133.8, 125.6, 122.0, 119.6, 62.0, 14.1.

IR (cm^{-1}): $\tilde{\nu}$ = 3037, 2980, 2932, 2904, 1702, 1573, 1533, 1464, 1444, 1391, 1366, 1292, 1243, 1218, 1171, 1111, 1094, 1040, 994, 973, 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).

HRMS for $C_7H_8O_2S_2$ (187.9966): found: 187.9948.

Synthesis of ethyl 2-(1,4-dithiin-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. $ZnCl_2$ 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·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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **40i** as red liquid (170 mg, 56%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ/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).

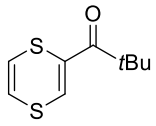
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 177.3, 161.8, 143.3, 129.8, 121.5, 118.4, 62.8, 14.0.

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).

HRMS for $C_8H_8O_3S_2$ (215.9915): found: 215.9914.

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. $ZnCl_2$ 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·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 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 96:4) yielding **40j** as red solid (84 mg, 62%).

m.p.: 102.5 - 103.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) 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).

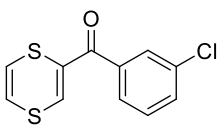
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 201.3, 134.1, 129.9, 122.8, 122.4, 44.1, 27.6.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) 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 $C_9H_{12}OS_2$ (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. $ZnCl_2$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 94:6) yielding **40k** as red oil (71 mg, 80%).

^{1}H-NMR (300 MHz, $CDCl_3$) 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).

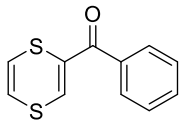
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 187.2, 138.6, 138.0, 134.8, 133.8, 132.5, 129.8, 129.0, 127.2, 122.5, 119.7.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) m/z (%) = 256 (28), 254 (62) [M^+], 139 (100), 111 (59), 75 (22).

HRMS for $C_{11}H_7ClOS_2$ (253.9627): found: 253.9623.

Synthesis of (1,4-dithiin-2-yl)(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. $ZnCl_2$ 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. NH_4Cl/NH_3 solution (8:1, 50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 94:6) yielding **40l** as red liquid (1.20 g, 78%).

^{1}H-NMR (300 MHz, $CDCl_3$) 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).

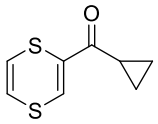
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 188.6, 137.0, 136.9, 134.2, 132.5, 129.1, 128.4, 122.6, 119.7.

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 $C_{11}H_8OS_2$ (220.0017): found: 220.0014.

Synthesis of cyclopropyl(1,4-dithiin-2-yl)methanone (40m)



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·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_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 9:1) yielding **40m** as red oil (168 mg, 65%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ/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).

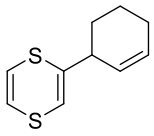
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 192.4, 135.0, 133.0, 122.2, 119.5, 17.1, 11.7.

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 $C_8H_8OS_2$ (184.0017): found: 184.0014.

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. $ZnCl_2$ 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. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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%).

^{1}H-NMR (300 MHz, $CDCl_3$) 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).

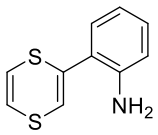
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 142.4, 129.8, 127.7, 123.4, 122.6, 115.6, 42.4, 28.6, 25.0, 20.1.

IR (cm^{-1}): $\tilde{\nu}$ = 3019, 2926, 2856, 2831, 1720, 1647, 1584, 1535, 1444, 1429, 1343, 1212, 1159, 1134, 1086, 1045, 1019, 978, 964, 898, 887, 869, 805, 793, 784, 772, 734, 723, 708, 669, 652, 624, 612, 596, 587, 576, 571, 568, 564, 555.

MS (70 eV, EI) m/z (%) = 196 (20) [M^+], 79 (23), 77 (21), 53 (34), 52 (22), 45 (100).

HRMS for $C_{10}H_{12}S_2$ (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. $ZnCl_2$ 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. NH_4Cl solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. 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 **40o** as yellow oil (1.56 g, 94%).

^{1}H-NMR (400 MHz, $CDCl_3$) 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).

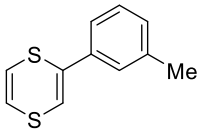
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 143.9, 135.0, 130.7, 129.7, 123.0, 122.8, 122.8, 119.1, 118.5, 116.0.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) 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 $C_{10}H_9NS_2$ (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. $ZnCl_2$ 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 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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were

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).

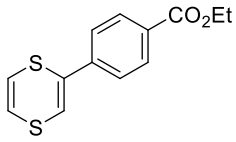
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 138.2, 138.0, 137.0, 129.4, 128.4, 127.7, 124.2, 123.4, 122.8, 115.8, 21.4.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) 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_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 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).

^{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}): $\tilde{\nu}$ = 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 $C_{13}H_{12}O_2S_2$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*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).

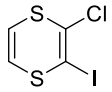
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 123.5, 84.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_4H_2I_2S_2$ (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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **41b** as yellow solid (73 mg, 71%).

m.p.: 55.0 – 56.3 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 6.54 (d, *J* = 6.3 Hz, 1H), 6.34 (d, *J* = 6.3 Hz, 1H).

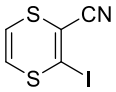
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 125.8, 123.6, 122.9, 74.0.

IR (cm^{-1}): $\tilde{\nu}$ = 3033, 2921, 1591, 1550, 1518, 1354, 1275, 1260, 1133, 922, 879, 817, 787, 736, 712, 675, 613, 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 $C_4H_2ICIS_2$ (275.8331): 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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column

chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **41c** as orange liquid (106 mg, 86%).

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 6.63 (d, *J* = 6.3 Hz, 1H), 6.32 (d, *J* = 6.3 Hz, 1H).

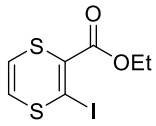
^{13}C-NMR (151 MHz, $CDCl_3$) δ/ppm = 124.3, 122.1, 116.0, 109.0, 96.6.

IR (cm^{-1}): $\tilde{\nu}$ = 3039, 3028, 2954, 2920, 2851, 2212, 1594, 1573, 1553, 1522, 1502, 1463, 1373, 1281, 1262, 1130, 1072, 1054, 1022, 892, 874, 841, 802, 791, 730, 679, 601, 557.

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 $C_5H_2NIS_2$ (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. $Na_2S_2O_3$ solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **41d** as orange liquid (793 mg, 62%).

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

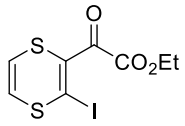
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 162.2, 126.6, 124.4, 123.5, 83.2, 62.5, 14.0.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_7H_7O_2IS_2$ (313.8932): found: 313.8929.

Synthesis of ethyl 2-(3-iodo-1,4-dithiin-2-yl)-2-oxoacetate (41e)



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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **41e** as red oil (120 mg, 50%).

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*/ppm = 6.61 (d, *J* = 6.1 Hz, 1H), 6.42 (d, *J* = 6.2 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.45 – 1.35 (m, 3H).

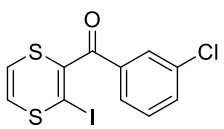
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 180.9, 161.0, 127.6, 126.1, 122.5, 89.4, 63.0, 13.9.

IR (cm^{-1}): $\tilde{\nu}$ = 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.

MS (70 eV, EI) *m/z* (%) = 342 (43) [M^+], 269 (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 $C_8H_7O_3IS_2$ (341.8881): found: 341.8871.

Synthesis of (3-chlorophenyl)(3-iodo-1,4-dithiin-2-yl)methanone (41f)



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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

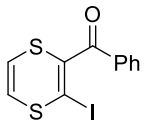
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 189.9, 135.3, 135.1, 134.3, 132.3, 130.2, 129.7, 128.1, 126.1, 122.2, 76.8.

IR (cm^{-1}): $\tilde{\nu}$ = 3064, 3029, 2922, 2849, 1950, 1885, 1779, 1667, 1595, 1567, 1522, 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, EI) *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 $C_{11}H_6OClIS_2$ (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 (**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 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. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

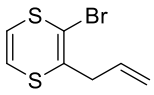
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 191.2, 134.4, 133.4, 133.0, 130.0, 128.9, 125.9, 122.4, 75.8.

IR (cm^{-1}): $\tilde{\nu}$ = 3031, 2923, 1963, 1656, 1594, 1578, 1528, 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) [M^+], 220 (13), 219 (14), 191 (16), 190 (25), 147 (21), 105 (100), 77 (72), 51 (26), 43 (45).

HRMS for $C_{11}H_7OIS_2$ (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. CuCN·2LiCl 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_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_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, $CDCl_3$) *δ*/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).

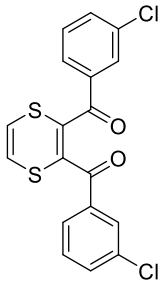
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 132.1, 132.0, 123.7, 123.4, 117.7, 103.2, 41.5.

IR (cm^{-1}): $\tilde{\nu}$ = 3032, 3018, 2925, 2853, 2832, 1718, 1648, 1585, 1563, 1556, 1520, 1500, 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) [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 $C_7H_7BrS_2$ (233.9171): found: 233.9178.

Synthesis of (1,4-dithiin-2,3-diyl)bis((3-chlorophenyl)methanone) (41i)



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 3-chlorobenzoyl chloride (61 mg, 0.35 mmol) and $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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%).

^{1}H-NMR (300 MHz, $CDCl_3$) *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).

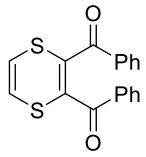
^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 188.5, 139.9, 136.8, 134.9, 133.8, 129.9, 129.0, 127.5, 125.1.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 394 (27), 392 (34) [M^+], 360 (16), 249 (22), 139 (100), 111 (49), 75 (16).

HRMS for $C_{18}H_{10}O_2Cl_2S_2$ (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 benzoyl chloride (98 mg, 0.7 mmol) and $Pd(PPh_3)_4$ (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. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 6:1) yielding **41j** as red oil (134 mg, 59%).

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 190.0, 139.5, 135.5, 133.8, 129.4, 128.5, 125.2.

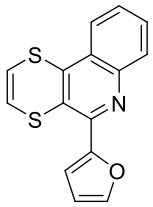
IR (cm^{-1}): $\tilde{\nu}$ = 3043, 2920, 2849, 1722, 1708, 1682, 1659, 1631, 1595, 1573, 1548, 1530, 1445, 1312, 1294, 1252, 1241, 1177, 1095, 1072, 1036, 1018, 996, 955, 935, 901, 836, 797, 747, 718, 689, 675, 663.

MS (70 eV, EI) *m/z* (%) = 325 (10), 324 (50) [M^+], 105 (100), 77 (56).

HRMS for $C_{18}H_{12}O_2S_2$ (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 (**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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **42a** as yellow solid (74 mg, 52%).

m.p.: 118.3 – 121.6 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

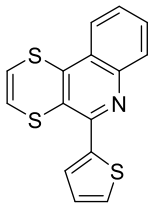
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 151.3, 146.4, 146.1, 144.3, 142.6, 130.1, 129.7, 127.4, 126.5, 126.1, 126.0, 124.2, 123.6, 114.4, 111.6.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{15}H_9ONS_2$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc/NEt_3, 98:2:0.05) yielding **42b** as yellow solid (90 mg, 60%).

m.p.: 128.8 – 131.2 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

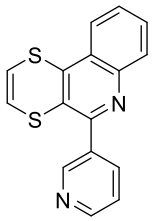
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 149.8, 146.3, 142.6, 142.5, 130.0, 130.0, 129.5, 128.8, 127.4, 127.2, 126.6, 126.3, 125.9, 124.1, 123.5.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 301 (14), 300 (25), 299 (100) [M^+], 298 (46), 267 (14), 266 (45), 222 (10).

HRMS for $C_{15}H_9NS_3$ (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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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.

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

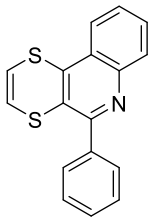
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 153.9, 150.1, 149.8, 146.5, 142.9, 137.0, 135.2, 130.3, 129.8, 127.8, 126.7, 126.3, 126.2, 123.6, 123.5, 123.0.

IR (cm^{-1}): $\tilde{\nu}$ = 3324, 3081, 3052, 3037, 3001, 2968, 2929, 1944, 1916, 1825, 1800, 1725, 1610, 1583, 1568, 1546, 1530, 1473, 1431, 1410, 1374, 1346, 1327, 1292, 1257, 1238, 1230, 1190, 1156, 1121, 1105, 1076, 1040, 1025, 995, 969, 946, 924, 896, 879, 848, 836, 799, 776, 748, 711, 701, 692, 683, 674.

MS (70 eV, EI) *m/z* (%) = 295 (14), 294 (69) [M^+], 293 (19), 270 (10), 269 (16), 268 (100), 261 (15).

HRMS for $C_{16}H_{10}N_2S_2$ (294.0285): found: 294.0281.

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. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc/NEt_3, 98:2:0.05) yielding **42d** as yellow solid (79 mg, 54%).

m.p.: 175.8 – 179.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

^{13}C-NMR (101 MHz, $CDCl_3$) 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.

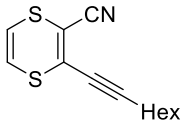
IR (cm^{-1}): $\tilde{\nu}$ = 3050, 3029, 3015, 2921, 2852, 1949, 1921, 1894, 1834, 1806, 1770, 1731, 1699, 1600, 1578, 1545, 1533, 1493, 1474, 1448, 1441, 1374, 1339, 1330, 1312, 1286, 1251, 1235, 1173, 1162, 1151, 1134, 1092, 1074, 1024, 1000, 993, 976, 948, 921, 902, 893, 863, 844, 818, 803, 781, 771, 751, 711, 702, 685, 656.

MS (70 eV, EI) *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 $C_{17}H_{11}NS_2$ (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)



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), CuI (7.6 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol) in NEt_3 (10 mL) at 25 °C. The reaction mixture was stirred at this temperature for 4 h and was then quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **43a** as orange oil (454 mg, 91%).

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

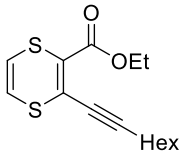
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 136.4, 124.1, 121.9, 114.5, 106.6, 104.2, 75.3, 31.2, 28.4, 27.9, 22.4, 19.9, 14.0.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{13}H_{15}NS_2$ (249.0646): found: 249.0641.

Synthesis of ethyl 3-(3-oxooct-1-yn-1-yl)-1,4-dithiin-2-carboxylate (43b)



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), CuI (14 mg, 0.07 mmol) and $Pd(PPh_3)_2Cl_2$ (25 mg, 0.04 mmol) in NEt_3 (18 mL) at 25 °C. The reaction mixture was stirred at this temperature for

4 h and was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with EtOAc (3 x 70 mL) and dried over anhydrous Na_2SO_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 **43b** as orange oil (817 mg, 77%).

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

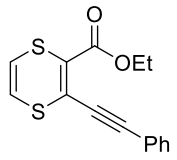
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 161.7, 128.5, 128.2, 123.7, 123.6, 102.7, 61.9, 31.3, 28.6, 28.1, 22.5, 20.1, 14.1, 14.0. (One signal not observed; possible coincidental isochronicity).

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *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 $C_{15}H_{20}O_2S_2$ (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), CuI (9 mg, 0.05 mmol) and $Pd(PPh_3)_2Cl_2$ (17 mg, 0.03 mmol) in NEt_3 (12 mL) at 25 °C. The reaction mixture was stirred at this temperature for 3 h and was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with EtOAc (3 x 70 mL) and dried over anhydrous Na_2SO_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 **43c** as red oil (634 mg, 93%).

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

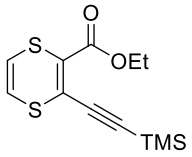
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 161.5, 131.9, 129.9, 129.4, 128.4, 127.3, 124.1, 123.6, 122.1, 99.2, 85.3, 62.1, 14.2.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 290 (11), 289 (19), 288 (100) [M^+], 260 (11), 259 (17), 243 (12), 229 (12), 216 (20), 215 (28), 214 (17), 171 (47), 145 (47), 145 (21), 113 (11).

HRMS for $C_{15}H_{12}O_2S_2$ (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), CuI (3 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (6 mg, 0.01 mmol) in NEt_3 (4.5 mL) at 25 °C. The reaction mixture was stirred at this temperature for 3 h and was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with EtOAc (3 x 70 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **43d** as red oil (206 mg, 80%).

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 161.5, 131.3, 126.5, 123.8 (2C), 106.2, 99.0, 62.1, 14.1, -0.4.

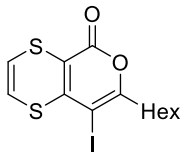
IR (cm^{-1}): $\tilde{\nu}$ = 3036, 2960, 2900, 2134, 1703, 1603, 1560, 1524, 1464, 1444, 1408, 1389, 1365, 1247, 1226, 1171, 1122, 1095, 1035, 992, 972, 838, 797, 758, 725, 676, 659.

MS (70 eV, EI) *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 $C_{12}H_{16}O_2S_2Si$ (284.0361): found: 284.0356.

5.7 Iodine-Mediated Electrophilic Cyclizations

Synthesis of 7-hexanoyl-8-iodo-5*H*-[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 CH_2Cl_2 (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 CH_2Cl_2 (35 mL) at 25 °C. The reaction mixture was stirred at this temperature for 2 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **44a** as red oil (972 mg, 88%).

^{1}H-NMR (400 MHz, $CDCl_3$) *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).

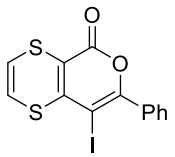
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 163.0, 156.9, 153.4, 125.2, 121.4, 113.9, 74.1, 37.3, 31.3, 28.7, 27.0, 22.4, 14.0.

IR (cm^{-1}): $\tilde{\nu}$ = 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, EI) *m/z* (%) = 396 (10), 395 (17), 394 (100) [M^+], 324 (34), 295 (10), 197 (24), 127 (23), 43 (23), 41 (10).

HRMS for $C_{13}H_{15}O_2IS_2$ (393.9558): found: 393.9553.

Synthesis of 8-iodo-7-phenyl-5*H*-[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 CH_2Cl_2 (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 CH_2Cl_2 (10 mL) at 25 °C. The reaction mixture was stirred at this temperature

for 12 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_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).

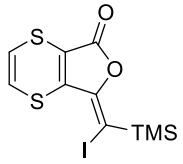
^{13}C-NMR (101 MHz, $CDCl_3$) δ/ppm = 158.8, 156.5, 153.9, 133.7, 130.9, 129.5, 128.2, 125.3, 121.8, 115.5, 73.9.

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 $C_{13}H_7O_2IS_2$ (385.8932): found: 385.8926.

Synthesis of (*E*)-7-(iodo(trimethylsilyl)methylene)-[1,4]dithiino[2,3-*c*]furan-5(7*H*)-one (44c)



According to **TP 5**, a solution of iodine (193 mg, 0.76 mmol) in dry CH_2Cl_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_2Cl_2 (8 mL) at 25 °C. The reaction mixture was stirred at this temperature for 3 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_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.

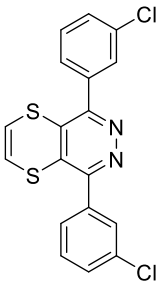
IR (cm^{-1}): $\tilde{\nu}$ = 3508, 3038, 2953, 2896, 2849, 2441, 2219, 2004, 1940, 1748, 1597, 1572, 1515, 1458, 1408, 1322, 1291, 1247, 1224, 1125, 1007, 991, 899, 860, 839, 816, 777, 758, 745, 711, 664, 653.

MS (70 eV, EI) *m/z* (%) = 384 (15), 383 (17), 382 (100) [M^+], 240 (15), 212 (10), 196 (21), 181 (14), 153 (15), 73 (78).

HRMS for $C_{10}H_{11}O_2IS_2Si$ (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)



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_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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 **45** as orange solid (314 mg, 62%).

m.p.: 116.9 – 119.0 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 7.72 (d, *J* = 1.7 Hz, 2H), 7.62 – 7.43 (m, 6H), 6.33 (s, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 156.6, 137.2, 135.5, 134.4, 129.9, 129.6 (2C), 127.8, 123.7.

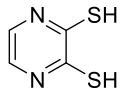
IR (cm^{-1}): $\tilde{\nu}$ = 3064, 3029, 2923, 2853, 1950, 1885, 1819, 1779, 1595, 1566, 1520, 1497, 1465, 1419, 1371, 1312, 1289, 1264, 1230, 1161, 1137, 1095, 1077, 1043, 998, 975, 911, 887, 824, 801, 787, 762, 719, 685, 668, 657.

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 $C_{18}H_{10}N_2Cl_2S_2$ (387.9662): found: 387.9666.

5.9 Preparation of 1,4-Dithiin-Fused Pyrazines

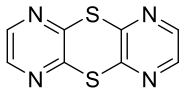
Synthesis of pyrazine-2,3-dithiol (47)



According to the literature,[74] 2,3-dichloropyrazine (**46**; 745 mg, 5.0 mmol) and $NaHS \cdot xH_2O$ (2.34 g, 5.0 mmol) were dissolved in H_2O (15 mL). The reaction mixture was heated to 120 °C for 5 h. The resulting precipitate was filtered, washed with H_2O (20 mL) and then dissolved in NaOH (2 M; 20 mL). Remained solids were removed by filtration and the filtrate was acidified with AcOH (50 mL). The resulting precipitate was filtered, washed with H_2O and dried under high vacuum yielding **47** as yellow solid (434 mg, 60%).

The analytical data matches those reported in the literature.[76]

Synthesis of [1,4]dithiino[2,3-*b*:5,6-*b*']dipyrazine (48)



2,3-Dichloropyrazine (**46**; 74 mg, 0.50 mmol), K_2CO_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_2O (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 8:1) yielding **48** as yellowish solid (84 mg, 76%).

m.p.: 130.4 – 136.2 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 8.22 (s, 4H).

[76] Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R. *Chem. Mater.* **2010**, *22*, 4120.

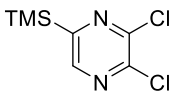
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 150.7, 141.8.

IR (cm^{-1}): $\tilde{\nu}$ = 2922, 2853, 1918, 1805, 1528, 1510, 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).

HRMS for $C_8H_4N_4S_2$ (219.9877): found: 219.9871.

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. TMPLi (**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. NH_4Cl solution (50 mL), extracted with EtOAC (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 96:4) yielding **49** as colorless liquid (1.68 g, 76%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 8.33 (s, 1H), 0.36 (s, 9H).

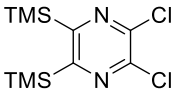
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 161.6, 148.5, 147.4, 145.4, -2.1.

IR (cm^{-1}): $\tilde{\nu}$ = 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 $C_7H_{10}N_2Cl_2Si$ (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. TMPLi

(**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. NH_4Cl solution (5 mL), extracted with EtOAC (3 x 10 mL) and dried over anhydrous Na_2SO_4. 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.

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 0.40 (s, 18H).

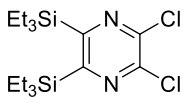
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 166.4, 145.9, 0.2.

IR (cm^{-1}): $\tilde{\nu}$ = 2956, 2900, 1502, 1464, 1409, 1348, 1282, 1264, 1247, 1168, 1092, 1068, 944, 897, 833, 754, 695, 659.

MS (70 eV, EI) 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 $C_{10}H_{18}N_2Cl_2Si_2$ (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. TMPLi (**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. NH_4Cl solution (50 mL), extracted with EtOAC (3 x 100 mL) and dried over anhydrous Na_2SO_4. 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%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 1.07 – 0.80 (m, 30H).

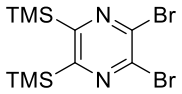
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 165.8, 145.6, 7.5, 4.2.

IR (cm^{-1}): $\tilde{\nu}$ = 2955, 2911, 2876, 1458, 1413, 1380, 1281, 1238, 1171, 1085, 1065, 1000, 970, 957, 886, 720, 660.

MS (70 eV, EI) 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).

HRMS for $C_{16}H_{30}N_2Cl_2Si_2$ (376.1325): found: 376.1317.

Synthesis of 2,3-dibromo-5,6-bis(trimethylsilyl)pyrazine (50c)



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. NH_4Cl solution (5 mL), extracted with EtOAC (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **50c** as colorless solid (151 mg, 63%).

m.p.: 92.7 – 95.2 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 0.44 (s, 18H).

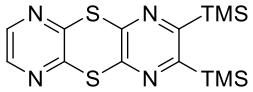
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 164.9, 146.7, -1.7.

IR (cm^{-1}): $\tilde{\nu}$ = 2957, 2899, 1459, 1409, 1320, 1250, 1234, 1205, 1190, 1100, 1056, 833, 755, 698.

MS (70 eV, EI) m/z (%) = 367 (39), 365 (15) [M-CH_3^+], 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 $C_9H_{15}N_2Br_2Si_2$ (364.9141): found: 364.9146.

Synthesis of 2,3-bis(trimethylsilyl)-[1,4]dithiino[2,3-*b*:5,6-*b*']dipyrazine (51a)



A suspension of 2,3-dichloro-5,6-bis(trimethylsilyl)pyrazine (**50a**; 291 mg, 1.0 mmol), K_2CO_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 EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_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 **51a** as yellow solid (139 mg, 38%).

m.p.: 101.6 – 103.0 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 8.19 (s, 2H), 0.37 (s, 18H).

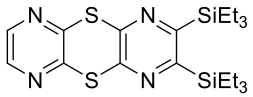
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 165.2, 151.8, 147.8, 141.3, 0.19.

IR (cm^{-1}): $\tilde{\nu}$ = 2953, 2897, 1456, 1421, 1408, 1348, 1277, 1248, 1179, 1146, 1088, 1062, 906, 835, 824, 755, 697, 660.

MS (70 eV, EI) *m/z* (%) = 366 (19), 365 (30), 364 (100) [M^+], 350 (10), 349 (36), 291 (20), 259 (14), 166 (63), 88 (14), 73 (48), 45 (11).

HRMS for $C_{14}H_{20}N_4S_2Si_2$ (364.0668): found: 364.0662.

Synthesis of 2,3-bis(triethylsilyl)-[1,4]dithiino[2,3-b:5,6-b']dipyrazine (51b)



A suspension of 2,3-dichloro-5,6-bis(triethylsilyl)pyrazine (**50b**; 1.76 g, 4.67 mmol), K_2CO_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 EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 8:1) yielding **51b** as yellow solid (1.07 g, 51%).

m.p.: 58.1 – 58.2 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) *δ*/ppm = 8.18 (s, 2H), 1.00 – 0.93 (m, 18H), 0.93 – 0.86 (m, 12H).

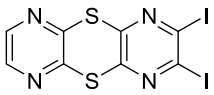
^{13}C-NMR (151 MHz, $CDCl_3$) *δ*/ppm = 164.5, 151.8, 147.5, 141.3, 7.6, 4.2.

IR (cm^{-1}): $\tilde{\nu}$ = 2953, 2933, 2873, 1538, 1500, 1454, 1414, 1378, 1345, 1277, 1235, 1180, 1146, 1076, 1061, 998, 970, 901, 844, 719, 704.

MS (70 eV, EI) *m/z* (%) = 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).

HRMS for $C_{20}H_{32}N_4S_2Si_2$ (448.1607): found: 448.1603.

Synthesis of 2,3-diiodo-[1,4]dithiino[2,3-*b*:5,6-*b*']dipyrazine (52a)



ICl (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 CH_2Cl_2 (1 mL) at 25 °C. The reaction mixture was stirred at 50 °C for 4 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_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.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 8.23 (s, 2H).

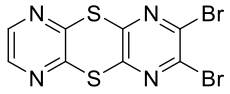
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 149.9, 149.0, 142.0, 126.0.

IR (cm^{-1}): $\tilde{\nu}$ = 2956, 2923, 2849, 1694, 1500, 1469, 1415, 1374, 1346, 1302, 1260, 1195, 1170, 1153, 1134, 1078, 1050, 910, 845.

MS (70 eV, EI) *m/z* (%) = 473 (11), 472 (100) [M^+], 166 (14), 88 (14), 84 (13), 83 (11), 70 (24).

HRMS for $C_8H_2I_2N_4S_2$ (471.7810): found: 471.7802.

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 CH_2Cl_2 (0.5 mL) at 25 °C. The reaction mixture was stirred for 20 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_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 **52b** as yellow solid (57 mg, 60%).

m.p.: 141.6 – 144.7 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ*/ppm = 8.24 (s, 2H).

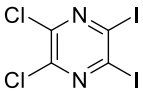
^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 149.7, 148.4, 142.1, 139.6.

IR (cm^{-1}): $\tilde{\nu}$ = 2956, 2922, 2853, 2604, 1919, 1462, 1418, 1349, 1264, 1197, 1175, 1139, 1078, 1052, 875, 849, 808, 735.

MS (70 eV, EI) *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 $C_8H_2Br_2N_4S_2$ (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 CH_2Cl_2 (10 mL) at 25 °C. The reaction mixture was stirred at 50 °C for 4 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 9:1) yielding **52c** as yellow solid (1.24 g, 62%).

m.p.: 127.6 – 131.9 °C.

^{13}C-NMR (75 MHz, $CDCl_3$) *δ*/ppm = 145.3, 125.3.

IR (cm^{-1}): $\tilde{\nu}$ = 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) [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 $C_4Cl_2I_2N_2$ (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 CH_2Cl_2-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-K_α radiation (λ = 0.71071 Å).

Data collection was performed with the CrysAlis CCD software;[77] CrysAlis RED software[78] was used for data reduction. Absorption correction using the SCALE3 ABSPACK multiscan method[79] was applied. The structures were solved with SHELXS-97,[80] refined with SHELXL-97[81] and finally checked using PLATON.[82] 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.

[77] CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).
[78] CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).
[79] SCALE3 ABSPACK – An Oxford Diffraction Program (1.0.4, gui:1.0.3) (C), Oxford Diffraction, Ltd., 2005.
[80] Sheldrick, G. M. (1997) SHELXS-97: *Program for Crystal Structure Solution*, University of Göttingen, Germany.
[81] Sheldrick, G. M. (1997) SHELXL-97: *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
[82] Spek, A. L. (1999) PLATON: *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.

Quinoxalines

Table 10: Details for X-ray data collection and structure refinement for compounds **15e** and **15m**.

	15e	**15m**
Empirical formula	$C_{30}H_{16}N_2O_2$	$C_{30}H_{16}N_2S_2$
Formula mass	436.45	468.57
T[K]	173(2)	173(2)
Crystal size [mm]	0.43 × 0.15 × 0.10	0.23 × 0.13 × 0.06
Crystal description	yellow rod	yellow block
Crystal system	monoclinic	Monoclinic
Space group	*P*21	*P*21/*c*
a [Å]	12.4504(11)	15.3378(10)
b [Å]	5.6333(4)	14.1481(8)
c [Å]	15.8276(11)	10.3748(5)
α [°]	90.0	90.0
β [°]	98.584(7)	94.934(5)
γ [°]	90.0	90.0
V [Å^3]	1097.66(15)	2243.0(2)
Z	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.321	1.388
μ [mm^{-1}]	0.084	0.260
F(000)	452	968
Θ range [°]	4.26 – 28.28	4.20 – 25.35
Index ranges	-13 ≤ *h* ≤ 13	-18 ≤ *h* ≤ 18
	-7 ≤ *k* ≤ 7	-16 ≤ *k* ≤ 17
	-16 ≤ *l* ≤ 21	-12 ≤ *l* ≤ 12
Reflns. collected	6781	14332
Reflns. obsd.	3072	2689
Reflns. unique	5140 (R_{int} = 0.0274)	4067 (R_{int} = 0.0782)
R_1, wR_2 (2σ data)	0.0572, 0.1008	0.0503, 0.0974
R_1, wR_2 (all data)	0.1064, 0.1279	0.0919, 0.1253
GOOF on F^2	0.984	1.033
Peak/hole [e Å^{-3}]	0.187 / -0.223	0.393 / -0.369

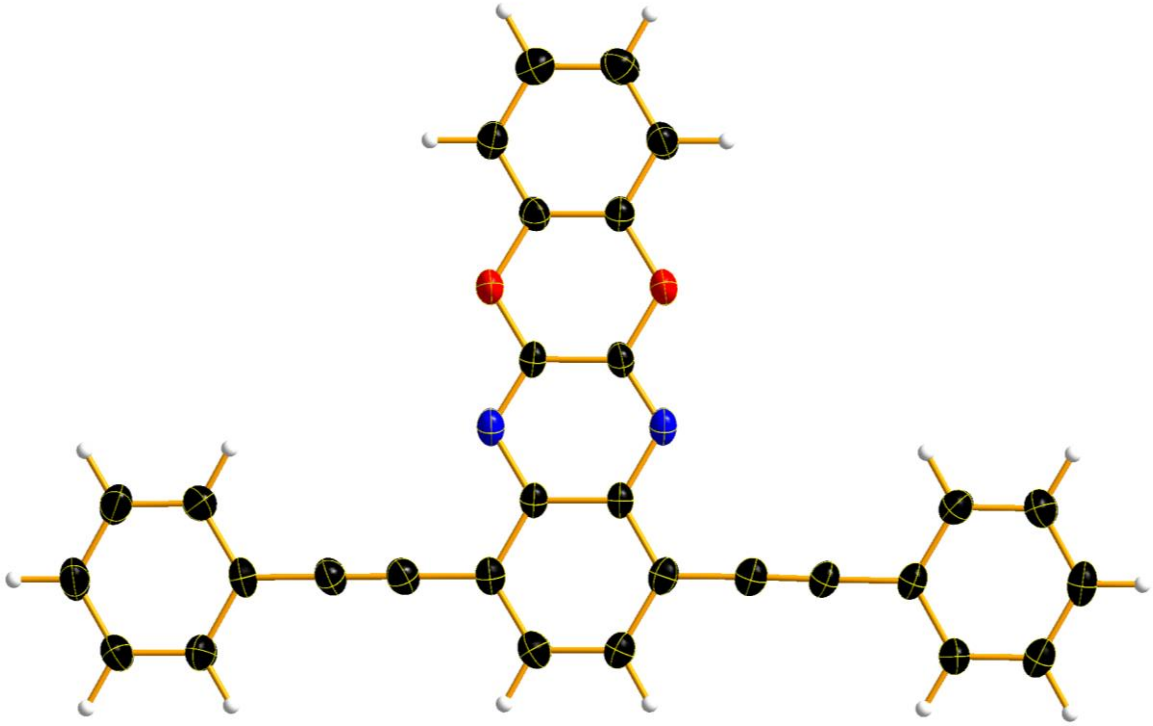


Figure 10: Molecular structure of compound **15e** in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50 % probability level.

Table 11: Selected bond lengths (Å) of compound **15e**.

C6 – N1	1.377(3)	C8 – C9	1.444(3)
C6 – C1	1.410(4)	C27 – C28	1.384(4)
C6 – C5	1.414(3)	C13 – C12	1.384(4)
C2 – C1	1.391(4)	C16 – C15	1.193(3)
C2 – C3	1.399(3)	C16 – C17	1.441(3)
O2 – C24	1.361(3)	C9 – C10	1.389(4)
O2 – C26	1.388(3)	C29 – C30	1.383(4)
C5 – N2	1.373(3)	C29 – C28	1.383(4)
C5 – C4	1.411(4)	C17 – C18	1.391(4)
C25 – C30	1.374(4)	C18 – C19	1.379(3)
C25 – O1	1.385(3)	C10 – C11	1.387(4)
C25 – C26	1.393(3)	C12 – C11	1.386(5)
C1 – C7	1.435(3)	C21 – C20	1.378(4)
C4 – C3	1.393(4)	C20 – C19	1.378(4)
C4 – C15	1.434(3)	C7 – C8	1.201(3)
O1 – C23	1.363(3)	C22 – C21	1.385(4)
N2 – C24	1.290(3)	C22 – C17	1.395(4)
N1 – C23	1.285(3)	C14 – C13	1.389(3)
C23 – C24	1.436(3)	C14 – C9	1.392(4)

C26 – C27	1.377(4)		

Table 12: Selected bond angles (°) of compound **15e**.

N1 – C6 – C1	119.3(2)	N2 – C24 – C23	121.8(2)
N1 – C6 – C5	120.4(2)	O2 – C24 – C23	121.5(2)
C1 – C6 – C5	120.2(3)	C12 – C13 – C14	119.5(3)
C1 – C2 – C3	120.7(3)	C15 – C16 – C17	179.7(4)
C24 – O2 – C26	117.1(2)	C10 – C9 – C14	119.6(2)
N2 – C5 – C4	118.7(2)	C10 – C9 – C8	119.9(3)
N2 – C5 – C6	121.1(3)	C14 – C9 – C8	120.5(3)
C4 – C5 – C6	120.2(3)	C16 – C15 – C4	179.1(3)
C30 – C25 – O1	118.2(2)	C30 – C29 – C28	120.6(3)
C30 – C25 – C26	120.3(3)	C18 – C17 – C22	119.4(2)
O1 – C25 – C26	121.5(2)	C18 – C17 – C16	120.5(3)
C2 – C1 – C6	119.0(2)	C22 – C17 – C16	120.0(3)
C2 – C1 – C7	120.4(3)	C25 – C30 – C29	119.2(3)
C6 – C1 – C7	120.6(3)	C29 – C28 – C27	120.2(3)
C3 – C4 – C5	118.5(2)	C19 – C18 – C17	120.1(3)
C3 – C4 – C15	120.8(3)	C11 – C10 – C9	120.0(3)
C5 – C4 – C15	120.6(3)	C13 – C12 – C11	120.5(3)
C23 – O1 – C25	117.6(2)	C12 – C11 – C10	120.0(3)
C4 – C3 – C2	121.4(3)	C20 – C21 – C22	120.1(3)
C24 – N2 – C5	116.9(2)	C19 – C20 – C21	120.3(3)
C23 – N1 – C6	116.5(2)	C20 – C19 – C18	120.3(3)
N1 – C23 – O1	116.1(2)	C8 – C7 – C1	177.7(3)
N1 – C23 – C24	123.2(2)	C21 – C22 – C17	119.8(3)
O1 – C23 – C24	120.7(2)	C13 – C14 – C9	120.3(3)
C27 – C26 – O2	118.0(2)	C7 – C8 – C9	177.7(3)
C27 – C26 – C25	120.4(3)	C26 – C27 – C28	119.3(3)
O2 – C26 – C25	121.6(2)	N2 – C24 – O2	116.6(2)

Table 13: Selected torsion angles (°) of compound **15e**.

N1 – C6 – C5 – N2	-0.5(4)	O1 – C25 – C26 – O2	-0.1(4)
C1 – C6 – C5 – N2	-179.5(2)	O2 – C26 – C27 – C28	179.8(2)
N1 – C6 – C5 – C4	178.2(2)	C25 – C26 – C27 – C28	1.4(4)
C1 – C6 – C5 – C4	-0.9(4)	C5 – N2 – C24 – O2	179.8(2)
C3 – C2 – C1 – C6	-0.4(4)	C5 – N2 – C24 – C23	-0.2(4)
C3 – C2 – C1 – C7	-179.7(3)	C26 – O2 – C24 – N2	-177.3(2)
N1 – C6 – C1 – C2	-178.1(2)	C26 – O2 – C24 – C23	2.7(3)
C5 – C6 – C1 – C2	1.0(4)	N1 – C23 – C24 – N2	-0.9(4)
N1 – C6 – C1 – C7	1.1(4)	O1 – C23 – C24 – N2	178.7(3)
C5 – C6 – C1 – C7	-179.8(2)	N1 – C23 – C24 – O2	179.1(3)

N2 – C5 – C4 – C3	178.9(2)	O1 – C23 – C24 – O2	-1.4(4)
C6 – C5 – C4 – C3	0.2(4)	C9 – C14 – C13 – C12	-1.0(4)
N2 – C5 – C4 – C15	2.0(4)	C13 – C14 – C9 – C10	0.2(4)
C6 – C5 – C4 – C15	-176.7(3)	C13 – C14 – C9 – C8	178.4(3)
C30 – C25 – O1 – C23	-178.4(2)	C21 – C22 – C17 – C18	0.2(4)
C26 – C25 – O1 – C23	1.5(4)	C21 – C22 – C17 – C16	179.5(3)
C5 – C4 – C3 – C2	0.3(4)	O1 – C25 – C30 – C29	-178.5(3)
C15 – C4 – C3 – C2	177.2(3)	C26 – C25 – C30 – C29	1.6(4)
C1 – C2 – C3 – C4	-0.2(4)	C28 – C29 – C30 – C25	-0.9(5)
C4 – C5 – N2 – C24	-177.9(2)	C30 – C29 – C28 – C27	0.4(5)
C6 – C5 – N2 – C24	0.8(4)	C26 – C27 – C28 – C29	-0.6(5)
C1 – C6 – N1 – C23	178.5(2)	C22 – C17 – C18 – C19	-0.8(5)
C5 – C6 – N1 – C23	-0.6(4)	C16 – C17 – C18 – C19	179.9(3)
C6 – N1 – C23 – O1	-178.4(2)	C14 – C9 – C10 – C11	0.1(4)
C6 – N1 – C23 – C24	1.2(4)	C8 – C9 – C10 – C11	-178.1(3)
C25 – O1 – C23 – N1	178.8(2)	C14 – C13 – C12 – C11	1.3(4)
C25 – O1 – C23 – C24	-0.8(3)	C13 – C12 – C11 – C10	-0.9(5)
C24 – O2 – C26 – C27	179.7(2)	C9 – C10 – C11 – C12	0.2(5)
C24 – O2 – C26 – C25	-2.0(4)	C17 – C22 – C21 – C20	0.3(5)
C30 – C25 – C26 – C27	-1.9(4)	C22 – C21 – C20 – C19	-0.2(5)
O1 – C25 – C26 – C27	178.2(3)	C21 – C20 – C19 – C18	-0.3(5)
C30 – C25 – C26 – O2	179.7(3)	C17 – C18 – C19 – C20	0.9(5)

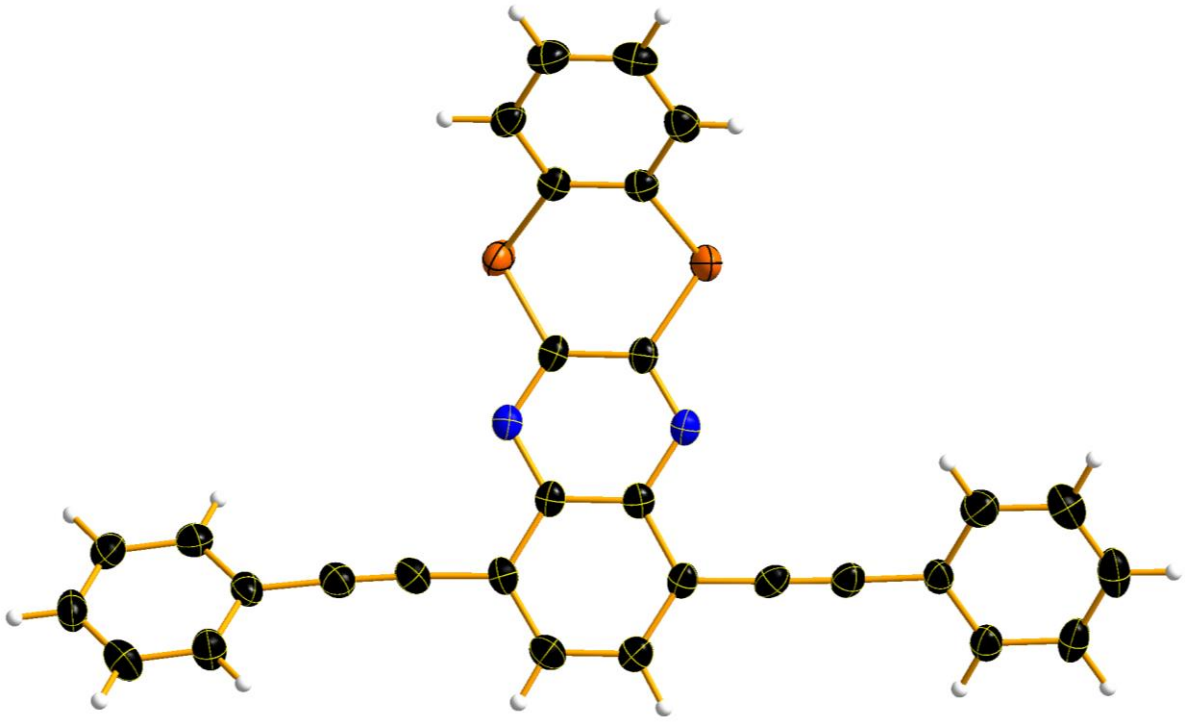


Figure 11: Molecular structure of compound **15m** in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50 % probability level.

Table 14: Selected bond lengths (Å) of compound **15m**.

S1 – C23	1.757(3)	C29 – C28	1.386(4)
S1 – C30	1.773(3)	C8 – C7	1.196(4)
S2 – C25	1.756(3)	C8 – C9	1.437(4)
S2 – C24	1.763(3)	C12 – C13	1.369(4)
N2 – C24	1.307(4)	C12 – C11	1.380(4)
N2 – C3	1.379(3)	C9 – C10	1.387(4)
N1 – C23	1.310(3)	C9 – C14	1.393(4)
N1 – C4	1.369(4)	C13 – C14	1.374(4)
C23 – C24	1.424(4)	C17 – C22	1.387(4)
C25 – C26	1.386(4)	C10 – C11	1.372(4)
C25 – C30	1.389(4)	C26 – C27	1.374(4)
C16 – C15	1.199(4)	C20 – C21	1.383(4)
C16 – C17	1.434(4)	C28 – C27	1.378(4)
C30 – C29	1.385(4)	C21 – C22	1.373(4)
C2 – C1	1.388(4)	C5 – C6	1.372(4)
C2 – C3	1.421(4)	C5 – C15	1.421(4)
C2 – C7	1.430(4)	C18 – C19	1.384(4)
C4 – C3	1.396(4)	C18 – C17	1.398(4)

C4 – C5	1.431(4)	C19 – C20	1.381(5)
C1 – C6	1.392(4)		

Table 15: Selected bond angles (°) of compound **15m**.

C23 – S1 – C30	102.4(1)	C13 – C12 – C11	119.4(3)
C25 – S2 – C24	101.7(1)	C10 – C9 – C14	118.0(3)
C24 – N2 – C3	116.5(2)	C10 – C9 – C8	120.2(3)
C23 – N1 – C4	116.6(2)	C14 – C9 – C8	121.7(3)
N1 – C23 – C24	122.0(3)	C12 – C13 – C14	120.7(3)
N1 – C23 – S1	115.1(2)	C22 – C17 – C18	119.2(3)
C24 – C23 – S1	122.8(2)	C22 – C17 – C16	120.3(3)
N2 – C24 – C23	122.4(2)	C18 – C17 – C16	120.5(3)
N2 – C24 – S2	116.1(2)	C13 – C14 – C9	120.6(3)
C23 – C24 – S2	121.2(2)	C11 – C10 – C9	121.0(3)
C26 – C25 – C30	119.4(3)	C8 – C7 – C2	176.4(3)
C26 – C25 – S2	117.9(2)	C10 – C11 – C12	120.3(3)
C30 – C25 – S2	122.7(2)	C27 – C26 – C25	120.6(3)
C15 – C16 – C17	175.7(3)	C5 – C6 – C1	121.6(3)
C29 – C30 – C25	120.0(3)	C19 – C20 – C21	119.7(3)
C29 – C30 – S1	117.3(2)	C27 – C28 – C29	120.3(3)
C25 – C30 – S1	122.6(2)	C26 – C27 – C28	119.9(3)
C1 – C2 – C3	117.9(3)	C22 – C21 – C20	120.2(3)
C1 – C2 – C7	120.5(3)	C21 – C22 – C17	120.7(3)
C3 – C2 – C7	121.6(2)	C16 – C15 – C5	178.7(3)
N1 – C4 – C3	121.6(2)	C19 – C18 – C17	119.6(3)
N1 – C4 – C5	118.3(2)	C20 – C19 – C18	120.6(3)
C3 – C4 – C5	120.1(3)	N2 – C3 – C4	120.8(2)
C2 – C1 – C6	121.5(3)	N2 – C3 – C2	118.7(2)
C6 – C5 – C15	122.2(2)	C4 – C3 – C2	120.5(2)
C6 – C5 – C4	118.3(3)	C30 – C29 – C28	119.7(3)
C15 – C5 – C4	119.5(3)	C7 – C8 – C9	177.7(3)

Table 16: Selected torsion angles (°) of compound **15m**.

C4 – N1 – C23 – C24	-0.4(4)	C5 – C4 – C3 – N2	-175.4(3)
C4 – N1 – C23 – S1	-176.7(2)	N1 – C4 – C3 – C2	-177.9(3)
C30 – S1 – C23 – N1	-150.2(2)	C5 – C4 – C3 – C2	3.0(4)
C30 – S1 – C23 – C24	33.5(3)	C1 – C2 – C3 – N2	177.0(3)
C3 – N2 – C24 – C23	-3.0(4)	C7 – C2 – C3 – N2	-1.8(4)
C3 – N2 – C24 – S2	170.4(2)	C1 – C2 – C3 – C4	-1.4(4)
N1 – C23 – C24 – N2	3.7(4)	C7 – C2 – C3 – C4	179.7(3)
S1 – C23 – C24 – N2	179.7(2)	C25 – C30 – C29 – C28	-2.1(4)
N1 – C23 – C24 – S2	-169.4(2)	S1 – C30 – C29 – C28	176.1(2)

S1 – C23 – C24 – S2	6.6(4)	C11 – C12 – C13 – C14	-0.2(5)
C25 – S2 – C24 – N2	143.6(2)	C19 – C18 – C17 – C22	0.5(4)
C25 – S2 – C24 – C23	-42.9(3)	C19 – C18 – C17 – C16	-177.0(3)
C24 – S2 – C25 – C26	-142.6(2)	C12 – C13 – C14 – C9	-0.4(5)
C24 – S2 – C25 – C30	39.9(3)	C10 – C9 – C14 – C13	0.7(4)
C26 – C25 – C30 – C29	0.4(4)	C8 – C9 – C14 – C13	178.7(3)
S2 – C25 – C30 – C29	177.9(2)	C14 – C9 – C10 – C11	-0.4(5)
C26 – C25 – C30 – S1	-177.7(2)	C8 – C9 – C10 – C11	-178.4(3)
S2 – C25 – C30 – S1	-0.2(3)	C9 – C10 – C11 – C12	-0.2(5)
C23 – S1 – C30 – C29	144.6(2)	C13 – C12 – C11 – C10	0.5(5)
C23 – S1 – C30 – C25	-37.2(3)	C30 – C25 – C26 – C27	1.4(4)
C23 – N1 – C4 – C3	-3.0(4)	S2 – C25 – C26 – C27	-176.3(2)
C23 – N1 – C4 – C5	176.1(3)	C15 – C5 – C6 – C1	-178.0(3)
C3 – C2 – C1 – C6	-0.2(4)	C4 – C5 – C6 – C1	1.3(4)
C7 – C2 – C1 – C6	178.7(3)	C2 – C1 – C6 – C5	0.2(5)
N1 – C4 – C5 – C6	177.9(3)	C18 – C19 – C20 – C21	-1.3(5)
C3 – C4 – C5 – C6	-2.9(4)	C30 – C29 – C28 – C27	2.0(4)
N1 – C4 – C5 – C15	-2.7(4)	C25 – C26 – C27 – C28	-1.4(5)
C3 – C4 – C5 – C15	176.5(3)	C29 – C28 – C27 – C26	-0.3(5)
C17 – C18 – C19 – C20	0.6(4)	C19 – C20 – C21 – C22	0.9(5)
C24 – N2 – C3 – C4	-0.5(4)	C20 – C21 – C22 – C17	0.2(5)
C24 – N2 – C3 – C2	-179.0(2)	C18 – C17 – C22 – C21	-0.9(5)
N1 – C4 – C3 – N2	3.7(4)	C16 – C17 – C22 – C21	176.6(3)

Tetrathiafulvalenes

Table 17: Details for X-ray data collection and structure refinement for compounds **27a** and **27b.**

	27a	**27b**
Empirical formula	$C_6H_2Br_2S_4$	$C_6H_2Br_2S_4$
Formula mass	362.12	362.12
T[K]	173(2)	173(2)
Crystal size [mm]	0.48 × 0.11 × 0.06	0.13 × 0.06 × 0.03
Crystal description	orange red rod	Orange red platelet
Crystal system	0rthorhombic	Monoclinic
Space group	*Pna*21	*C*2/*c*
a [Å]	18.5221(11)	19.4634(7)
b [Å]	3.9448(2)	3.9238(1)
c [Å]	26.9282(16)	12.6797(4)

	27a	**27b**
α [°]	90	90
β [°]	90	93.194(3)
γ [°]	90	90
V [Å^3]	1967.5(2)	966.85(5)
Z	8	4
$\rho_{calcd.}$ [g cm^{-3}]	2.445	2.488
μ [mm^{-1}]	9.026	9.184
F(000)	1376	688
Θ range [°]	4.38 – 28.28	4.19 – 30.50
Index ranges	-17 ≤ *h* ≤ 24	-27 ≤ *h* ≤ 27
	-5 ≤ *k* ≤ 5	-5 ≤ *k* ≤ 5
	-34 ≤ *l* ≤ 35	-13 ≤ *l* ≤ 18
Reflns. collected	14939	4480
Reflns. obsd.	3245	1274
Reflns. unique	4717 (R_{int} = 0.0853)	1476 (R_{int} = 0.0293)
R_1, wR_2 (2σ data)	0.0803, 0.1816	0.0238, 0.0492
R_1, wR_2 (all data)	0.1222, 0.2242	0.0316, 0.0526
GOOF on F^2	1.089	1.043
Peak/hole [e Å^{-3}]	5.850 / -1.146	0.494 / -0.573

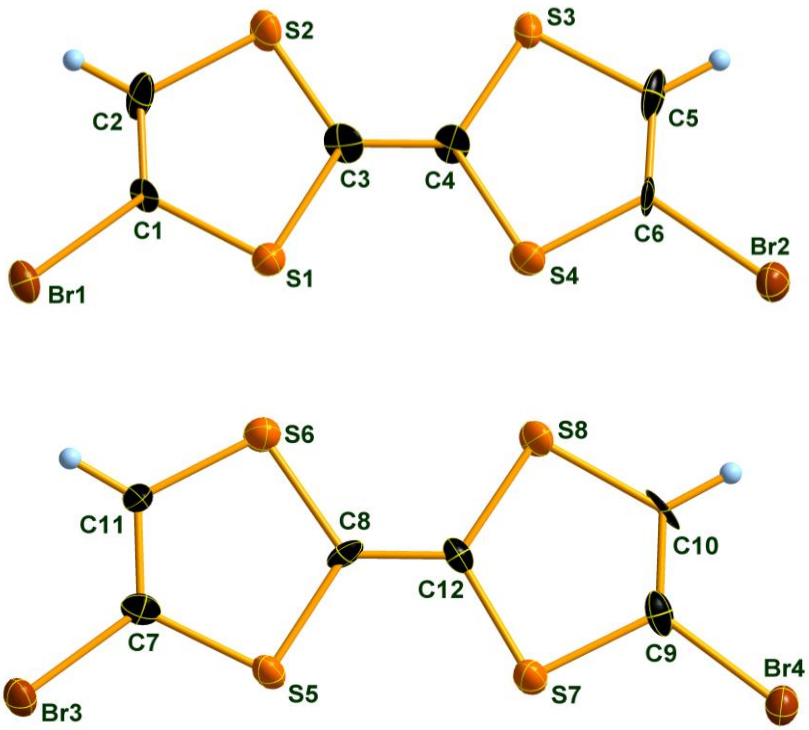


Figure 12: Molecular structure of compound **27a** in the crystal, view of the two crystallographically independent molecules, DIAMOND representation; thermal ellipsoids are drawn at 50 % probability level.

Table 18: Selected bond lengths (Å) of compound **27a**.

Br1 – C1	1.88(3)	S3 – C4	1.76(3)
Br3 – C7	1.86(3)	S8 – C12	1.76(3)
Br2 – C6	1.907(2)	S8 – C10	1.760(2)
Br4 – C9	1.864(2)	S4 – C6	1.709(2)
S7 – C12	1.74(2)	S4 – C4	1.75(2)
S7 – C9	1.774(2)	C4 – C3	1.34(3)
S5 – C7	1.73(2)	C2 – C1	1.29(4)
S5 – C8	1.746(2)	C6 – C5	1.32(2)
S2 – C3	1.757(2)	C7 – C11	1.39(4)
S2 – C2	1.78(3)	C9 – C10	1.30(2)
S6–C11	1.72(3)	C8–C12	1.37(3)
S6–C8	1.792(2)	S1–C3	1.771(2)
S1–C1	1.75(3)	S3–C5	1.755(2)

Table 19: Selected bond angles (°) of compound **27a**.

C12 – S7 – C9	92.6(1)	S7 – C9 – Br4	115.(1)
C7 – S5 – C8	95.9(1)	C2 – C1 – S1	120.(2)
C3 – S2 – C2	94.9(1)	C2 – C1 – Br1	125.(2)
C11 – S6 – C8	95.7(1)	S1 – C1 – Br1	114.7(2)
C1 – S1 – C3	94.0(1)	C12 – C8 – S5	122.0(2)
C5 – S3 – C4	95.4(1)	C12 – C8 – S6	124.0(2)
C12 – S8 – C10	93.7(9)	S5 – C8 – S6	114.0(9)
C6 – S4 – C4	93.6(1)	C9 – C10 – S8	117.2(1)
C3 – C4 – S4	123.(2)	C4 – C3 – S2	123.7(2)
C3 – C4 – S3	122.5(2)	C4 – C3 – S1	121.8(2)
S4 – C4 – S3	114.8(2)	S2 – C3 – S1	114.5(1)
C1 – C2 – S2	116.4(2)	C6 – C5 – S3	114.0(1)
C5 – C6 – S4	122.1(1)	C8 – C12 – S7	120.1(2)
C5 – C6 – Br2	122.1(1)	C8 – C12 – S8	122.8(2)
S4 – C6 – Br2	115.8(9)	S7 – C12 – S8	117.0(2)
C11 – C7 – S5	118.(2)	C7 – C11 – S6	116.6(2)
C11 – C7 – Br3	126.(2)	C10 – C9 – S7	119.5(1)
S5 – C7 – Br3	116.4(1)	C10 – C9 – Br4	125.4(1)

Table 20: Selected torsion angles (°) of compound **27a**.

C6 – S4 – C4 – C3	177.8(2)	S4 – C4 – C3 – S2	-178.1(1)
C6 – S4 – C4 – S3	-1.2(1)	S3 – C4 – C3 – S2	1.(3)
C5 – S3 – C4 – C3	-177.1(2)	S4 – C4 – C3 – S1	0.(3)
C5 – S3 – C4 – S4	1.9(1)	S3 – C4 – C3 – S1	178.7(1)
C3 – S2 – C2 – C1	0.6(2)	C2 – S2 – C3 – C4	179.2(2)
C4 – S4 – C6 – C5	-0.3(2)	C2 – S2 – C3 – S1	1.2(1)
C4 – S4 – C6 – Br2	178.8(1)	C1 – S1 – C3 – C4	179.8(2)
C8 – S5 – C7 – C11	-0.4(2)	C1 – S1 – C3 – S2	-2.1(1)
C8 – S5 – C7 – Br3	-177.8(1)	S4 – C6 – C5 – S3	1.6(2)
C12 – S7 – C9 – C10	-0.1(2)	Br2 – C6 – C5 – S3	-177.3(8)
C12 – S7 – C9 – Br4	178.4(1)	C4 – S3 – C5 – C6	-2.1(2)
S2 – C2 – C1 – S1	-2.0(3)	S5 – C8 – C12 – S7	2.0(2)
S2 – C2 – C1 – Br1	178.4(1)	S6 – C8 – C12 – S7	-178.5(1)
C3 – S1 – C1 – C2	2.7(22)	S5 – C8 – C12 – S8	178.6(1)
C3 – S1 – C1 – Br1	-178.0(1)	S6 – C8 – C12 – S8	-2.(2)
C7 – S5 – C8 – C12	178.1(2)	C9 – S7 – C12 – C8	176.7(2)
C7 – S5 – C8 – S6	-1.4(1)	C9 – S7 – C12 – S8	0.1(1)
C11 – S6 – C8 – C12	-177.2(2)	C10 – S8 – C12 – C8	-176.6(2)
C11 – S6 – C8 – S5	2.2(1)	C10 – S8 – C12 – S7	0.0(1)
S7 – C9 – C10 – S8	0.0(2)	S5 – C7 – C11 – S6	2.(2)
Br4 – C9 – C10 – S8	-178.3(8)	Br3 – C7 – C11 – S6	179.3(1)

C12 – S8 – C10 – C9	0.0(2)	C8 – S6 – C11 – C7	-2.5(2)

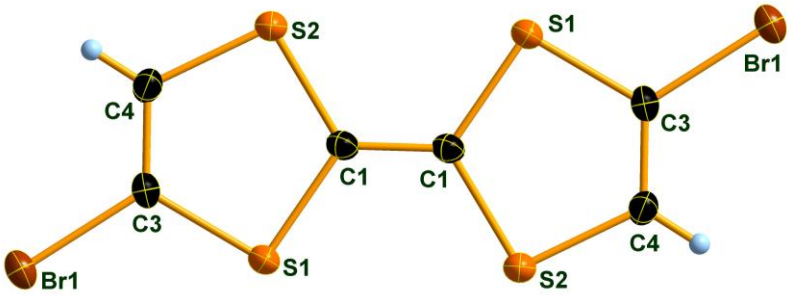


Figure 13: Molecular structure of compound **27b** in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50 % probability level.

Table 21: Selected bond lengths (Å) of compound **27b**.

Br1 – C3	1.882(2)	S2 – C1	1.766(2)
S1 – C3	1.741(2)	C3 – C4	1.329(3)
S1 – C1	1.762(2)	C1 – C1^{i}	1.343(4)
S2 – C4	1.739(2)		

Table 22: Selected bond angles (°) of compound **27b**.

C3 – S1 – C1	93.7(1)	C1^{i} – C1 – S1	122.7(3)
C4 – S2 – C1	95.1(1)	C1^{i} – C1 – S2	122.5(2)
C4 – C3 – S1	119.7(2)	S1 – C1 – S2	114.8(1)
C4 – C3 – Br1	123.4(2)	C3 – C4 – S2	116.6(2)
S1 – C3 – Br1	116.9(1)		

Table 23: Selected torsion angles (°) of compound **27b**.

C1 – S1 – C3 – C4	-1.6(2)	C3 – S1 – C1 – C1^{i}	-179.0(3)
C1 – S1 – C3 – Br1	178.9(1)	C3 – S1 – C1 – S2	1.95(14)
S1 – C3 – C4 – S2	0.6(3)	C4 – S2 – C1 – C1^{i}	179.2(3)
Br1 – C3 – C4 – S2	-179.9(1)	C4 – S2 – C1 – S1	-1.7(1)
C1 – S2 – C4 – C3	0.7(2)		

Table 24: Details for X-ray data collection and structure refinement for compounds **32g**, **35c** and **35d**.

	32g	**35c**	**35d**
Empirical formula	$C_9H_8O_2S_4$	$C_{30}H_{28}O_8S_4$	$C_{26}H_{18}N_2O_4S_4 \cdot (H_2O)_{0.11}$
Formula mass	276.39	644.76	552.65
T[K]	173(2)	173(2)	123(2)
Crystal size [mm]	0.22 × 0.17 × 0.11	0.37 × 0.26 × 0.11	0.23 × 0.17 × 0.13
Crystal description	orange red block	dark red block	red block
Crystal system	triclinic	Triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a [Å]	7.4753(3)	14.0157(6)	10.4341(5)
b [Å]	7.5350(3)	15.870(6)	10.5898(6)
c [Å]	20.4016(12)	16.2834(8)	13.6768(5)
α [°]	85.359(4)	61.914(5)	70.307(4)
β [°]	88.611(4)	72.352(4)	86.343(3)
γ [°]	89.943(4)	82.966(4)	64.261(5)
V [Å^3]	1145.04(9)	3044.2(11)	1275.57(11)
Z	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.603	1.407	1.439
μ [mm^{-1}]	0.804	0.361	0.409
F(000)	568	1344	570
Θ range [°]	4.21 – 25.35	4.17 – 25.35	4.09 – 25.35
Index ranges	-8 ≤ *h* ≤ 9	-16 ≤ *h* ≤ 13	-12 ≤ *h* ≤ 12
	-9 ≤ *k* ≤ 9	-18 ≤ *k* ≤ 19	-12 ≤ *k* ≤ 12
	-24 ≤ *l* ≤ 24	-19 ≤ *l* ≤ 19	-16 ≤ *l* ≤ 16
Reflns. collected	8066	22722	17681
Reflns. obsd.	3404	8250	3826
Reflns. unique	4130	11073	4642
	(R_{int} = 0.0347)	(R_{int} = 0.0284)	(R_{int} = 0.0344)
R_1, wR_2 (2σ data)	0.0619, 0.1421	0.0472, 0.1123	0.0307, 0.0748
R_1, wR_2 (all data)	0.0760, 0.1503	0.0689, 0.1271	0.0410, 0.0803
GOOF on F^2	1.088	1.023	1.032
Peak/hole [e Å^{-3}]	1.379 / -0.461	1.381 / -0.515	0.269 / -0.231

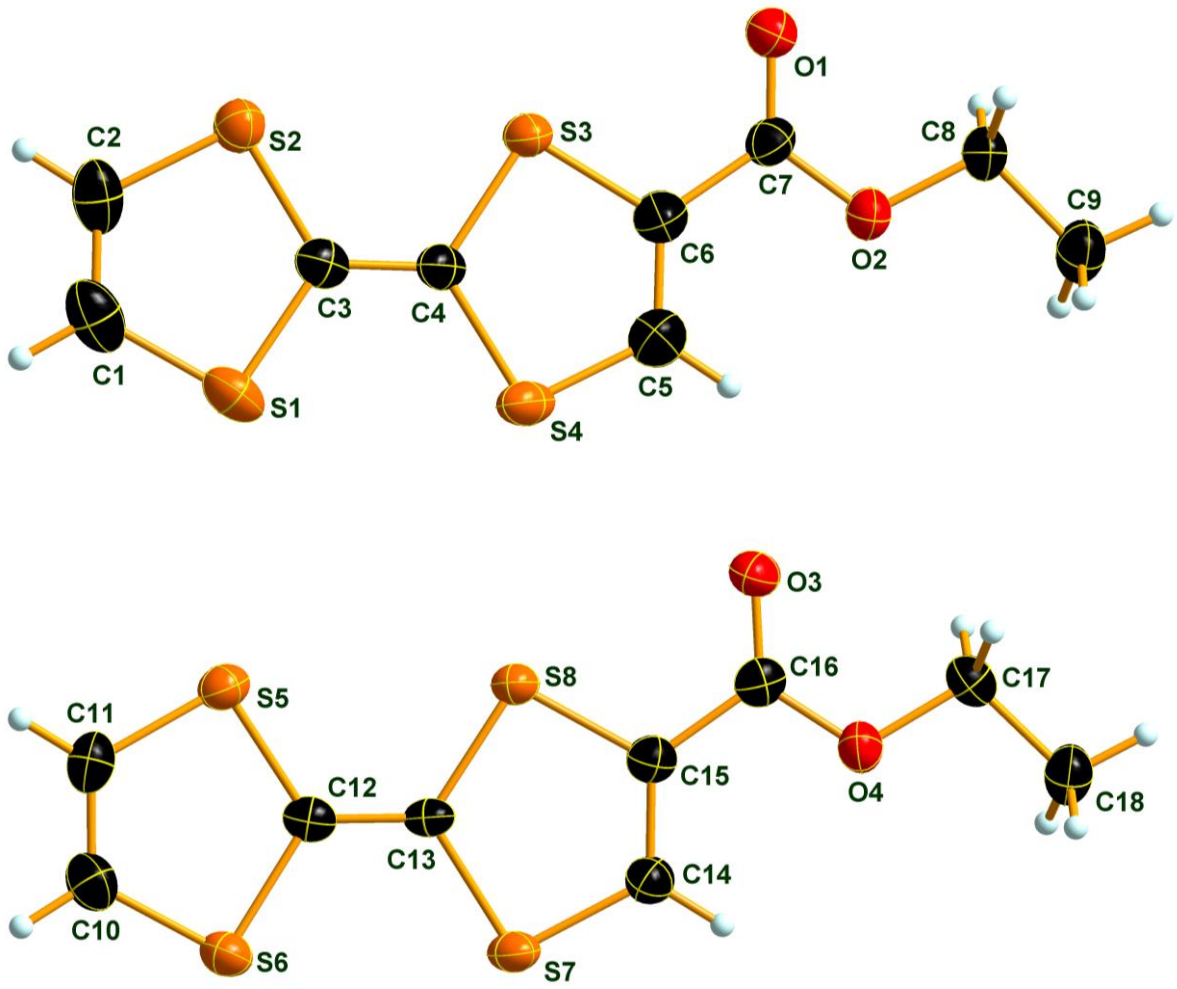


Figure 14: Molecular structure of compound **32g** in the crystal, view of the two crystallographically independent molecules, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.

Table 25: Selected bond lengths (Å) of compound **32g**.

S8 – C15	1.739(5)	C12 – C13	1.338(7)
S8 – C13	1.761(5)	O3 – C16	1.207(6)
S2 – C2	1.740(6)	C10 – C11	1.329(8)
S2 – C3	1.763(5)	C7 – C6	1.506(8)
S4 – C5	1.660(6)	C17 – C18	1.522(7)
S4 – C4	1.757(5)	C5 – C6	1.339(8)
S7 – C14	1.708(5)	C8 – C9	1.503(7)
S7 – C13	1.772(5)	C2 – C1	1.314(8)
S1 – C1	1.733(7)	O4 – C16	1.334(6)
S1 – C3	1.763(5)	O4 – C17	1.450(6)
S5 – C11	1.740(5)	O2 – C7	1.340(6)

S5 – C12	1.758(5)	O2 – C8	1.446(6)
S6 – C10	1.746(6)	C4 – C3	1.336(7)
S6 – C12	1.765(5)	C15 – C14	1.345(7)
S3 – C6	1.725(6)	C15 – C16	1.482(7)
S3 – C4	1.766(5)	O1 – C7	1.196(6)

Table 26: Selected bond angles (°) of compound **32g**.

C15 – S8 – C13	94.0(2)	C6 – C5 – S4	118.6(5)
C2 – S2 – C3	94.6(3)	C5 – C6 – C7	126.3(5)
C5 – S4 – C4	95.5(3)	C5 – C6 – S3	118.5(5)
C14 – S7 – C13	94.7(2)	C7 – C6 – S3	115.2(4)
C1 – S1 – C3	94.9(3)	O2 – C8 – C9	106.9(4)
C11 – S5 – C12	94.5(2)	C10 – C11 – S5	118.4(4)
C10 – S6 – C12	94.4(2)	C1 – C2 – S2	118.2(5)
C6 – S3 – C4	93.1(3)	C2 – C1 – S1	118.2(5)
C16 – O4 – C17	116.6(4)	C4 – C3 – S1	123.5(4)
C7 – O2 – C8	116.5(4)	S2 – C3 – S1	113.8(3)
C3 – C4 – S4	123.0(4)	O3 – C16 – O4	125.5(5)
C3 – C4 – S3	122.8(4)	O3 – C16 – C15	122.6(4)
S4 – C4 – S3	114.2(3)	O4 – C16 – C15	111.9(4)
C14 – C15 – C16	125.9(5)	C12 – C13 – S8	123.5(4)
C14 – C15 – S8	118.1(4)	C12 – C13 – S7	121.8(4)
C16 – C15 – S8	115.9(3)	S8 – C13 – S7	114.7(3)
C15 – C14 – S7	118.4(4)	C11 – C10 – S6	117.6(4)
C13 – C12 – S5	122.5(4)	O1 – C7 – O2	125.6(5)
C13 – C12 – S6	122.8(4)	O1 – C7 – C6	124.0(5)
S5 – C12 – S6	114.7(3)	O2 – C7 – C6	110.1(4)
C4 – C3 – S2	122.7(4)	O4 – C17 – C18	106.1(4)

Table 27: Selected torsion angles (°) of compound **32g**.

C5 – S4 – C4 – C3	-179.7(5)	S5 – C12 – C13 – S8	0.4(6)
C5 – S4 – C4 – S3	-0.9(3)	S6 – C12 – C13 – S8	-176.8(3)
C6 – S3 – C4 – C3	179.8(5)	S5 – C12 – C13 – S7	-178.9(3)
C6 – S3 – C4 – S4	1.0(3)	S6 – C12 – C13 – S7	3.8(6)
C13 – S8 – C15 – C14	0.0(4)	C15 – S8 – C13 – C12	179.7(4)
C13 – S8 – C15 – C16	179.6(4)	C15 – S8 – C13 – S7	-0.9(3)
C16 – C15 – C14 – S7	-178.5(4)	C14 – S7 – C13 – C12	-179.3(4)
S8 – C15 – C14 – S7	0.9(6)	C14 – S7 – C13 – S8	1.3(3)
C13 – S7 – C14 – C15	-1.3(4)	C12 – S6 – C10 – C11	3.6(5)

C11 – S5 – C12 – C13	-171.6(4)	C8 – O2 – C7 – O1	0.3(7)
C11 – S5 – C12 – S6	5.8(3)	C8 – O2 – C7 – C6	-173.4(4)
C10 – S6 – C12 – C13	171.6(4)	C16 – O4 – C17 – C18	-174.3(4)
C10 – S6 – C12 – S5	-5.9(3)	C4 – S4 – C5 – C6	0.3(6)
S4 – C4 – C3 – S2	177.9(3)	S4 – C5 – C6 – C7	-179.4(5)
S3 – C4 – C3 – S2	-0.7(6)	S4 – C5 – C6 – S3	0.4(7)
S4 – C4 – C3 – S1	-2.4(6)	O1 – C7 – C6 – C5	-174.6(6)
S3 – C4 – C3 – S1	178.9(3)	O2 – C7 – C6 – C5	-0.8(8)
C2 – S2 – C3 – C4	174.0(4)	O1 – C7 – C6 – S3	5.6(7)
C2 – S2 – C3 – S1	-5.7(3)	O2 – C7 – C6 – S3	179.4(4)
C1 – S1 – C3 – C4	-174.0(4)	C4 – S3 – C6 – C5	-0.9(5)
C1 – S1 – C3 – S2	5.7(3)	C4 – S3 – C6 – C7	178.9(4)
C17 – O4 – C16 – O3	-2.8(7)	C7 – O2 – C8 – C9	177.3(4)
C17 – O4 – C16 – C15	175.3(4)	S6 – C10 – C11 – S5	-0.1(6)
C14 – C15 – C16 – O3	176.6(5)	C12 – S5 – C11 – C10	-3.5(5)
S8 – C15 – C16 – O3	-2.9(6)	C3 – S2 – C2 – C1	3.5(5)
C14 – C15 – C16 – O4	-1.6(7)	S2 – C2 – C1 – S1	0.0(6)
S8 – C15 – C16 – O4	178.9(3)	C3 – S1 – C1 – C2	-3.5(5)

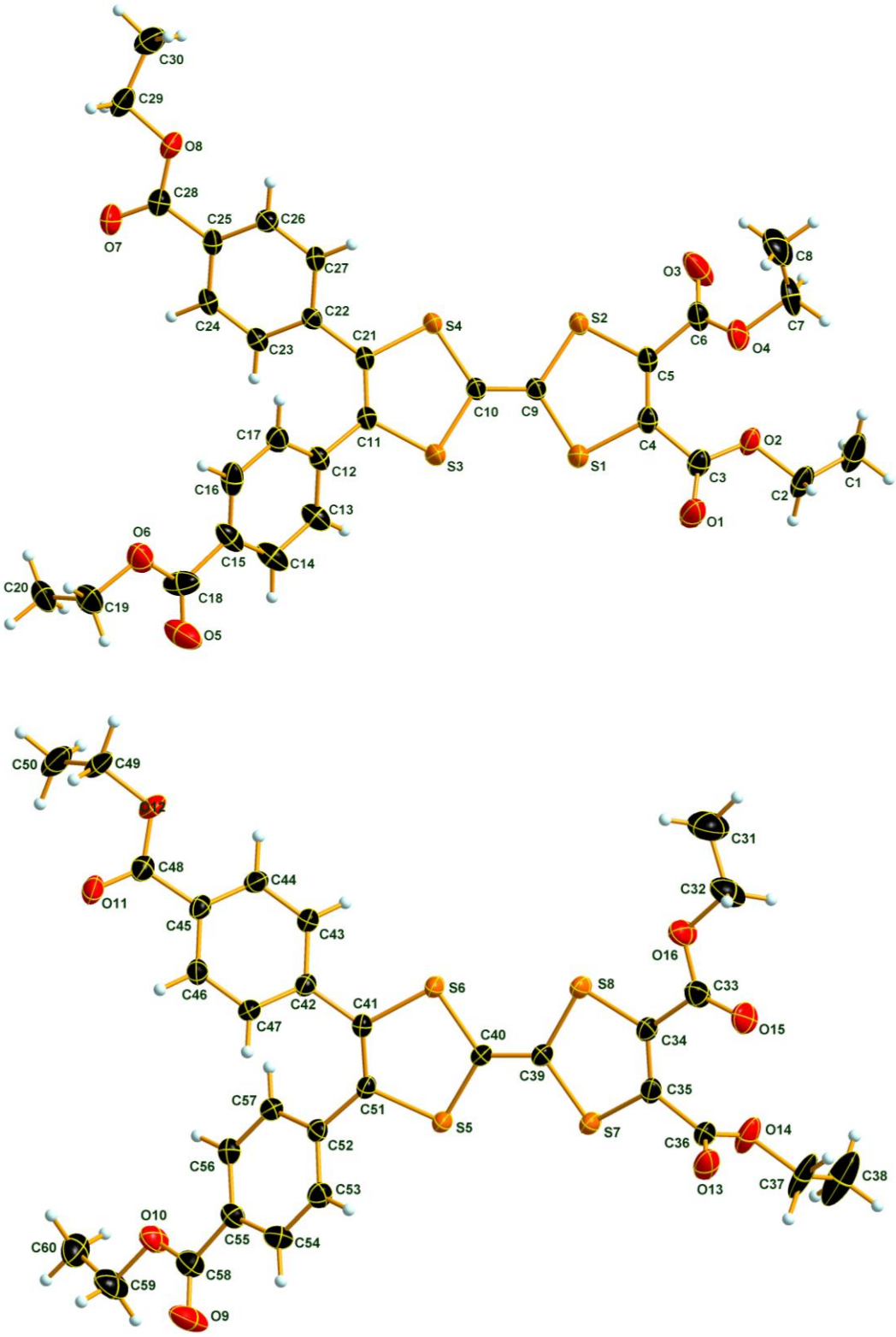


Figure 15: Molecular structure of compound **35c** in the crystal, view of the two crystallographically independent molecules, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.

Table 28: Selected bond lengths (Å) of compound **35c**.

S1 – C4	1.754(3)	C56 – C55	1.389(4)
S1 – C9	1.760(3)	C26 – C25	1.396(4)
S5 – C40	1.750(3)	O6 – C18	1.332(4)
S5 – C51	1.762(3)	O6 – C19	1.488(4)
S2 – C9	1.752(3)	C44 – C43	1.385(4)
S2 – C5	1.754(3)	O1 – C3	1.202(4)
S3 – C10	1.748(3)	O4 – C6	1.307(3)
S3 – C11	1.761(3)	O4 – C7	1.465(4)
S4 – C10	1.751(3)	O3 – C6	1.197(4)
S4 – C21	1.767(3)	C16 – C17	1.394(4)
S8 – C34	1.751(3)	C24 – C25	1.391(4)
S8 – C39	1.754(3)	C2 – C1	1.468(5)
S6 – C40	1.752(3)	C25 – C28	1.485(4)
S6 – C41	1.773(3)	O5 – C18	1.194(4)
S7 – C35	1.742(3)	C59 – C60	1.494(5)
S7 – C39	1.758(3)	C13 – C14	1.381(4)
C5 – C4	1.343(4)	C19 – C20	1.545(5)
C5 – C6	1.492(4)	C30 – C29	1.499(5)
C51 – C41	1.352(4)	C50 – C49	1.497(5)
C51 – C52	1.479(4)	C7 – C8	1.487(5)
O2 – C3	1.327(4)	C37 – C38	1.448(5)
O2 – C2	1.467(3)	C32 – C31	1.477(5)
O16 – C33	1.331(4)	C12 – C13	1.392(4)
O16 – C32	1.463(4)	C12 – C17	1.396(4)
C23 – C24	1.379(4)	C21 – C22	1.475(4)
C23 – C22	1.397(4)	O13 – C36	1.190(3)
C39 – C40	1.343(4)	O14 – C36	1.322(4)
C9 – C10	1.343(4)	O14 – C37	1.460(4)
C41 – C42	1.476(4)	C45 – C44	1.387(4)
C48 – O11	1.202(3)	C45 – C46	1.390(4)
C48 – O12	1.342(3)	C34 – C35	1.339(4)
C48 – C45	1.489(4)	C34 – C33	1.484(4)
C54 – C53	1.383(4)	C42 – C47	1.395(4)
C54 – C55	1.395(4)	C42 – C43	1.397(4)
C15 – C14	1.374(5)	C47 – C46	1.378(4)
C15 – C16	1.392(5)	O12 – C49	1.461(3)
C15 – C18	1.521(5)	C58 – O9	1.201(4)
C52 – C53	1.395(4)	C58 – O10	1.344(4)
C52 – C57	1.397(4)	C58 – C55	1.489(4)

C57 – C56	1.388(4)	O7 – C28	1.203(4)
C4 – C3	1.484(4)	C36 – C35	1.505(4)
O15 – C33	1.194(4)	O8 – C28	1.333(4)
C27 – C26	1.378(4)	O8 – C29	1.459(4)
C27 – C22	1.390(4)	O10 – C59	1.456(3)
C11 – C21	1.352(4)	C11 – C12	1.474(4)

Table 29: Selected bond angles (°) of compound **35c**.

C4 – S1 – C9	94.5(1)	O2 – C2 – C1	108.5(3)
C40 – S5 – C51	96.2(1)	C24 – C25 – C26	119.1(3)
C9 – S2 – C5	94.0(1)	C24 – C25 – C28	118.7(3)
C10 – S3 – C11	95.8(1)	C26 – C25 – C28	122.1(3)
C10 – S4 – C21	95.7(1)	O5 – C18 – O6	127.1(3)
C34 – S8 – C39	93.9(1)	O5 – C18 – C15	123.6(3)
C40 – S6 – C41	95.9(1)	O6 – C18 – C15	109.2(3)
C35 – S7 – C39	94.0(1)	O10 – C59 – C60	108.2(3)
C4 – C5 – C6	129.8(3)	C14 – C13 – C12	121.3(3)
C4 – C5 – S2	117.6(2)	O6 – C19 – C20	109.7(3)
C6 – C5 – S2	112.5(2)	C16 – C17 – C12	119.4(3)
C41 – C51 – C52	129.9(2)	O7 – C28 – O8	123.7(3)
C41 – C51 – S5	116.8(2)	O7 – C28 – C25	123.9(3)
C52 – C51 – S5	113.1(2)	O8 – C28 – C25	112.3(2)
C3 – O2 – C2	115.6(2)	O3 – C6 – O4	126.4(3)
C33 – O16 – C32	116.2(2)	O3 – C6 – C5	120.8(3)
C24 – C23 – C22	120.5(3)	O4 – C6 – C5	112.7(3)
C40 – C39 – S8	122.7(2)	O1 – C3 – O2	124.2(3)
C40 – C39 – S7	122.3(2)	O1 – C3 – C4	122.0(3)
S8 – C39 – S7	115.0(2)	O2 – C3 – C4	113.7(3)
C10 – C9 – S2	123.6(2)	C15 – C14 – C13	119.9(3)
C10 – C9 – S1	122.1(2)	O4 – C7 – C8	111.0(3)
S2 – C9 – S1	114.3(2)	C38 – C37 – O14	109.0(3)
C51 – C41 – C42	129.3(2)	O8 – C29 – C30	106.5(3)
C51 – C41 – S6	116.4(2)	O12 – C49 – C50	111.9(3)
C42 – C41 – S6	114.3(2)	O16 – C32 – C31	107.2(3)
O11 – C48 – O12	123.9(3)	C5 – C4 – C3	130.3(3)
O11 – C48 – C45	124.0(3)	C5 – C4 – S1	116.9(2)
O12 – C48 – C45	112.1(2)	C3 – C4 – S1	112.7(2)
C53 – C54 – C55	120.1(3)	C39 – C40 – S5	123.8(2)
C14 – C15 – C16	119.7(3)	C39 – C40 – S6	122.4(2)

C14 – C15 – C18	115.0(3)	S5 – C40 – S6	113.8(2)
C16 – C15 – C18	125.2(3)	C26 – C27 – C22	121.0(3)
C53 – C52 – C57	118.3(3)	C21 – C11 – C12	128.4(2)
C53 – C52 – C51	120.1(2)	C21 – C11 – S3	116.7(2)
C57 – C52 – C51	121.3(2)	C12 – C11 – S3	114.9(2)
C56 – C57 – C52	120.6(3)	C9 – C10 – S3	122.5(2)
C9 – C10 – S4	123.2(2)	C36 – O14 – C37	115.9(2)
S3 – C10 – S4	114.3(2)	C44 – C45 – C46	118.9(3)
C13 – C12 – C17	118.9(3)	C44 – C45 – C48	122.9(3)
C13 – C12 – C11	119.4(2)	C46 – C45 – C48	118.2(2)
C17 – C12 – C11	121.7(3)	C35 – C34 – C33	123.6(3)
C11 – C21 – C22	128.5(2)	C35 – C34 – S8	117.5(2)
C11 – C21 – S4	116.6(2)	C33 – C34 – S8	118.7(2)
C22 – C21 – S4	114.4(2)	C47 – C42 – C43	118.5(3)
C47 – C42 – C41	120.3(2)	C56 – C55 – C58	123.2(3)
C43 – C42 – C41	121.0(2)	C54 – C55 – C58	117.6(3)
C46 – C47 – C42	120.6(3)	C27 – C26 – C25	120.2(3)
C48 – O12 – C49	116.2(2)	C54 – C53 – C52	121.2(3)
O9 – C58 – O10	123.2(3)	C18 – O6 – C19	111.3(3)
O9 – C58 – C55	124.2(3)	C43 – C44 – C45	120.5(3)
O10 – C58 – C55	112.6(3)	C6 – O4 – C7	116.4(3)
C27 – C22 – C23	118.7(3)	C34 – C35 – C36	125.1(3)
C27 – C22 – C21	121.3(2)	C34 – C35 – S7	117.8(2)
C23 – C22 – C21	119.7(2)	C36 – C35 – S7	117.1(2)
O13 – C36 – O14	125.7(3)	C47 – C46 – C45	120.8(3)
O13 – C36 – C35	123.9(3)	C15 – C16 – C17	120.7(3)
O14 – C36 – C35	110.4(2)	C23 – C24 – C25	120.5(3)
C28 – O8 – C29	116.6(2)	O15 – C33 – O16	125.9(3)
C58 – O10 – C59	114.6(2)	O15 – C33 – C34	124.2(3)
C57 – C56 – C55	120.6(3)	O16 – C33 – C34	109.8(2)
C56 – C55 – C54	119.2(3)	C44 – C43 – C42	120.7(3)

Table 30: Selected torsion angles (°) of compound **35c**.

C9 – S2 – C5 – C4	12.3(2)	C52 – C57 – C56 – C55	-1.1(4)
C9 – S2 – C5 – C6	-169.3(2)	C57 – C56 – C55 – C54	1.1(4)
C40 – S5 – C51 – C41	4.0(2)	C57 – C56 – C55 – C58	-178.2(3)
C40 – S5 – C51 – C52	179.2(2)	C53 – C54 – C55 – C56	-0.3(4)
C34 – S8 – 39 – C40	168.8(2)	C53 – C54 – C55 – C58	179.1(3)
C34 – S8 – C39 – S7	-12.6(2)	O9 – C58 – C55 – C56	-173.0(3)
C35 – S7 – C39 – C40	-168.6(2)	O10 – C58 – C55 – C56	7.6(4)
C35 – S7 – C39 – S8	12.8(2)	O9 – C58 – C55 – C54	7.7(5)
C5 – S2 – C9 – C10	162.6(3)	O10 – C58 – C55 – C54	-171.8(3)
C5 – S2 – C9 – S1	-16.3(2)	C22 – C27 – C26 – C25	-0.6(4)
C4 – S1 – C9 – C10	-164.2(2)	C55 – C54 – C53 – C52	-0.5(4)
C4 – S1 – C9 – S2	14.8(2)	C57 – C52 – C53 – C54	0.5(4)
C52 – C51 – C41 – C42	9.8(5)	C51 – C52 – C53 – C54	-173.2(3)
S5 – C51 – C41 – C42	-175.9(2)	C46 – C45 – C44 – C43	-0.1(4)
C52 – C51 – C41 – S6	-171.9(2)	C48 – C45 – C44 – C43	-179.3(3)
S5 – C51 – C41 – S6	2.4(3)	C33 – C34 – C35 – C36	3.0(5)
C40 – S6 – C41 – C51	-7.4(2)	S8 – C34 – C35 – C36	179.1(2)
C40 – S6 – C41 – C42	171.1(2)	C33 – C34 – C35 – S7	-175.7(2)
C41 – C51 – C52 – C53	-148.9(3)	S8 – C34 – C35 – S7	0.4(3)
S5 – C51 – C52 – C53	36.7(3)	O13 – C36 – C35 – C34	90.3(4)
C41 – C51 – C52 – C57	37.6(4)	O14 – C36 – C35 – C34	-92.9(3)
S5 – C51 – C52 – C57	-136.9(2)	O13 – C36 – C35 – S7	-91.0(3)
C53 – C52 – C57 – C56	0.3(4)	O14 – C36 – C35 – S7	85.9(3)
C51 – C52 – C57 – C56	174.0(2)	C39 – S7 – C35 – C34	-7.9(2)
C6 – C5 – C4 – C3	-6.7(5)	C39 – S7 – C35 – C36	173.2(2)
S2 – C5 – C4 – C3	171.4(2)	C42 – C47 – C46 – C45	-1.7(4)
C6 – C5 – C4 – S1	177.9(2)	C44 – C45 – C46 – C47	1.3(4)
S2 – C5 – C4 – S1	-4.0(3)	C48 – C45 – C46 – C47	-179.5(2)
C9 – S1 – C4 – C5	-6.6(2)	C14 – C15 – C16 – C17	0.9(5)
C9 – S1 – C4 – C3	177.3(2)	C18 – C15 – C16 – C17	-177.8(3)
S8 – C39 – C40 – S5	178.7(2)	C22 – C23 – C24 – C25	0.6(4)
S7 – C39 – C40 – S5	0.1(4)	C32 – O16 – C33 – O15	-1.7(5)
S8 – C39 – C40 – S6	0.6(4)	C32 – O16 – C33 – C34	179.2(3)
S7 – C39 – C40 – S6	-178.0(2)	C35 – C34 – C33 – O15	-4.5(5)
C51 – S5 – C40 – C39	172.9(2)	S8 – C34 – C33 – O15	179.4(3)
C51 – S5 – C40 – S6	-8.9(2)	C35 – C34 – C33 – O16	174.6(3)
C41 – S6 – C40 – C39	-171.9(2)	S8 – C34 – C33 – O16	-1.5(3)
C41 – S6 – C40 – S5	9.9(2)	C45 – C44 – C43 – C42	-0.7(4)
C10 – S3 – C11 – C21	8.3(2)	C47 – C42 – C43 – C44	0.3(4)

C10 – S3 – C11 – C12	-173.2(2)	C41 – C42 – C43 – C44	-175.3(2)
S2 – C9 – C10 – S3	-176.6(2)	C3 – O2 – C2 – C1	177.3(3)
S1 – C9 – C10 – S3	2.2(4)	C23 – C24 – C25 – C26	-0.1(4)
S2 – C9 – C10 – S4	4.2(4)	C23 – C24 – C25 – C28	178.4(3)
S1 – C9 – C10 – S4	-177.0(2)	C27 – C26 – C25 – C24	0.1(4)
C11 – S3 – C10 – C9	171.7(2)	C27 – C26 – C25 – C28	-178.3(3)
C11 – S3 – C10 – S4	-9.0(2)	C19 – O6 – C18 – O5	-7.5(5)
C21 – S4 – C10 – C9	-173.7(2)	C19 – O6 – C18 – C15	174.9(3)
C21 – S4 – C10 – S3	7.1(2)	C14 – C15 – C18 – O5	7.2(5)
C21 – C11 – C12 – C13	146.7(3)	C16 – C15 – C18 – O5	-173.9(3)
S3 – C11 – C12 – C13	-31.6(3)	C14 – C15 – C18 – O6	-175.0(3)
C21 – C11 – C12 – C17	-35.3(4)	C16 – C15 – C18 – O6	3.8(4)
S3 – C11 – C12 – C17	146.4(2)	C58 – O10 – C59 – C60	-178.9(3)
C12 – C11 – C21 – C22	-11.5(5)	C17 – C12 – C13 – C14	0.4(4)
S3 – C11 – C21 – C22	166.8(2)	C11 – C12 – C13 – C14	178.5(3)
C12 – C11 – C21 – S4	177.0(2)	C18 – O6 – C19 – C20	-83.5(4)
S3 – C11 – C21 – S4	-4.7(3)	C15 – C16 – C17 – C12	2.1(4)
C10 – S4 – C21 – C11	-1.4(2)	C13 – C12 – C17 – C16	-2.7(4)
C10 – S4 – C21 – C22	-174.2(2)	C11 – C12 – C17 – C16	179.3(3)
O11 – C48 – C45 – C44	176.2(3)	C29 – O8 – C28 – O7	-0.5(5)
O12 – C48 – C45 – C44	-3.3(4)	C29 – O8 – C28 – C25	177.3(3)
O11 – C48 – C45 – C46	-3.1(4)	C24 – C25 – C28 – O7	4.3(5)
O12 – C48 – C45 – C46	177.5(2)	C26 – C25 – C28 – O7	-177.3(3)
C39 – S8 – C34 – C35	7.4(2)	C24 – C25 – C28 – O8	-173.5(3)
C39 – S8 – C34 – C33	-176.3(2)	C26 – C25 – C28 – O8	4.9(4)
C51 – C41 – C42 – C47	36.6(4)	C7 – O4 – C6 – O3	-6.0(5)
S6 – C41 – C42 – C47	-141.7(2)	C7 – O4 – C6 – C5	177.6(3)
C51 – C41 – C42 – C43	-147.8(3)	C4 – C5 – C6 – O3	148.5(3)
S6 – C41 – C42 – C43	33.9(3)	S2 – C5 – C6 – O3	-29.7(4)
C43 – C42 – C47 – C46	0.9(4)	C4 – C5 – C6 – O4	-34.9(4)
C41 – C42 – C47 – C46	176.6(2)	S2 – C5 – C6 – O4	146.9(2)
O11 – C48 – O12 – C49	0.6(4)	C2 – O2 – C3 – O1	-5.8(4)
C45 – C48 – O12 – C49	180.0(2)	C2 – O2 – C3 – C4	178.4(2)
C26 – C27 – C22 – C23	1.1(4)	C5 – C4 – C3 – O1	157.2(3)
C26 – C27 – C22 – C21	175.5(2)	S1 – C4 – C3 – O1	-27.3(4)
C24 – C23 – C22 – C27	-1.1(4)	C5 – C4 – C3 – O2	-26.9(4)
C24 – C23 – C22 – C21	-175.6(3)	S1 – C4 – C3 – O2	148.6(2)
C11 – C21 – C22 – C27	149.6(3)	C16 – C15 – C14 – C13	-3.3(5)
S4 – C21 – C22 – C27	-38.8(3)	C18 – C15 – C14 – C13	175.6(3)

C11 – C21 – C22 – C23	-36.1(4)	C12 – C13 – C14 – C15	2.6(5)
S4 – C21 – C22 – C23	135.6(2)	C6 – O4 – C7 – C8	83.3(4)
C37 – O14 – C36 – O13	-3.1(5)	C36 – O14 – C37 – C38	172.6(4)
C37 – O14 – C36 – C35	-179.8(3)	C28 – O8 – C29 – C30	-169.1(3)
O9 – C58 – O10 – C59	1.1(5)	C48 – O12 – C49 – C50	-85.6(3)
C55 – C58 – O10 – C59	-179.5(3)	C33 – O16 – C32 – C31	170.3(3)

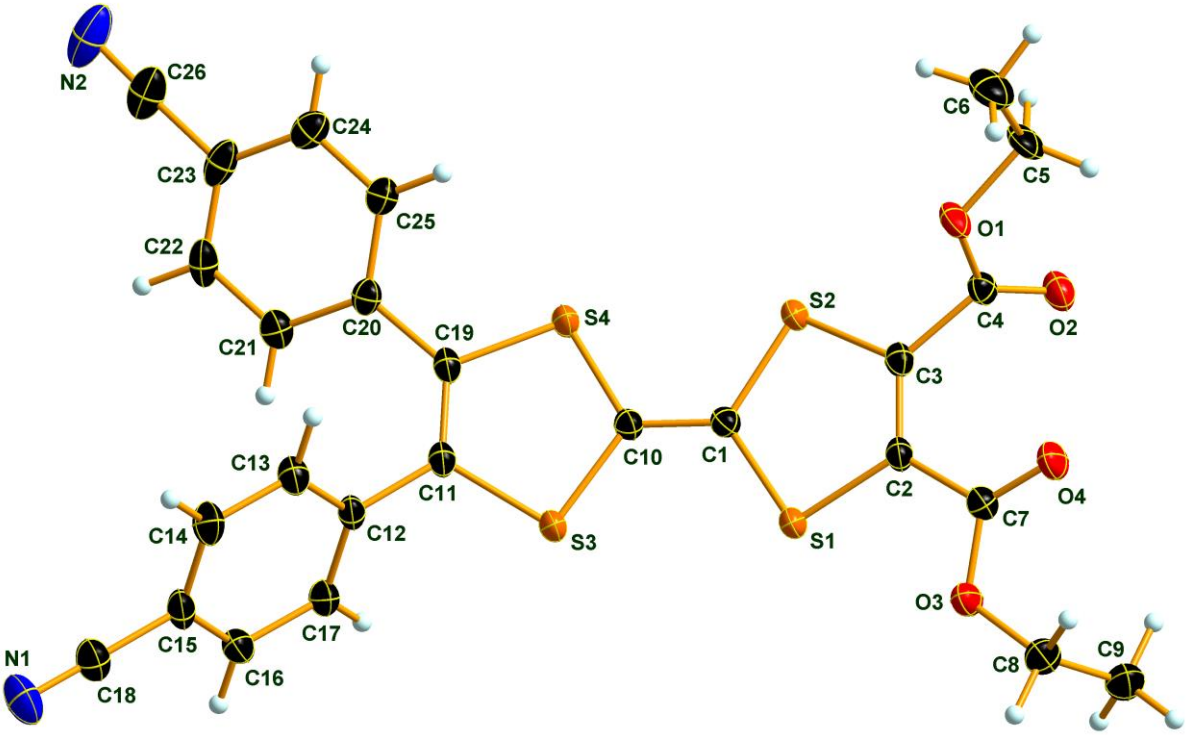


Figure 16: Molecular structure of compound **35d** in the crystal, DIAMOND representation; thermal ellipsoids are drawn at 50% probability level.

Table 31: Selected bond lengths (Å) of compound **35d**.

S1 – C1	1.757(2)	C22 – C23	1.390(3)
S1 – C2	1.760(2)	C2 – C7	1.480(3)
S4 – C10	1.758(2)	C21 – C20	1.397(3)
S4 – C19	1.766(2)	C20 – C25	1.400(3)
S3 – C10	1.751(2)	C15 – C14	1.395(3)
S3 – C11	1.763(2)	C15 – C18	1.445(3)
S2 – C3	1.739(2)	C18 – N1	1.148(3)
S2 – C1	1.761(2)	C25 – C24	1.380(3)
O1 – C4	1.329(2)	C14 – C13	1.382(3)
O1 – C5	1.460(2)	C5 – C6	1.495(3)
O2 – C4	1.194(2)	C24 – C23	1.390(3)
C3 – C2	1.347(2)	C23 – C26	1.448(3)

C3 – C4	1.505(2)	N2 – C26	1.145(3)
O4 – C7	1.203(2)	C12 – C13	1.393(3)
C10 – C1	1.343(3)	C16 – C15	1.388(3)
C11 – C19	1.350(3)	C16 – C17	1.393(3)
C11 – C12	1.478(2)	C8 – C9	1.501(3)
O3 – C7	1.338(2)	C19 – C20	1.476(2)
O3 – C8	1.465(2)	C22 – C21	1.388(3)
C12 – C17	1.391(3)		

Table 32: Selected bond angles (°) of compound **35d**.

C1 – S1 – C2	94.37(8)	C21 – C20 – C25	118.66(17)
C10 – S4 – C19	95.27(8)	C21 – C20 – C19	121.49(17)
C10 – S3 – C11	95.08(8)	C25 – C20 – C19	119.69(16)
C3 – S2 – C1	94.60(8)	C16 – C15 – C14	120.64(17)
C4 – O1 – C5	116.43(14)	C16 – C15 – C18	120.17(18)
C2 – C3 – C4	126.06(16)	C14 – C15 – C18	119.18(18)
C2 – C3 – S2	117.92(14)	N1 – C18 – C15	179.0(2)
C4 – C3 – S2	116.01(13)	C24 – C25 – C20	120.72(18)
C1 – C10 – S3	124.70(14)	C13 – C14 – C15	119.48(18)
C1 – C10 – S4	121.45(14)	O1 – C5 – C6	106.95(16)
S3 – C10 – S4	113.83(10)	C14 – C13 – C12	120.39(18)
C10 – C1 – S1	123.68(14)	C25 – C24 – C23	120.1(2)
C10 – C1 – S2	121.53(14)	O4 – C7 – O3	125.48(17)
S1 – C1 – S2	114.8(1)	O4 – C7 – C2	124.12(17)
C19 – C11 – C12	126.20(16)	O3 – C7 – C2	110.40(15)
C19 – C11 – S3	117.19(14)	C24 – C23 – C22	120.09(18)
C12 – C11 – S3	116.62(13)	C24 – C23 – C26	119.4(2)
C7 – O3 – C8	115.94(14)	C22 – C23 – C26	120.53(19)
C17 – C12 – C13	119.92(17)	N2 – C26 – C23	178.5(3)
C17 – C12 – C11	120.76(16)	C11 – C19 – S4	116.34(14)
C13 – C12 – C11	119.32(16)	C20 – C19 – S4	114.49(13)
O2 – C4 – O1	126.09(16)	C21 – C22 – C23	119.74(19)
O2 – C4 – C3	125.22(16)	C12 – C17 – C16	119.99(18)
O1 – C4 – C3	108.63(15)	C3 – C2 – C7	124.34(16)
C15 – C16 – C17	119.57(18)	C3 – C2 – S1	117.11(14)
O3 – C8 – C9	110.75(16)	C7 – C2 – S1	118.54(13)
C11 – C19 – C20	128.84(17)	C22 – C21 – C20	120.72(19)

Table 33: Selected torsion angles (°) of compound **35d**.

C1 – S2 – C3 – C2	6.8(2)	C15 – C16 – C17 – C12	-0.7(3)
C1 – S2 – C3 – C4	-174.6(1)	C4 – C3 – C2 – C7	1.4(3)
C11 – S3 – C10 – C1	163.6(2)	S2 – C3 – C2 – C7	179.9(1)
C11 – S3 – C10 – S4	-14.8(1)	C4 – C3 – C2 – S1	-179.0(1)
C19 – S4 – C10 – C1	-163.8(2)	S2 – C3 – C2 – S1	-0.4(2)
C19 – S4 – C10 – S3	14.6(1)	C1 – S1 – C2 – C3	-6.2(2)
S3 – C10 – C1 – S1	2.3(2)	C1 – S1 – C2 – C7	173.5(1)
S4 – C10 – C1 – S1	-179.4(1)	C23 – C22 – C21 – C20	0.5(3)
S3 – C10 – C1 – S2	-177.5(1)	C22 – C21 – C20 – C25	0.0(3)
S4 – C10 – C1 – S2	0.7(2)	C22 – C21 – C20 – C19	-175.5(2)
C2 – S1 – C1 – C10	-169.3(2)	C11 – C19 – C20 – C21	-31.3(3)
C2 – S1 – C1 – S2	10.6(1)	S4 – C19 – C20 – C21	141.8(2)
C3 – S2 – C1 – C10	169.1(2)	C11 – C19 – C20 – C25	153.2(2)
C3 – S2 – C1 – S1	-10.8(1)	S4 – C19 – C20 – C25	-33.7(2)
C10 – S3 – C11 – C19	9.3(2)	C17 – C16 – C15 – C14	0.9(3)
C10 – S3 – C11 – C12	-171.0(1)	C17 – C16 – C15 – C18	-178.6(2)
C19 – C11 – C12 – C17	122.1(2)	C21 – C20 – C25 – C24	-0.3(3)
S3 – C11 – C12 – C17	-57.5(2)	C19 – C20 – C25 – C24	175.3(2)
C19 – C11 – C12 – C13	-57.3(3)	C16 – C15 – C14 – C13	-0.6(3)
S3 – C11 – C12 – C13	123.1(2)	C18 – C15 – C14 – C13	178.8(2)
C5 – O1 – C4 – O2	0.0(3)	C4 – O1 – C5 – C6	-166.3(2)
C5 – O1 – C4 – C3	-177.4(2)	C15 – C14 – C13 – C12	0.1(3)
C2 – C3 – C4 – O2	69.5(3)	C17 – C12 – C13 – C14	0.0(3)
S2 – C3 – C4 – O2	-109.1(2)	C11 – C12 – C13 – C14	179.5(2)
C2 – C3 – C4 – O1	-113.1(2)	C20 – C25 – C24 – C23	0.1(3)
S2 – C3 – C4 – O1	68.3(2)	C8 – O3 – C7 – O4	1.0(3)
C7 – O3 – C8 – C9	-84.9(2)	C8 – O3 – C7 – C2	-178.6(1)
C12 – C11 – C19 – C20	-7.2(3)	C3 – C2 – C7 – O4	9.6(3)
S3 – C11 – C19 – C20	172.5(2)	S1 – C2 – C7 – O4	-170.0(2)
C12 – C11 – C19 – S4	179.9(1)	C3 – C2 – C7 – O3	-170.8(2)
S3 – C11 – C19 – S4	-0.5(2)	S1 – C2 – C7 – O3	9.5(2)
C10 – S4 – C19 – C11	-8.6(2)	C25 – C24 – C23 – C22	0.4(3)
C10 – S4 – C19 – C20	177.4(1)	C25 – C24 – C23 – C26	-178.9(2)
C13 – C12 – C17 – C16	0.2(3)	C21 – C22 – C23 – C24	-0.7(3)
C11 – C12 – C17 – C16	-179.2(2)	C21 – C22 – C23 – C26	178.6(2)

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
*i*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

mmol	millimole
MS	mass spectronomy
MW	microwave
NMP	*N*-methyl-2-pyrrolidine
NMR	nuclear magnetic resonance
o	ortho
p	para
PEPPSI-*i*Pr	[1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene](3-chloropyridyl)palladium(II) dichloride
Ph	phenyl
q	quartet
R	organic substituent
s	singlet
sat	saturated
SPhos	2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl
t	triplet
*t*Bu	*tert*-butyl
TFA	trifluoroacetic acid
tfp	tris-(2-furyl)phosphine
THF	tetrahydrofuran
TLC	thin layer chromatography
TMP	2,2,6,6-tetramethylpiperidyl
TMS	trimethylsilyl
Tos	4-toluenesulfonyl
TP	typical procedure
TTF	tetrathiafulvalene
W	Watt