Synthesis of aromatic monopyrrolo-tetrathiafulvalene derivatives with variable degree of π-conjugation

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By

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A word of thanks to my family for supporting me throughout my journey and patience.

Declaration

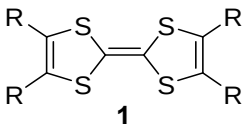
I, Sibusiso Nicko Mncwangi, hereby declare that my thesis entitled “Synthesis of aromatic monopyrrolo-tetrathiafulvalene derivatives with variable degree of π-conjugation” was composed by myself, that the research work contained herein is my own except where explicitly stated otherwise in the text and references, and that this work has not been submitted for any other degree or processional qualification except as specified. The research was performed under the supervision of Prof. Vladimir Azov.

Sibusiso N. Mncwangi: _____ signature

Date: 29 Novermber 2021

Abstract

Tetrathiafulvalene (TTF, **1**) and its derivatives have attracted much interest and found widespread applications in molecular, supramolecular and materials chemistry.[1] Monopyrrolo-tetrathiafulvalenes (MPTTF, **59**) possess more extended π–system in comparison to the parent TTF **1**, better π–stacking capability and, therefore, they are capable of forming stronger charge-transfer complexes with molecular acceptors.[2]



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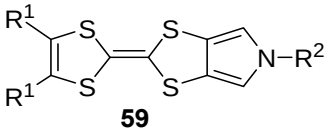

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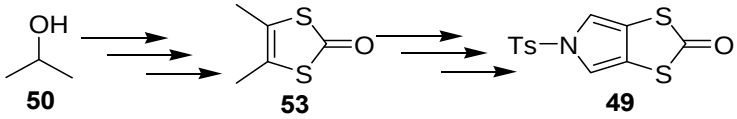
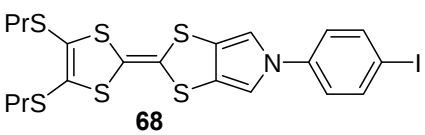
R = H, alkyl, aryl, ...

Herein, I present an efficient synthesis of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49**, the key intermediate in the synthesis of monopyrrolo-tetrathiafulvalenes **59**, which is performed using the inexpensive starting material and the convenient purification methods and permits the scale-up to 100 g. This modified synthetic pathway offers the benefits of avoiding the use of toxic carbon tetrachloride for radical bromination, of mercury derivatives for transchalcogenation and does not require complex chromatographic separation for most of the reaction steps.



50 **53** **49**

Thiopropyl-substituted MPTTF **59** (R^1=SPr, R^2=H) were tested in Cu(I)-catalyzed Ullman *N*-arylation reaction to prepare aromatic *bis*-MPTTF derivatives with various degree of π–conjugation between two TTF units. For that, spacer groups such as phenyl, biphenyl, stilbene should have been used. Unfortunately, only mono coupling products resulted instead of the desired di-coupling products. Three new MPTTF derivatives with the appended phenyl **69**, biphenyl **70** and stilbene **72** residues have been prepared and characterised within the framework of this project. Unfortunately, attempts to prepare di-azobenzene-MPTTF derivative **73** using several possible methods (Ullmann coupling between MPTTF **59** and 4,4'-dibromoazobenzene **62**, diazo coupling of aromatic amino MPTTF derivative **66**) were also unsuccessful.



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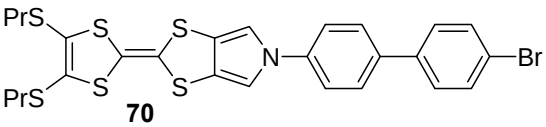
SPr = thioproply



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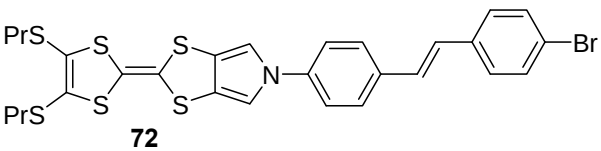

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List of abbreviation

AB	Azobenzene
AIBN	Azobisisobutyronitrile
Ag/AgCl	Standard silver/silver chloride electrode
BEDT-TTF	Bis(ethylenedithio)tetrathiafulvalene
BPTTF	Bispyrrolotetrathiafulvalene
BuLi	n-Butyllithium
$(BzO)_2$	Benzoyl peroxide
$CBPQT^{4+}$	Cyclobis(paraquat-*p*-phenylene)
CPK	*Cory-Pauling-Koltun*
DACH	(+/-)-*trans*-1,2-Diaminocyclohexane
DBU	1,8-Diazobicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DDQ	2,3-Dichloro-5,6-dicyano quinone
DMF	*N,N*-Dimethylformamide
DMIT	1,3-Dithiole-2-thione
DMSO	Dimethyl sulfoxide
DNP	1,5-dioxynaphthalene
Et_4NBr	Tetraethylammonium bromide
eq.	Equivalent
IR	Infrared
KO^tBu	Potassium tert-butoxide
LDA	Diisopropylamide
LiO^tBu	Lithium tert-butoxide
MeOH	Methanol
MIM's	Mechanical interlocked molecules
MPTTF	Monopyrrolotetrathiafulvalene
NaO^tBu	Sodium tert-butoxide
NaOEt	Sodium ethoxide

NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinamide
NEt_3	Triethylamine
NMR	Nuclear Magnetic Resonance
NOR	Not Or
$P(OEt)_3$	Triethyl phosphite
PPh_3	Triphenylphosphine
ppm	Parts per million
Pyrrolo-TTF	Pyrrolo-tetrathiafulvalene
p-TTF-phanes	Tetrathiafulvalenoparacyclophanes
R_f	Retention factor
TCNE	Tetracyanoethylene
TCNQ	Tetracyanoquinodimethene
TMS	Tetramethylsilane
TMTSF	Tetramethyltetraselenafulvalene
TTF	Tetrathiafulvalene
TTF-AB	Tetrathiafulvalene-azobenzene
TTF-phanes	Tetrathiafulvalenoparacyclophanes
TTF-TCNQ	Tetrathiafulvalene-tetracyanoquinodimethene
TTF^+	Tetrathiafulvalene radical-cation
TTF^{2+}	Tetrathiafulvalene dication
TTFVs	Tetrathiafulvalene vinylogues
TTN	Tetrathianaphthalene
THF	Tetrahydrofuran
Ts	Tosyl
TsNHNa	Toluene sulphonamide monosodium salt
TNT	2,4,6-Trinitrotoluene
TNB	1,3,5-Trinitrobenzene
UV; UV/Vis	Ultraviolet; Ultraviolet-visible

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Chapter 1 : Tetrathiafulvalenes

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Chapter 1 : Tetrathiafulvalenes

1.1 Introduction

Tetrathiafulvalene (TTF, **1**) and its derivatives[3] have attracted much attention from chemists and material scientists due to their fascinating structure, low potential redox properties and electron-donating capabilities. Since the discovery of TTF it has been widely used in several fields of chemistry and material science.[4] Overall, TTF derivatives belong to very active area of research[5] being successfully employed as building blocks for multiple applications in different research fields, as depicted in Figure 1.1. This planar electron rich molecule has proved itself to be a popular molecular building block in the preparation of conductive and superconductive organic phases[6] and charge-transfer salts, e.g., with tetracyanoquinodimethene (TCNQ, **3**),[7] in supramolecular chemistry and in chemistry of macrocyclic compounds, as well as in the field of material chemistry[8] and molecular systems such as sensors, polymers, receptors. TTFs found application in interlocked supramolecular architectures, such as catenanes and rotaxanes, forming redox-switchable molecular devices, in which they play a role of molecular motors.[9] TTFs were used as building blocks for redox-active molecular receptors or chemosensors that are capable of selective binding of certain molecular targets.[10] Such versatility is attained due to the possibility of stepwise reversible oxidation of TTFs, in which first a radical-cation and then a dication are being formed. Their properties differ dramatically from the parent non-oxidized TTF, since they lose electron-donating nature and become electron acceptors upon oxidation.

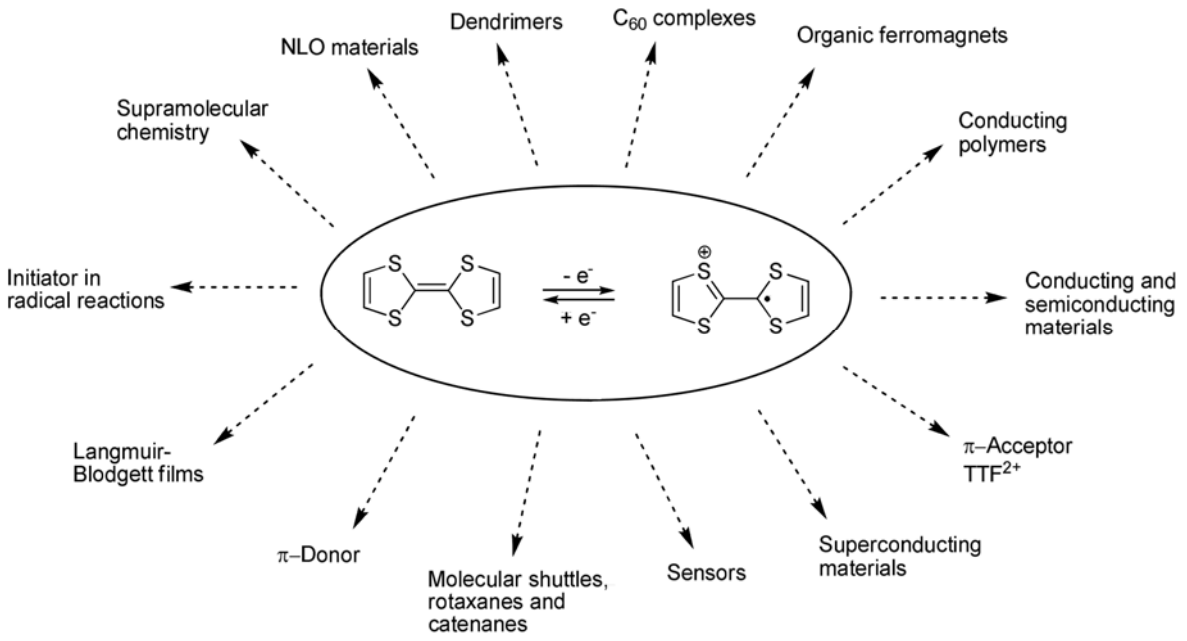


Figure 1.1: Applications of TTF derivatives in various research fields.

1.2 Discovery of tetrathiafulvalenes

In 1960s dithiolonium salt was synthesized by *Klingsberg*[11] and later used by *Wudl* in 1970 to prepare tetrathiafulvalene (TTF, **1**) by its dimerization.[12] It was soon established that TTF can be used as a donor molecule: in 1972 it was demonstrated to be an organic conducting material in the form of its chloride salt.[13] The discovery of the tetrathiafulvalene-tetracyanoquinodimethene (TTF-TCNQ) conductive phase[14] in 1973 (Figure 1.2), the first electric current conducting organic phase motivated chemists all around the world to study TTFs and their derivatives. The preparation of Bechgaard salts, conductive and even superconductive organic materials, started in 1979 using selenium-TTF (TMTSF, **2**)[15] and paved the way for the extensive application of TTFs in materials chemistry.[16] Later TTFs started to be broadly used as building block for macrocyclic and supramolecular chemistry due to their appealing electrochemical properties.[17–21]

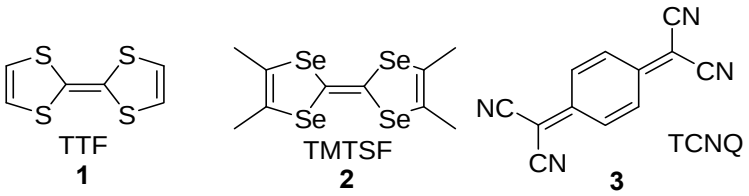


Figure 1.2: The structures of TTF **1**, TMTSF **2** and TCNQ **3** molecules.

1.3 Properties of tetrathiafulvalenes and its derivatives

The 14-electron π-system allows for TTF to be almost a planar molecule, but it lacks proper conjugation, since both of the rings do not fulfil the Hückel 4n+2 rule to become aromatic. TTF has a C_{2v} symmetry with a boat-shape structure (Figure 1.3) in its non-oxidized state, although it inversion barrier is very shallow and boat-type distortion from planarity is minimal. Therefore, it is considered that in the non-oxidized state TTF has three localized double bonds with some degree of conjugation between them. The oxidation of TTF occurs reversibly first to form the radical cation (TTF^{+}, **1a**$^{\cdot}$), which has a planar D_{2h} symmetry due to its aromatization, and then the dication ($TTF^{2+,}$ **1b**), which has a twisted conformation with D_2 symmetry[16–18] and free rotation around the central bond. Aromatization of heterocyclic rings upon oxidation leads to low oxidation potentials and to high thermodynamic stability of both radical-cationic and dicationic species (Figure 1.3).

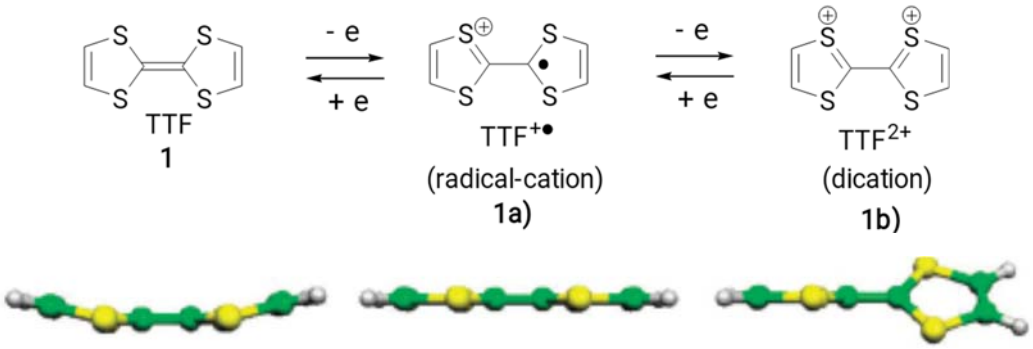


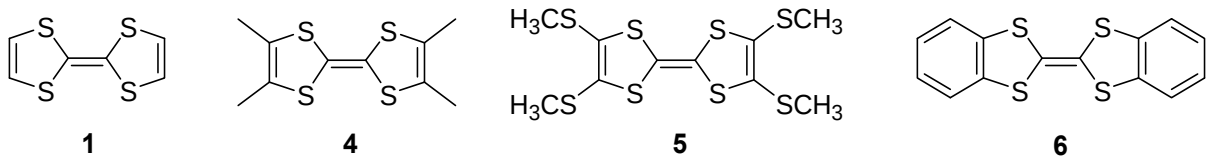
Figure 1.3: TTF **1** is a redox active molecule that can be reversibly stepwise oxidized to give the radical-cation (TTF^{+}, **1a**) ($E_{1/2}$ = 0.34 V) and the dication (TTF^{2+}, **1b**) ($E_{1/2}$ = 0.78 V). Oxidation potentials are measured with Ag/AgCl as a reference electrode in acetonitrile (CH_3CN).[14] Minimal energy conformations are shown below each of the oxidation states of the TTF molecule.[16]

Parent TTF **1** has proven to be quite flexible in its non-oxidized state, and the degree of its boat-type distortion depends on the donor-acceptor and π-π interactions in the crystalline phases. Due to the free rotation around the central bond in the dicationic state TTF^{2+} (Figure 1.3), asymmetrically substituted TTF that exist in either *cis*- or *trans*-isomeric form in its ground state will undergo isomerization upon oxidation-reduction cycle. The electron-withdrawing and electron-donating substituents affect the oxidation potentials of TTFs.[18,22] Thio-alkyl groups are very easy to introduce, but they act as electron-withdrawing groups, thus raising the TTF oxidation potential. Alkyl groups are electron-donating and lower oxidation potentials of TTFs, but such derivatives are much more difficult to prepare. Finally, extension of the TTF backbone can be performed by fusing it to unsaturated cycles or heterocycles, such as benzene or pyrrole rings. The symmetric and asymmetric substitution of TTF moiety allows its integration into different types of molecular structures.[17–21]

TTF is known to be a strong electron donor due to its electron-rich extended π–system.[16–20] Self-assembly between the molecules of TTF and TTF-derivatives occurs due to S ··· S and π-π attractive interactions.[20] TTF's forms conductive solid phases with different charge transfer acceptors, such as DDQ (dichlorodicyanoquinone), TCNE (tetracyanoethylene) and TCNQ,[14,16,19] or upon partial oxidation of TTF molecules in the solid phase.[13] In the dicationic form both rings possess six electrons in their π-systems, giving them an aromatic character and making them particularly stable. Dicationc species TTF^{2+} with both oxidised rings can be easily isolated in crystalline form due to the effective resonance stabilization.[20] By changing oxidation state, it is possible to induce structural and conformational switching in TTF-containing molecules.[1] During synthetic protocols that make use of strong oxidising agent and strong acidic condition, TTF molecules were found to be unstable due to their over oxidation followed by decomposition.

Synthetic chemistry of TTFs is quite flexible and different types of substituents can be attached to the TTF backbone, as well as the backbone itself can be modified by fusing it with

additional ring systems (Figure 1.4).[16] As mentioned above, different substituents influence redox and electron-donating properties of TTFs. Alkyl substituents, like in **4**, make TTF derivatives more electron-rich than parent TTF **1**, thus lowering their oxidation potential and making them better electron donors. On the contrary, thioalkyl substituents, like in **5**, act as electron-withdrawing groups because of the inductive effect of the sulphur atoms along the C-S bonds, thus increasing oxidation potential of TTFs and diminishing their electron-donating properties. Fusion of the TTF backbone with other π–systems, like in **6**, may both increase or decrease the electron-donating properties of TTFs, depending on the π–electron density of the rings fused with the TTF backbone.



1 **4** **5** **6**

Figure 1.4: The parent TTF structure **1** and TTF-derivatives with different substituent such as methyl **4**, thiomethyl **5**, and with two fused benzene rings **6**.

It is necessary to note that TTF derivatives **4, 5** and **6** are all symmetric structures with a plane of symmetry going along the central double bond perpendicular to the plane of the molecule. If they have only one substituent on each side, e.g., compound **4** would have only one methyl group on each cycle, then the formation of *cis*- and *trans*-isomers would be possible. Due to similarity in their properties and polarities separation of such stereoisomers is quite difficult and often impossible. In addition, slow *cis/trans*-isomerization takes place upon light irradiation or under slightly acidic conditions and scrambling of *cis/trans* isomers is imminent upon oxidation-reduction cycle.

There are multiple pathways that can be used for the preparation of tetrathiafulvalene and its derivatives (Figure 1.5).[23,24] The most practical pathways are **A**, **B** and **C** because of their efficiency, universality, accessibility of starting materials and good yields. The cross-coupling pathway **B** that is based on 1,3-dithiole-2-chalcogenones and mediated by triethyl phosphite was used as the method of choice for the synthesis of pyrrolo-tetrathiafulvalene (pyrrolo-TTF) and its derivatives during previous investigations[23] held in our group.

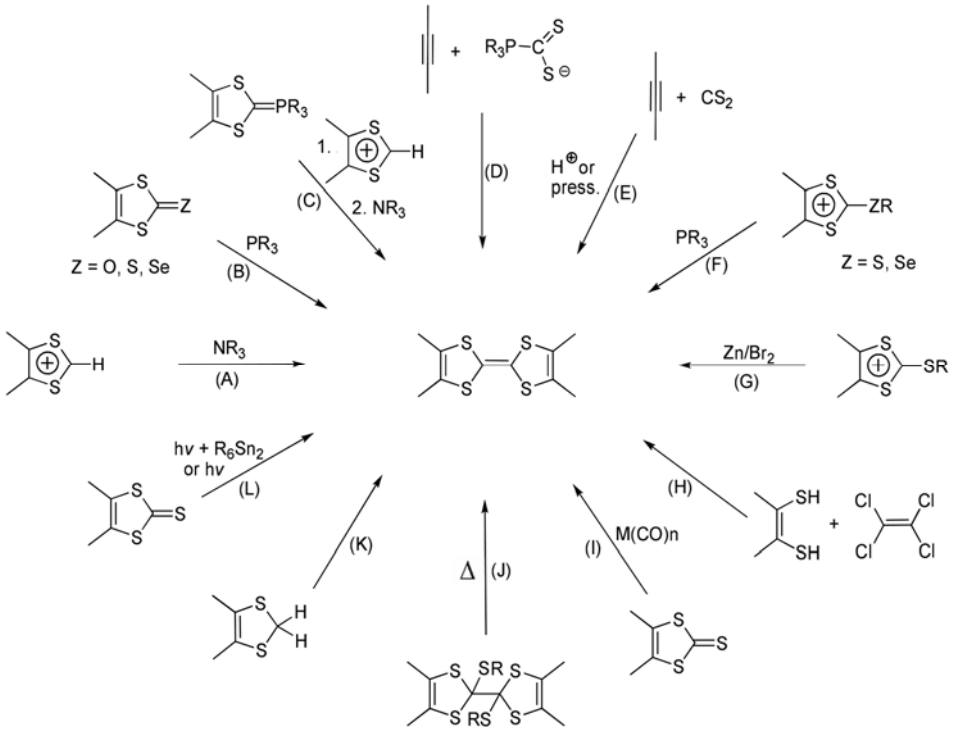


Figure 1.5: Different synthetic routes of the preparations of TTF and its derivatives.[24]

1.4 Synthetic approaches to the preparation of tetrathiafulvalenes

Extensive work has been done to develop efficient pathways for the preparation of substituted TTFs and their incorporation into supramolecular and macrocyclic systems. Initially, scientists encountered problems when it came to selective functionalization of TTF which possesses D_{2h} symmetry with four identical attachment sides (Figure 1.6). Several TTF building blocks have been prepared in the past years and multiple problems concerning functionalization of the TTF core have been solved. TTFs with two or four thiolate groups have proved to be excellent building blocks for the synthesis of supramolecular TTF-based molecular architectures by simple alkylation of the thiolate anions generated by removal of cyanoethyl protective groups under basic conditions.[25,26]

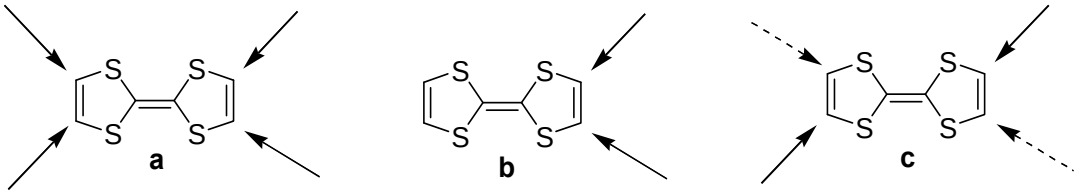
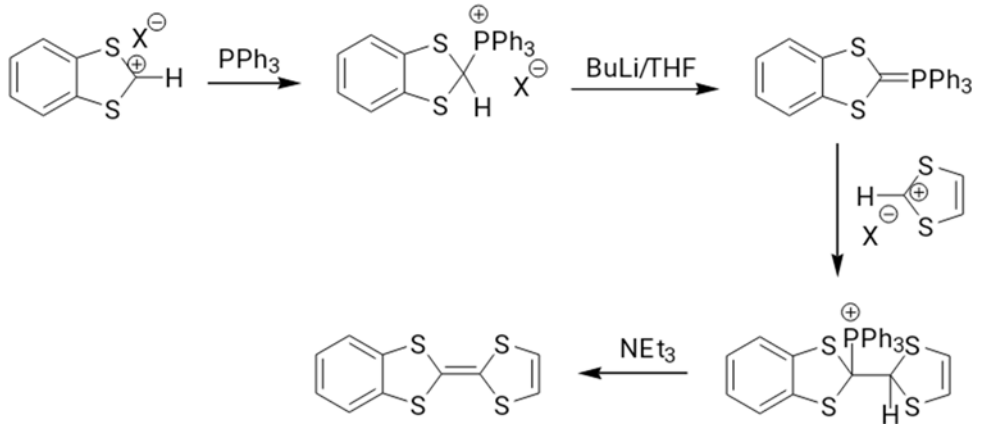


Figure 1.6: Symmetry properties of substituted TTF for four-fold symmetrical (**a**), two-fold asymmetrical (**b**) and pseudo-symmetrical (**c**) substitution patterns.

In the 1990's, the development of TTF chemistry was challenging when it came to modification of parent-TTF **1** for application in charge transfer and electric conducting materials. Most strategies were focused on the parent-TTF looking at peripheral position and the preparation of derivatives with extended π-electron donor system.[27,28] In the past years, a remarkable progress on the electron donor organic metals based on radical cation salt of unsymmetrical TTF-derivatives have been achieved for several applications.[29] In 1992 *Misaki* presented synthesis and investigation of the *bis*-fused TTF molecules and its analogues, in which several asymmetric TTF-fused donors displayed the formation of charge-transfer complexes that were found to be stable at low temperatures. Synthesis of symmetrical TTF-based donors is often achieved by triethyl phosphite-induced coupling reaction, which forms the TTF backbone by the formation of the central C=C bond. When this synthetic approach is applied to the synthesis of unsymmetrical TTFs with different substituents on each side of it, symmetric product is also formed together with the target asymmetric product.[30,31] Asymmetric TTF derivatives are often difficult to prepare due to the lack of general synthetic method and purification.

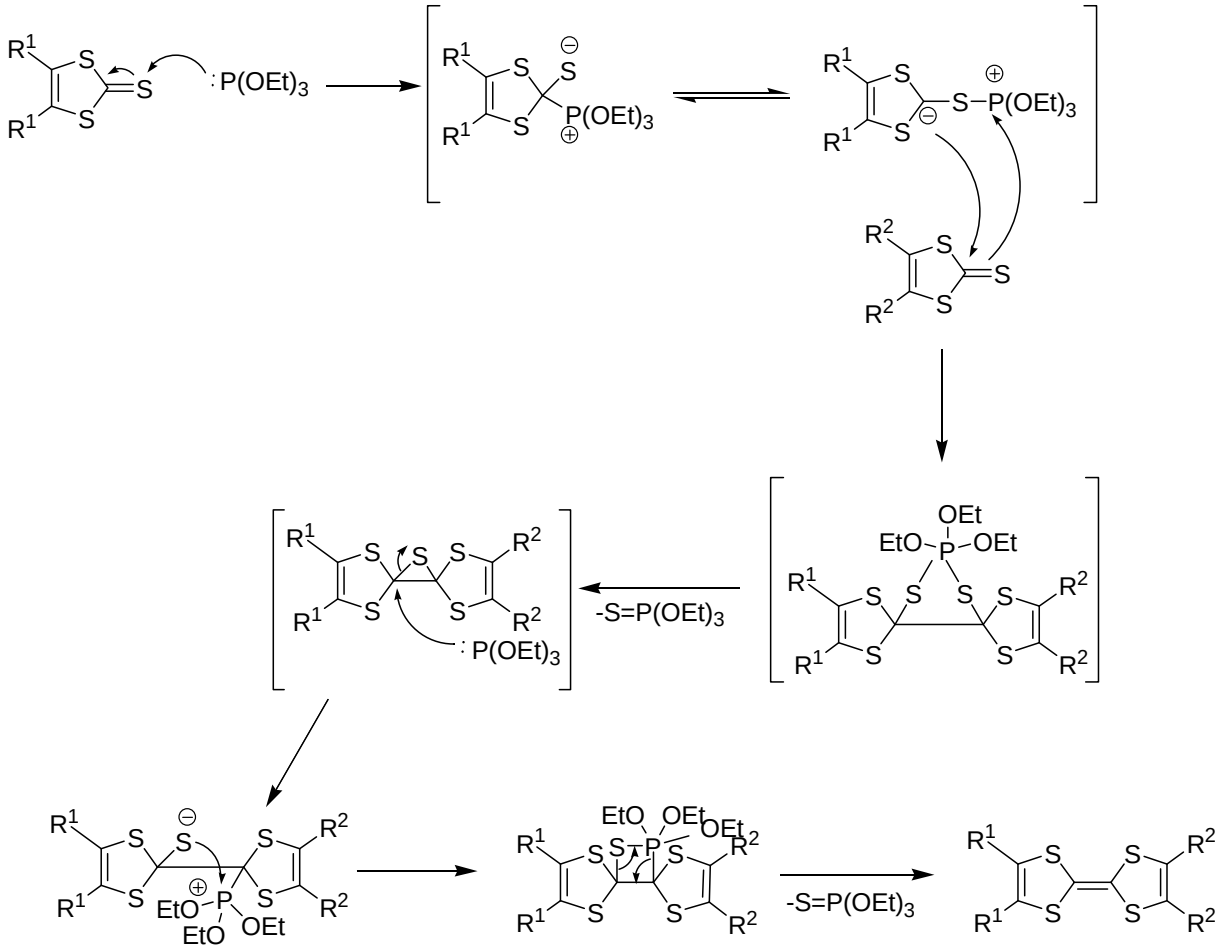
In 1970, *Hartzler et al.* performed a cross coupling reaction from dechalcogenation of chalcogenones with 1,3-dichalcogenole-2-chalcogenones using a phosphine (Scheme 1.1) or phosphite[32,33] reagents and including dithiolium intermediates. This is one of the methods which is particularly useful for the asymmetric synthesis of tetrathiafulvalenes, since it involves the formation of the stable ylene intermediate.



Scheme 1.1: Synthesis of asymmetric *bis*-cyanoethyl-TTF derivatives using phosphine-mediated coupling.

Asymmetric and quadruple substituted TTFs have been also prepared using a phosphite-mediated cross-coupling of dithiole-thiones/dithiolones (Scheme 1.2). Firstly, nucleophilic attack of triethyl phosphite ($P(OEt)_3$) on C=S bond results in formation of ylide intermediate that is in equilibrium phosphonium sulphide. Carbophilic attack of the ylide on the C=S bond of the second thione gives a cyclic intermediate, that after the loss of $–S=P(OEt)_3$ forms an episulfide cyclic derivative. A nucleophilic attack of $P(OEt)_3$ on it results in formation of four-membered cyclic thiaphosphetane intermediate. Lastly, the loss of $S=P(OEt)_3$ affords a TTF

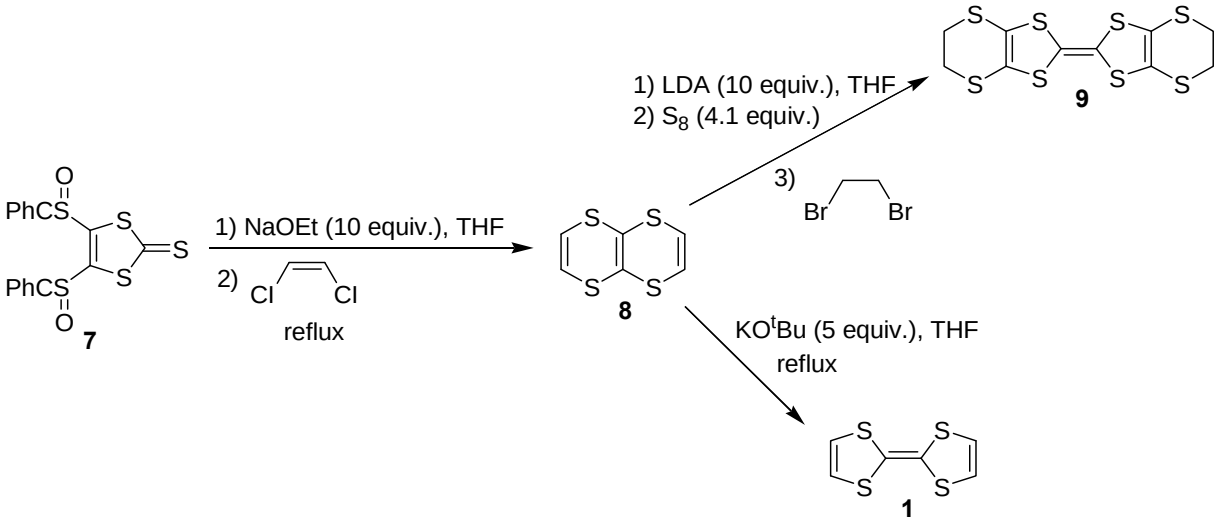
molecule.[34] This coupling reaction can be performed with dithiole-thiones, dithiolones, or with their mixtures. In the latter case, the major product will be the one formed by the asymmetric coupling between dithiole-thione and dithiolone molecules, whereas the formation of symmetric products is usually suppressed. Reaction condition such as temperature, nature of the substituents and concentration can significantly influence the yield.[35]



Scheme 1.2: Mechanism of the phosphite-mediated coupling of dithiole-thiones. Note that dithiolones (one or both reagents) can be used instead.

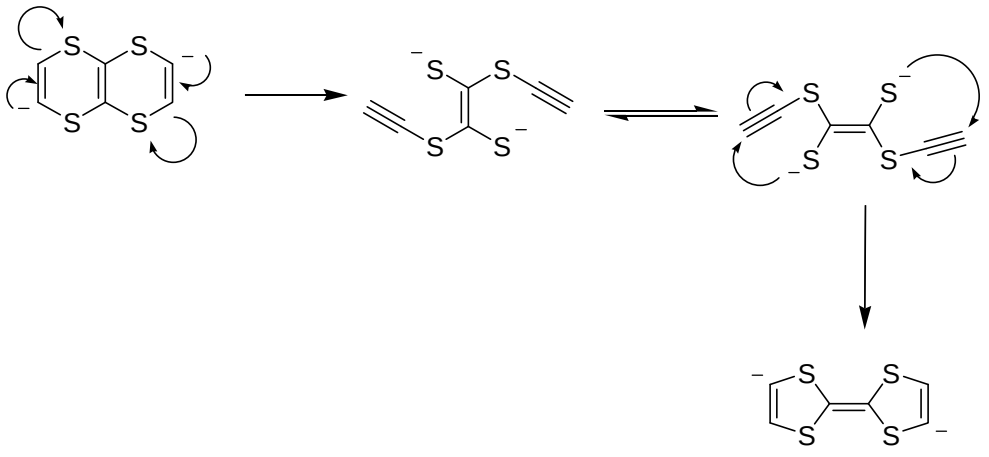
Phosphite-mediated coupling (Scheme 1.4) has been successfully used in the synthesis of several *bis*-cyanoethyl protected-TTF derivatives and usually it gives good yields of unsymmetrical cross-coupled tetrathiafulvalenes. TTF derivatives often precipitate from the reaction mixture and can be filtered off, while they can be easy purified by the use of flash chromatography afterwards. These derivatives are also very stable and can be stored for long period of time without any decomposition.[22] Preparation of functionalized TTF using this pathway has been frequently used due to easy separation and purification.[36] Such functionalised TTFs play an important role in the preparation of macrocyclic and supramolecular systems.[34] To increase the solubility of the TTF derivatives, flexible spacers between the TTF cores and functional groups can be introduced.[37]

High cost of parent TTF **1** from commercial sources has led to studies of new synthetic pathways, affording the cost-effective syntheses with high yields,[38] which is performed via tetrathianaphthalene (TTN, **8**) intermediate. The compound that was prepared by *Cava et al*. with a multi-step synthesis but without further preparation of its derivatives.[39,40] *Yoshida et al.* reported that TTN can be electrochemically oxidized into TTF molecules.[41–43] *Anzai et al*. proved that TTN can be rearranged into TTF with good yield via base-induced rearrangement and can also be used to prepare bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **9**) by sublimation of elementary sulfur and then reacting with an excess of 1,2-dibromoethane.[38,41,42] This synthesis uses low cost commercially available starting materials (Scheme 1.3). An inexpensive mixture of *cis*- and *trans*-1,2-dichoroethylene can be used instead of costly pure *cis*-isomer, because the *trans*-isomer during a reaction does not cause any hindrance for the preparation of the target TTN.[44] TTN can be prepared in one step from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione **7** with good yield by using sodium ethoxide (in excess) and a *cis*-1,2-dichoroethylene (Scheme 1.1). Then, TTN is re-arranged into TTF **1** using a strong base.[38]



Scheme 1.3: Non-coupling pathway to TTF **1** and BEDT-TTF **9** from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione **7**.

TTN rearrangement is preferentially performed using BuLi or KO^{t}Bu affording good reaction yields, whereas the usage of LiO^{t}Bu and NaO^{t}Bu bases (reflux in THF) showed a recovery of the starting material.[45] Mechanistically, the reaction is likely to proceed via the ring opening – ring closing process (Scheme 1.4), though it was not possible to prove it directly.



Scheme 1.4: Rearrangement of TTN **8** into TTF **1.**

Different functional groups can be appended to the backbone of TTF **1**, such as: carboxylic acid (COOH), amide ($CONH_2$), phenol (ArOH), aldehyde (CHO), nitrile (CN) and halogen (Cl, Br, I) (Figure 1.7). This functionalization is performed in the sequence including (i) deprotonation of TTF **1** using lithium diisopropylamide (LDA) (ii) followed by the reaction with a corresponding electrophilic reagent, such as CO_2, alkylbromides, and others.[34]

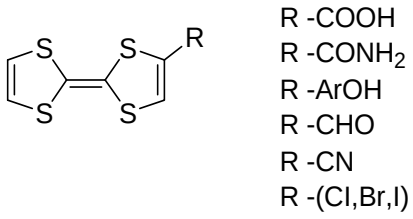


Figure 1.7: Structure of TTF-derivatives with different functional groups.

1.5 Pyrrolo-Tetrathiafulvalenes and their properties

TTF derivatives in which parent TTF core is annealed to phenyl **6**, pyrrole **10**, furane **11**, selenophene **11**, thiophene **11**, are well known and commonly called "extended tetrathiafulvalenes" (Figure 1.8). Most of them demonstrate higher oxidation potentials compere to parent TTF **1,**[46,47] but pyrrolo-TTFs, which are annealed to electron-rich pyrrole, have lower oxidation potentials. Attachment of different aromatic groups on another side of pyrrolo-TTF core alters TTF properties, such as the span and nature of the π-system, dipole moment, redox potentials, flexibility of the molecular backbone, and others.[48]

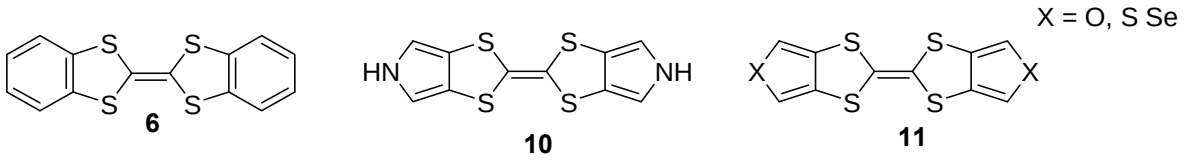


Figure 1.8: Structures of TTF core annealed derivatives.

Researchers have been interested in working with pyrrolo-annealed TTFs (Figure 1.9) in order to use them for the preparation of supramolecular and macrocyclic structures, since pyrrolo-TTFs allow straightforward substitution of their N-atoms with various groups.[49] *Cava* and co-workers have reported a detailed and efficient the synthesis of the pyrrolo-annealed TTF **12** and its related monopyrrolo-annealed TTF (MPTTF) derivative **13**.[46,49] Introducing of two 2,5-dimethlypyrrole rings into TTF gives lower oxidation potential compere to parent TTF **1** and the presence of two functional site (-NH) in pyrrolo-annelated **12** results in higher symmetric system compared to other non-annealed-TTF derivatives containing four attachment sites. The problem with 2,5-dimethylpyrrolo-annealed TTF **12** is the possible unfavourable steric hindrance due to the methyl groups in the cases when the molecules is used in supramolecular and macrocyclic architectures.[49–51]

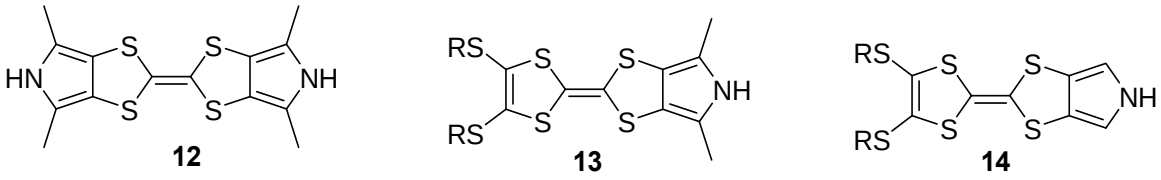
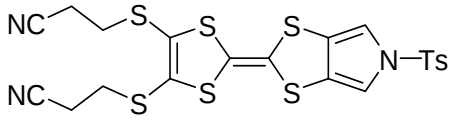


Figure 1.9: Structures of pyrrolo-annealed TTF's and MPTTF derivative.

Pyrrolo-TTFs, symmetric **10** and asymmetric **14** (Figure 1.9), have more extended π–system in comparison to the parent TTF **1**.[52] Their oxidation potentials are only slightly lower than those of the "parent" TTF, but they more easily form charge-transfer complexes with electron-deficient molecules due to large π–system and stronger π–stacking interactions. Pyrrolo-TTFs can be easily functionalized with two substituents by nucleophilic substitution reaction upon deprotonation of nitrogen atom of pyrrole groups followed by an addition of an electrophile. Unlike with "parent" TTF, which allow four-fold substitution, rotation around the central bound of pyrrolo-TTFs upon its oxidation will not lead to formation of *cis-/trans*-isomers. It is also possible to create hybrids between "normal" TTFs and pyrrolo-TTFs (Figure 1.8) called monopyrrolo-TTFs (MPTTFs, **14**), whereas symmetric pyrrolo-TTFs are called *bis*-pyrrolo-TTFs (BPTTFs, **10**). MPTTFs allow for asymmetric substitution patterns, and, similar to BPTTFs, they do not form *cis*- and *trans*-isomers due to the presence of just one *N*-substituent on one of their sides. This is a big advantage of pyrrolo-fused TTF derivatives in preparation of functional molecular architectures.[2]

Derivative **15** (Figure 1.10) is used as a common intermediate that can be selectively sequentially functionalized in all three positions under mild S- and N-alkaylation conditions. MPTTF derivatives have proven to be the very successful in a number of applications and was employed as the building block in cage molecules, amphiphilic bistable [2]rotaxanes, molecular receptors and porphyrins.[53]



15

Figure 1.10: Structure of a building block for TTF and TTF-derivatives **15.**

1.6 Functional tetrathiafulvalene-containing molecular architectures

1.6.1 TTF-based catenanes and rotaxanes

The beauty of nature and natural phenomena, such as molecular recognition, self-assembly and self-organization, has been the major inspiration for creation of molecular-based architectures, in which weak non-covalent bonding interactions play an important role.[54] Designer supramolecular systems and molecular switches have received a great attention in the past recent years due to promising applications in nano-machines and molecular devices.[55] Mechanically interlocked molecules (MIM's) without covalent bonding between their components, such as rotaxanes and catenanes (Figure 1.11),[56] can be prepared using self-assembly method based on molecular recognition between complementary π−electron rich/deficient molecular units. [2]Rotaxane constitutes a promising architecture for the development of molecular-based switches.[57] Synthesis of MIM's is usually driven by weak non-covalent bonding, such as π−π interactions, hydrogen bonding and donor−acceptor interactions.[58] Most contribution in the development of new nano-machines and molecular devices come from sir *JF Stoddart* (Nobel Prize 2016) and co-workers. They have showed a tremendous effort in studying, and preparing of rotaxanes, catenanes, pseudorotaxanes by exploiting the unique properties of "blue box" host cyclobis(paraquat-*p*-phenylene) macrocycle ($CBPQT^{4+}$, **16**).[59] Prime candidates are used in the preparation of artificial/molecular switches and for fabrication of electronic nano-devices based on [2]rotaxanes and [2]catenanes.[56,60,61]

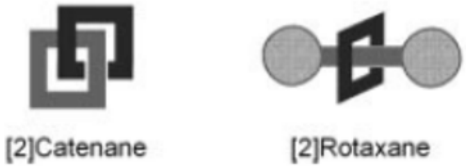
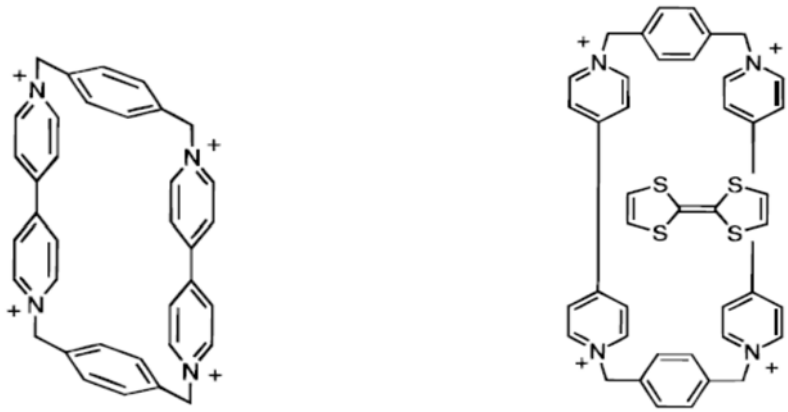


Figure 1.11: Schematic representation of a [2]catenane and a [2]rotaxane.[52]

In the past years, π-electron deficient macrocyclic host $CBPQT^{4+}$ (Figure 1.12) has been used with various π-electron rich guest to form complexes and applied in the preparation of template directed molecules.[62] *Stoddart* and co-workers were the first to study the interactions of parent TTF **1** donor molecule and $CBPQT^{4+}$.[63,64] Guest TTF donor molecule in it neutral TTF state is one of the most efficient to form 1:1 complex with electron accepter molecule $CBPQT^{4+}$.[65,66] Much efforts were invested to study donor guest interactions with the macrocyclic $CBPQT^{4+}$ ring. If a side chain with donating properties is covalently attached to the macrocycle, self-complexation has been observed.[67] Some electron donors do not influence $CBPQT^{4+}$ in terms of binding affinities, as observed by *Kaifer* and *Mirzoian*.[68,69] Recently, most groups are working towards strong charge transfer interactions in MIM's with π-donor molecule, such as TTF and 1,5-dioxynaphthalene (DNP).[70] Donor molecules that demonstrate high affinity for electron acceptor macrocycle $CBPQT^{4+}$ are non-substituted TTF **1** and its derivatives. Binding studies with different TTFs have shown that poor π-donor TTF derivatives form weaker complexes and TTF derivatives that have lower oxidation potentials form stronger complexes.[71]



16

Figure 1.12: Structure of $CBPQT^{4+}$ "blue box" **16** and a 1:1 complex with TTF.

Upon availability of certain functional groups, components of interlocked supramolecular architectures can be switched in their relative position to each other by photochemical or electrochemical stimuli (Figure 1.13) and subsequent movement of molecular components

can be tracked using different analytical methods, such as nuclear magnetic resonance (NMR). Catenanes and rotaxanes can serve as the starting point for fabrication of molecular electronics devices and artificial molecular machines.[52,72]

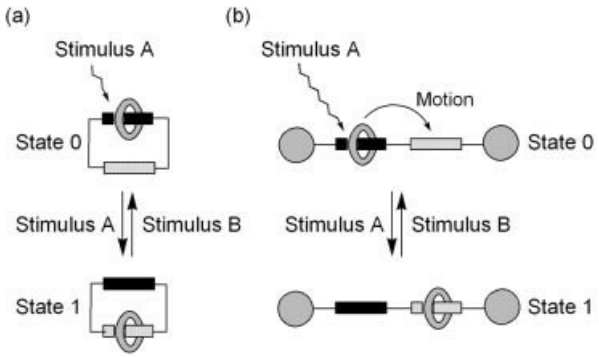


Figure 1.13: Switching of (a) [2]catenanes and (b) [2]rotaxanes. Note the dislocation of one of the macrocyclic components.[52]

The redox-controllable catenanes and rotaxanes are based on the possibility to reversibly oxidize TTF groups that are incorporated in their structures and in this manner to control their electron-donating properties. Redox-switchable rotaxanes were tested in fabrication of single molecule electrochemical junctions in electronic devices, while the redox-switchable catenanes can be used also in construction of a solid-state electronically reconfigurable molecular switches.[21] Sir *JF Stoddart* was one of three Nobel Prize awardees in Chemistry in the year of 2016[73] for his developments in the field of redox-switchable TTF-based catenanes and rotaxanes.

Template-directed method can be used to prepare mechanically interlocked such as macrocyclic polyether and CBPQT4^{+} ring. Steric interaction in CBPQT^{4+} ring prevents the formation of TTF$^{\cdot+}$ **1a** dimers.[74] [2]rotaxane incorporating electron-rich groups TTF, DNP and electron-accepting CBPQT^{4+} macrocycle (Figure 1.14) demonstrates excellent performance in redox-switchable supramolecular systems.[75]

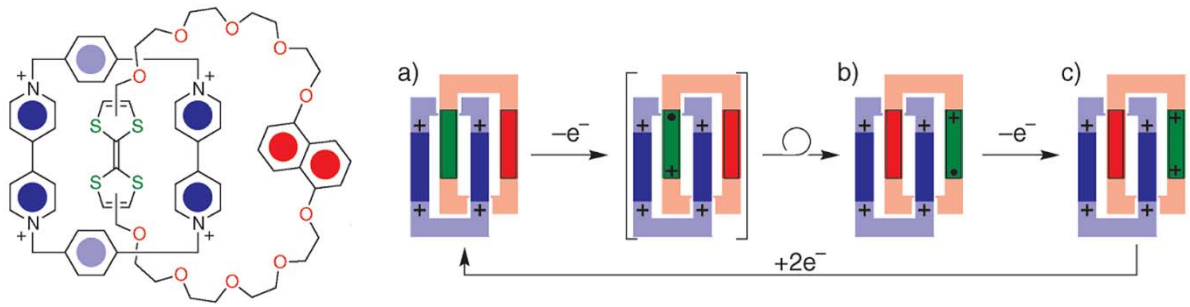


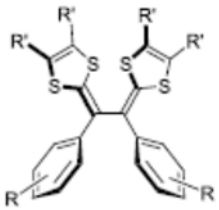
Figure 1.14: Redox-switchable system of a TTF-based catenane.[73]

Efficiency of molecular motion in [2]rotaxane-architecture can be influenced by changing the length of oligo ethylene glycol chains, thus modifying the basic flexibility of the system. The chain length influences the effects of temperature and solvent on the system.[76] Possible molecular building blocks, such as 1,2,3-triazole, do not change any thermodynamics and kinetics factors influencing switching abilities.[77]

1.6.2 TTF-based extended molecular architectures

The numerous preparation of extended TTF-systems came up after the proposal of *Wuld* and co-workers in 1977 stating that higher conductivity charge-transfer can be obtained from more than two TTF units in one molecules.[78] In addition, in 1980 after *Staab et al.* presented tetrathiafulvalenophanes (TTF-phanes) and tetrathiafulvalenoparacyclophanes (*p*-TTF-phanes) there has been a growing interest in macrocycle-based molecular systems.[79,80] Macrocyclic and supramolecular architectures based on more than one TTF units attract a particular interest in studies regarding their properties, redox behaviour and π-electron donating ability.[81] Over the past decade, several host-guest systems together with their complex super-structures have been investigated.[82] Incorporating of TTF and π-extended TTF units into macrocycle systems, such as designer receptors for interacting with electron deficient molecules,[83,84] is a field of current research interest, which has been exposed in several systems for development of molecular devices such as shuttles, molecular machines, sensors, switchable molecule and many more.[85]

There is an ongoing particular interest in new π-extended TTF systems. For example, π-extended TTF with π-conjugating spacer between the two 1,3-dithiolium rings are prime targets for the synthesis of molecular receptors.[86] *Yoshida et al*. was the first to report tetrathiafulvalene vinylogue (TTFV, **17**) derivatives.[87–89] TTFVs are π-extended derivatives of the parent TTF **1** donor molecule with a vinyl π-conjugated spacers between the two 1,3-dithiole rings (Figure 1.15).[90] In the absence of two aryl rings, the structure of TTFV usually adopts a planar geometry with *transoid* isomer, whereas when two aryl rings are present, they adopt non-planer geometry with *cisoid* form as a result of steric crowding.[91] *Yamashita* and co-workers made an assumption that when diaryl rings are introduced in TTFVs, diaryl-TTFVs will form a *transoid* isomer due to increase of steric interaction.[92,93] TTFVs and derivatives are excellent redox-active π-donor molecules and, in particular, diaryl-TTFVs demonstrate unique redox-controlled conformational switching. Neutral form of diaryl-TTFVs can be used in macrocyclic and tweezer-like systems.[94,95] Significant interest has been shown towards other π-extended TTF derivatives, which had several other various π-conjugated spacers, such as arylene, acetylene and quinoid moieties, placed between the 1,3-dithiole rings for tuning of their properties and use in molecular devices.[96–98]



17

Figure 1.15: Structure of TTFVs **17**.[90]

Diaryl-TTFVs demonstrate unique reversible redox properties with two electron oxidation and reduction process,[99,100] which occurs via one step two electron transfer, like for the parent TTF, forming a radical-cation and then a dication.[101] Low oxidation potential of diaryl-TTFVs is due to delocalization in the dication, whereas the conformational change is due to the increase of Coulombic repulsion upon their oxidation (Figure 1.16). Several TTFV-based switching ligands have been prepared and investigated over the past few years.[87–89,102]

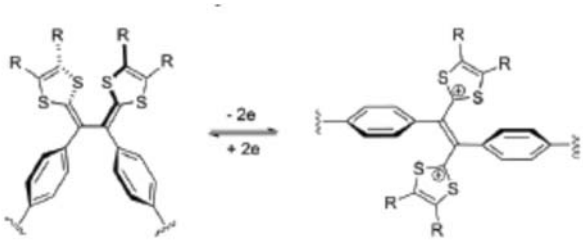
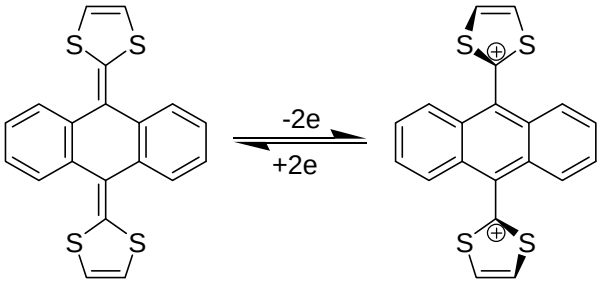


Figure 1.16: TTFV is a redox molecule that can be reversibly oxidized to give the dication.[96]

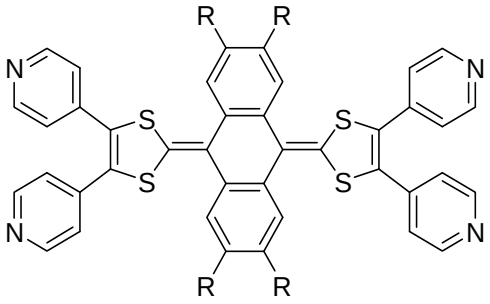
π-Extended tetrathiafulvalenes with an antracene spacer **18** also demonstrates unique electronic and structural properties. *N. Martín et al.* revealed its features and developed several covalent receptors-based on it.[47,103] *Yamashita* and *Bryce* groups were the first independent reporters in the preparation of π-extended TTF-derivatives.[104,105] Extended TTF **18** has been particularly interesting in design of molecular electronics due to favourable influence of its extended π-system.[106] Like π-extended TTFVs **17**, TTF derivative **18** can undergo a redox reversible process stimulated by electrochemical stimuli. In a neutral state, **18** adopts a non-planar saddle-shape structure due to steric hindrance between the anthracene moiety and two 1,3-dithiolium rings. Upon the release of two electrons, 1,3-dithiolium rings become aromatic, non-conjugated with anthracene spacer, and rotate orthogonal to the anthracene plane.[107–109] Due to this peculiar reversible reaction, π-extended-TTF system undergo a single step two electron oxidation to from a stable dicationic specie (Figure 1.17).[110,111]



18

Figure 1.17: Redox reversible reaction of pristine π-extended-TTF **18**.

Tetrapyridyl-π-extended TTF **19** (Figure 1.18) ligand is a redox-active molecule that can form metal complexes that disassemble via oxidation and reassemble via reduction.[112] Due to its saddle shape and excellent π-donating ability, tetrapyridyl π-extended TTF ligand readily interact with curved or spherical electron-deficient molecules, such as fullerene.[113,114] Self-assembly by co-ordination with metals leads to self-assembly of **19** into metalla-cages which can undergo transformations stimulated by guest exchange, irradiation, and other external stimuli.[115,116]

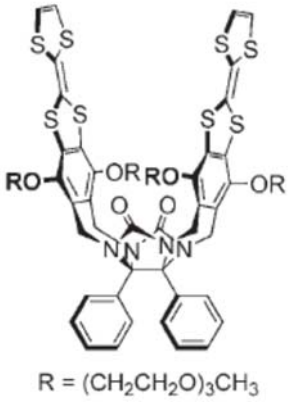


19

Figure 1.18: Structure of tetrapyridyl- π-extended-TTF ligand **19.**

Receptors with an open cavity that possess two or more interaction sites separated by a spacer are commonly called molecular tweezers or molecular clips. *Nolte* and co-workers have used glycoluril-based scaffold, which has attracted much attention as a building block for the preparation of molecular clips,[117,118] cucurbit[n]uril macrocycles and capsules, as well as served as the basis for the *bis*-TTF receptors with the architecture of molecular tweezers (Figure 1.19). Receptor **20** has a rigid and pre-organized structure[119] efficient for binding of electron-deficient guests, such as dicationic viologen (*N*,*N*′-dialkyl-4,4′-bipyridinium) derivatives, in between its two TTF "arms". Molecular clips **20** may differ in terms of the nature of substituents on TTF's side walls and possible incorporation of a rigid spacer between TTFs and glycoluril backbone.[120] Rigidity of the molecular tweezers prevents the collapse of

a free receptor, which can be expected due to possible stacking interactions of the opposite TTF units.[121] Stepwise oxidation of **20** causes self-association of the receptor **20** due to the formation of mixed-valence and radical cation dimers between the TTF units.[122] TTF-diphenylglycoluril molecular clips were used in switchable complexes with electron-deficient macrocycles. The switching behaviour between threaded and unthreaded states could be controlled by several multicomponent systems, such as NH_4^+/Et_3N (protonation/deprotonation), K^+/[2,2,2]cryptand (complexing of K^+), (p-BrPh)$_3$NSbCl$_6$/Zn (oxidation/reduction) and heating/cooling cycles. These abilities allow macrocycle-clip complex to operate as a molecular logic NOR (not or) gate.[123] Thus, in order to obtain host-guest systems with high binding affinity, pre-organized macrocyclic hosts of molecular clips/tweezers type represent a very promising molecular architectures to look at.[124]

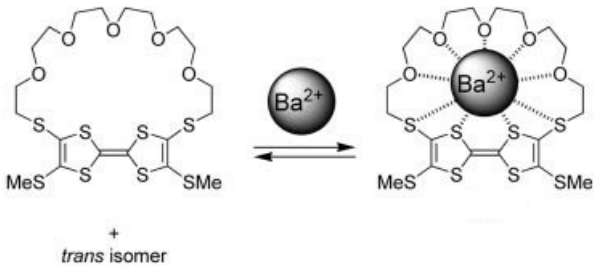


20

Figure 1.19: Structure of diphenylglycoluril molecular clip with TTF arms **20**.[124]

1.6.3 Use of pyrrolo-tetrathiafulvalenes in the synthesis of molecular receptors, sensors and cyclophanes

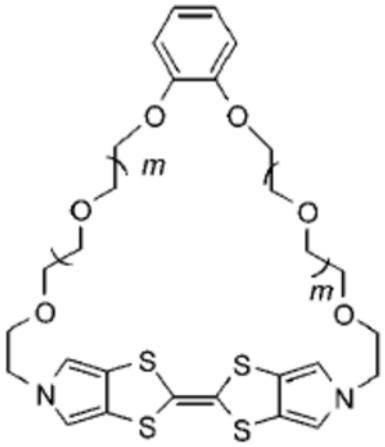
Host (donor)-guest (acceptor) system is often used in the development of macrocyclic and supramolecular sensors. Such sensors can be built by combining of a commonly used ligands, such as crown ethers for alkali metals, with a redox active group.[125] TTFs are the ideal redox active moieties with unique π-electron donating characteristics that change their spectroscopic properties upon close interaction with positively-charged molecules and ionic guest.[1] Molecular receptors for cations commonly have a binding site of crown-ether moiety. Sensing of several metal cations had been studied by electrochemical recognition with TTF-containing crown ethers **21** in the past years (Figure 1.20). One of the problems encountered was related to the incorporation of TTF moiety within the structure of a crown ether. *Cis/trans*-TTF mixtures of isomeric crown ethers were usually obtained, and *trans*-isomer usually did not interact well with metal cations due to steric reasons.[126]



21 **22**

Figure 1.20: Structure of TTF-crown ether **21** and its complex with Ba^{2+} **22** in its *cis*-isomeric form.[52]

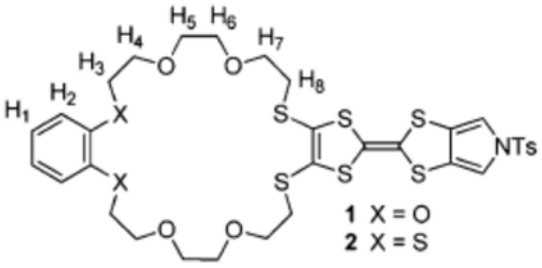
The problem can be solved by introducing BPTTF molecule into a crown ether, since they do not exhibit the problem of formation of *cis/trans* isomers and promote a close proximity of a bound metal cation and TTF group (Figure 1.21).[127] Thus, TTF-containing macrocycle can ensure the optimal feedback to the electro active TTF group upon cation binding.[126] BPTTF-crown ether **23** shows high binding affinities toward Ba^{2+} and Pb^{2+} in its neutral state. On another hand, such receptors can be modified to control the release and uptake of the cation from the ligand system upon redox switching of TTF moieties. Molecular architectures like this can be applied for the design of drug-carriers and sensors systems.[125]



23

Figure 1.21: Structure of BPTTF-crown **23,** while m can be 1 or 2.[125]

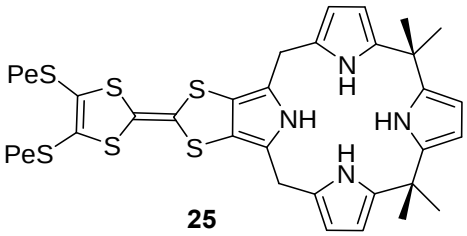
Often molecular receptors are targeted more for sensitivity and less for selectivity. Two unique MPTTFs receptors **24** (Figure 1.22) with optimal oxidation-reduction properties are coupled with dithiabenzo-crown or benzo-crown. MPTTF receptors showed a good affinity towards K^+ (X=O) and strong to Ag^+ (X=S), whereas it has very weak interactions with other metal cations.[128]



24

Figure 1.22: Structure of the molecular receptors **24**.[128]

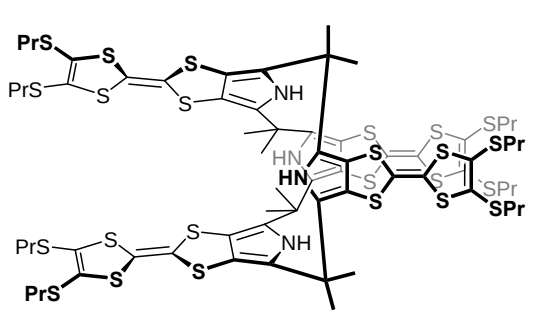
The first synthesis of calix[4]pyrrole was reported by *Baeyer* in the 19th century. Calix[4]pyrroles contain four pyrrole cycles interconnected by four sp^3 carbon bridges, and were often used as ligands towards neutral and anionic guests. Currently, redox-responsive calix[4]pyrroles comprising MPTTF moieties and related systems attract a lot of attention as possible molecular sensors and components for the construction of smart materials.[129,130] Molecular receptor representing MPTTF-calix[4]pyrrole conjugate **25** served as a chemosensors for detecting anions with electrochemical readout. Receptor shows excellent binding affinities toward F^-, Cl^- and Br^- ion species.[129]



25

Figure 1.23: Structure of the MPTTF-calix[4]pyrrole **25**.

The TTF-calix[4]pyrrole molecular receptors **26** were developed in collaboration of the groups of *Jeppensen* and *Sessler* (Figure 1.24). These receptors have four MPTTFs groups that form the molecular recognition centre of the receptor. Usually, they have two thio-propyl substituents on each TTF unit, but other groups have been also investigated. TTF-calix[4]pyrrole **26** has been reported as a binder of electron-deficient neutral aromatic molecules, such as 2,4,6-trinitro-toluene (TNT) and 1,3,5-trinitro-benzene (TNB), as well as of fullerenes C_{60} and their derivatives.[131] MPTTFs were used in preparation and studies of molecular tweezers **27** that were successfully tested as receptors for electron-deficient planar molecules, such as TCNQ, showing high binding affinity.[131,132]



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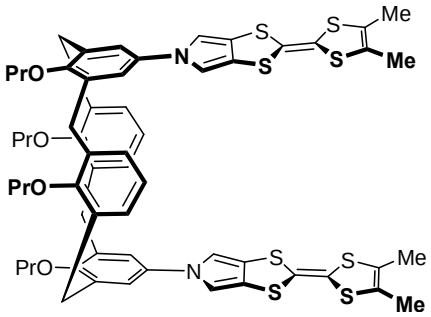
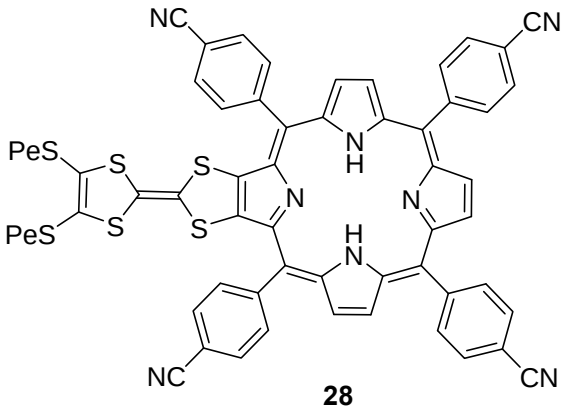


27

Figure 1.24: Structures of TTF-calix[4]pyrrole molecular receptor **26** and TTF-based molecular tweezers **27**.

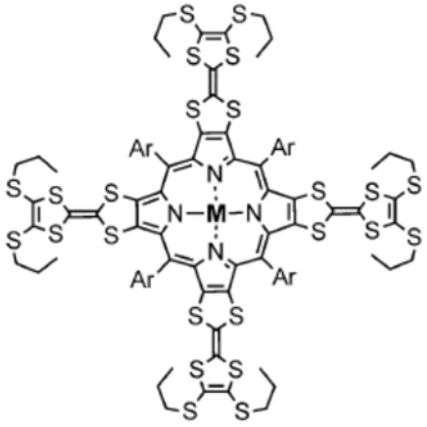
Porphyrins and associated tetra-pyrrolic macrocycles play an important role in biological systems, for example in haemoglobin, bacterial photosynthesis, and cytochrome C. Porphyrins have attracted researchers by their unique spectroscopic and physico-chemical properties.[133] They are also used in a fluorescence switch, where they can undergo a change between fluorescent and non-fluorescent species via oxidation of the TTF-groups.[134] Several methods have been investigated in order to prepare porphyrins annealed to pyrrolic and other π-extended TTF systems.[135] *Odense* and *Angers* groups, were able to design and synthesize the MPTTF-annealed porphyrin **28** (Figure 27), which was investigated as substrate for a photosynthetic reaction and as an optical sensor for anions.[133] In addition, porphyrin molecular systems have extended application in catalysis, molecular recognition, sensorics and other.[134]



28

Figure 1.25: Structure of MPTTF-based porphyrin **28**.

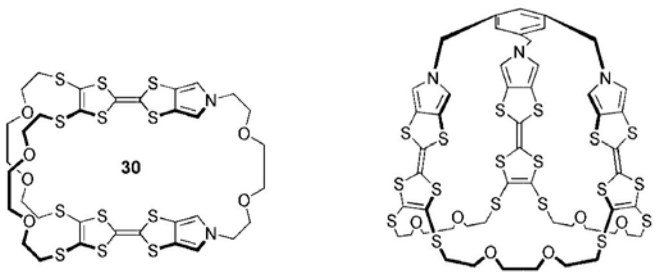
Another type of anion sensor has a structure of calix[4]pyrrole **29** comprising four MPTTF units.[136] Studies have shown that it has the strongest anion binding affinity between F^-, Br^- and Cl^- ions when compared to other calix[4]pyrrole derivatives.[137]



29

Figure 1.26: Structure of TTF-annealed porphyrins **29**.[137]

Several MPTTF containing macrocycles and poly-macrocycles[21] have been tested as ion sensors and as guest molecules for large electro-deficient organic molecules. MPTTF-belt **30** and MPTTF-cage **31** molecules (Figure 1.27) represent such molecular structures. MPTTF-belt **30** showed affinity to TCNQ, although it was shown that in the crystal structure the interaction happens outside the cavity of the nano-belt.[138] *Cory-Pauling-Koltun* (CPK) models suggested that MPTTF-cage **31** is more flexible in comparison to MPTTF-belt **30** and offers higher probability that a guest molecule such as TCNQ will fit into its cavity. Further analysis such as X-ray crystallography revealed that MPTTF-cage **31** was able to host molecules within a cavity in the solid state.[139] Recently, a modification of MPTTF-cage **31** with an extended triphenylmethyl spacer was reported to host fullerene C_{60} molecules, and complexation was confirmed with X-ray crystallography.[140]



30 **31**

Figure 1.27: MPTTF-based molecular belt **30** and molecular cage **31.**[52]

1.6.4 Tetrathiafulvalene conjugates with photoswitches

Tetrathiafulvalenes are excellent building blocks that allow control of their properties using redox-chemistry. Their combination with molecular elements capable of switching process using other stimuli, such as electromagnetic radiation (UV or visible light) seems to be obvious and promising, since it will allow construction of multi-stimuli-switchable molecular devices.

Surprisingly, only few examples of tetrathiafulvalene conjugates with photo/thermoswitches have been reported up to date, and they made use of azobenzene,[141–144] diarylethene,[145] and dihydroazulene/vinylheptafulvene[146] moieties. Most of the examples represent acyclic structures, though some of them were macrocycles (Figure 1.28).[143,144] Several photochromic TTF derivatives displayed influence of chromophore isomerization on the redox properties of the TTF unit, which were detectable using Cyclic Voltammetry (CV) method. Among all photoswitchable units, AB appears to be the most practical one due to the multitude of possible synthetic pathways and impressive application record.

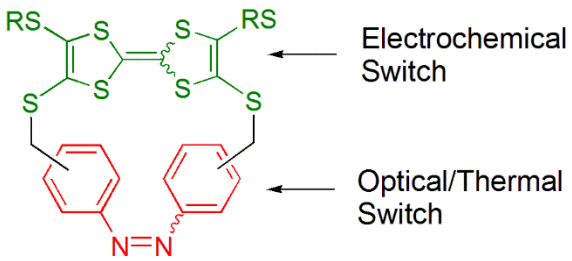
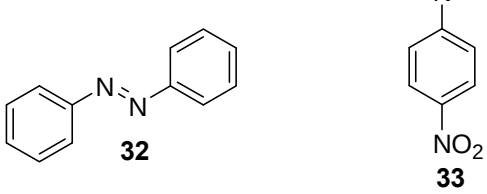


Figure 1.28 : An example of a multistate molecular device with orthogonal switching inputs.[144]

Chapter 2 : Azobenzenes

2.1 Discovery and structure of azobenzene

Azobenzene (AB, **32**, Figure 2.1) was discovered in the early 1800s. In 1834, it was the first time when AB was described in detail.[147] *Martius* discovered the first AB dye in 1863 and *Griess* in the following year reported the coupling reaction of diazonium compounds (**33**, Figure 2.1). These interesting discoveries opened the doors to many scientists for the research and development of AB dyes, which are versatile and important organic compounds.[147,148] In 1934, *Krollpfeiffer* and co-workers reported an explanation of photochemical reaction of AB derivatives.[149] In 1937, a study of *G.S Hartley* was published, where the influence of light on configuration of N=N double bonds was presented,[150] For the first time, *cis*-isomer of AB was observed after exposure to light of the *trans*-isomer and separated by making use of solvent extraction methods. This discovery was one of the first major developments in the history of organic molecular switches.[151] AB compounds are linked by an (N=N) azo group and their properties played an important role for their applications in industry and research.[152] AB derivatives have found use as dyes and pigments, therapeutic agents, radical reaction initiator, food additives, components of molecular switches and shuttles, chemo-sensors and units for the optical storage of information.[153]



32 **33**

Figure 2.1: Structure of AB **32** and diazonium **33** compounds.

ABs are excellent building blocks for molecular switches since they exist in two interconvertible forms, namely as the *trans* (E) and *cis* (Z) isomers.[151] Moreover, AB derivatives undergo a reversible controllable *trans* (E) – *cis* (Z) isomerization that can be induced by UV light,[154] whereas the backwards *cis* (Z) – *trans* (E) isomerization can be induced thermally or by visible light. Wavelength of light inducing isomerisation can be tuned by changing the substitution pattern of aromatic rings, for example by their fluorination. AB derivatives are excellent building blocks for dynamic molecular devices due to the possibility of their controllable isomerisation that is accompanied by the size and shape change of the AB moiety, with elongated *trans*-form and bent *cis*-form which is bent and more compact.[151,155] Due its light-controllable switching properties AB derivatives have been employed as photo-switches for changing conformation of biomolecules[156] and for induction of chirality.[155] There were reports on the use of AB derivatives for photo-control of switchable peptides, nucleic acid, stabilization of helical structures, in molecular scissors and

gated ion channels.[156] In addition, AB have shown a great potential in the development of the targeted drug delivery and molecular electronics.[153]

2.2 Photoisomerization of azobenzene: Substituent effects

AB derivatives are well-known for their change in configuration form *trans*- into *cis*- isomer in light-induced isomerization (Figure 2.2).[157] Since in 1954, AB isomerization between *trans*- and *cis*-isomer has been studied using photochemical methods.[158] It was found that AB photo-isomerization mechanism and quantum yields can be influenced with certain factors such temperature, substituent groups (e.g phenyl), irradiation wavelength, pressure, and solvent properties. Studies have shown that knowledge of photo-isomerization mechanism for practical purpose is not as important as the knowledge of the isomerization rates and quantum yields. Both properties are dependent on the isomerization pathway.[158–160]

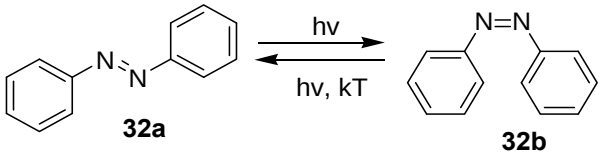
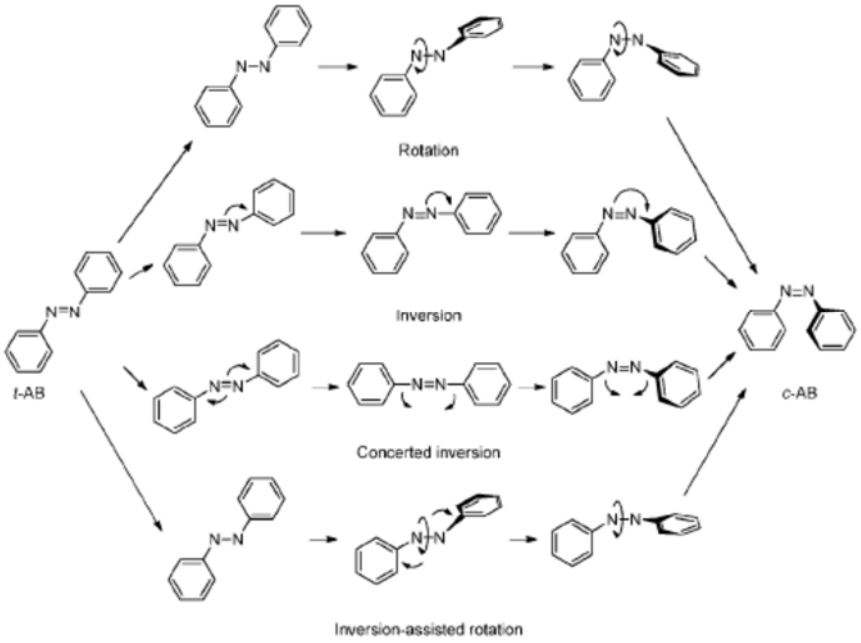


Figure 2.2: The photo-isomerization of AB, trans- (**32a**) to cis- (**32b**) isomers. AB isomer that is more stable is *trans*- than *cis*- isomer.

Proposed possible isomerization mechanism of AB's are inversion-assisted rotation, concerted inversion, inversion, and rotation, as shown in Scheme 2.1. In the Inversion-assisted rotation, both N=N-C angles undergo a significant simultaneous change. The Concerted inversion mechanism leads to two *sp*-hybridized nitrogen atoms in the transition state, which has no dipole moment due to its linear form. In the Inversion mechanism, the change in angles leads to the transition state with one *sp*-hybridized nitrogen atom. In the Rotation mechanism, N=N bond undergoes the loss of its double bond character, allowing for a free rotation around it. In principle, *cis*- or *trans*- isomer can be formed after relaxation of the corresponding transition states in all four cases.[159,160] The photo-irradiation induced step from *trans*- to *cis*-isomer undergoes a Rotation or Inversion mechanism, whereas heat induced transition from *cis*- to *trans*-isomer undergoes an Inversion mechanism.

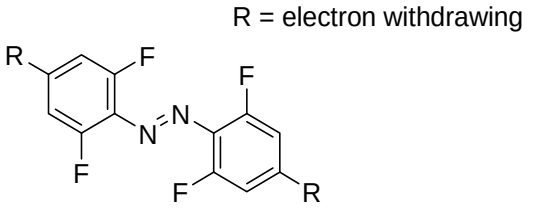


Scheme 2.1: Photo-isomerization of AB mechanisms. Bent arrows denote rotation/movement of AB **32** fragments.[160]

Rotation and inversion mechanism can take place starting from the ground state, S_0. When *trans*-AB is excited by light to S_1 (n → π*) first singlet state, isomerisation takes place very rapidly due to induced ultrafast rotation around the N-N bond and radiationless decay.[161] It was found that substituents play a significant role in isomerisation: electron withdrawing groups decrease the isomerization barrier and electron donating groups increase it for the inversion pathway in S_0 state. It can be said that after n → π* excitation ($S_0 \rightarrow S_1$ transition) the rotation pathway dominate over the inversion pathway. Concerted-inversion may happen for π → π* excitation ($S_0 \rightarrow S_2$ transition), as suggested by *Diau.*[162] For the *trans*-isomer a weak absorption band can be seen at the wavelength of 447 nm leading to S_1 state (n → π* excitation) and a strong band can be seen at 316 nm leading to S_2 state (π → π*, S_2) in the UV/Vis spectra.[163] *Kasha's* rule states that excitation wavelength determines the isomerisation quantum yield. An n → π* (S_1) and π → π* (S_2) excitations imply that different isomerization mechanism take place from these different excited states.[164] Recent reports showed large enhancement for the *trans*- to *cis*- isomerzation quantum yield for bridged AB excited to the S_1 state.[165] Isomerization of azobenzene-based architectures and derivatives is influenced by steric hindrance. Increasing bulkiness of the alkyl groups as substituents at the *meta*-position leads in a decrease of thermal rate of Z to E isomerization of ABs.[166,167]

Ortho-fluoroazobenzenes **34** have been developed to optimize the switching properties of the AB group. There is no sterical distortion of planar geometry in the *trans*-AB form because fluorine has a relatively small van der Waals radius, which is comparable to the one of hydrogen.[168] The electron density of the π-system of aromatic rings is reduced by *ortho*-fluorination and *n*-orbital energy is lowered, which helps for the effective separation of n →

π* excitation bands in its absorption spectrum, thus allowing for the selective induction of *trans*/*cis*-isomerization and enhancement of thermal stability of *cis*-isomer. Electron withdrawing group at *para* position can further enhance separation of n → π* transitions.[169]



34

Figure 2.3: Structure of *ortho*-fluoroazobenzene derivative **34**.

2.3 Azobenzene-based switchable molecular architectures

Azobenzenes have proved to be efficient photo-switching units in various functional molecular systems[170] because of the possibility to control their shapes and sizes using selective photo- and thermo-isomerization. These properties have led to the development of optically-switchable molecular structures that can be potentially used for the information storage.[171] At room temperature, AB can serve as photo-switch when immobilized between two gold electrodes.[172] Transformation reversibility leads to high photo-stabilities and possibility of multiple switching cycles.[173,174] The control of photo-isomerization of AB's is important in azobenzene-based molecular switches and derivatives for development of light-responsive materials.[175]

In supramolecular chemistry, macrocyclic molecules play very important role as a hosts for neutral and charged guest molecules and metal ions,[176] which can bind to intramolecular cavities via specific weak interactions.[177] The potential use of molecular-switches in preparation of adaptive surfaces, information storage and in nanotechnology has resulted in fast increase in their research.[178]

2.3.1 Macrocyclic azobenzenophanes and molecular machines

Since the discovery of functional macrocycles containing nitrogen and oxygen atoms, many laboratories around the world have been studying macrocyclic compounds. First ground-breaking results were achieved in 1970s, when *Pedersen* synthesized crown ethers, *Lehn* prepared and studied cryptands, whereas *Cram* investigated spherands,[179,180] all of them being effective and selective binders of alkali and alkali earth cations. Various functional groups can be introduced into macrocycles, which are used to tune their physical and chemical properties.[181]

Introducing an AB group inside of a macrocyclic structure opens a possibility to control its conformational states by stimulating it with electromagnetic radiation of a suitable wavelength.[182] For example, macrocyclic azobenzenophanes consists of two AB groups linked together by a bridge of variable length (Figure 2.4). Macrocycle **35**, containing -CH_2-S-CH_2- bridge at *para* position of two AB groups, was prepared by *Rau* and co-workers with the goal to study the mutual influence of photo-isomerization of two AB units in macrocyclic structure. Thermal *cis*- to *trans*-isomerization was affected by steric hindrance and chain length.[183,184] An AB containing macrocycle **36** with -CH_2-CH_2- bridges was reported by *Tamaoki* and co-workers, who reported that *trans,cis*-form was less stable then *trans,trans*-form.[185,186] It was also found that thermal *trans,cis*-form → *trans,trans*-form isomerization was faster than *cis,cis*-form → *trans,cis*-form thermal isomerization in different solvents.[187] AB macrocycle **38**, interconnected at 4,4'-positions, was prepared by *Grutzmacher et al.*[188,189] Investigation of absorption spectra and theoretical study of molecular motion in the excited states shed light onto the effects of rigid macrocyclic structure on rates and mechanisms of isomerization of macrocyclic *bis*-AB derivatives.[190]

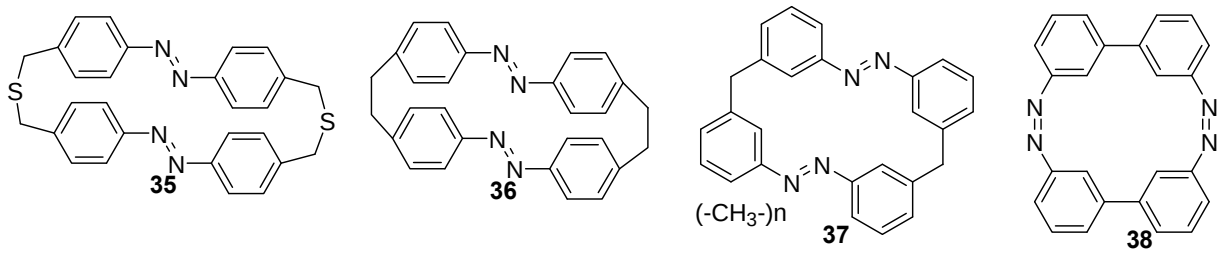


Figure 2.4: Structures of macrocyclic azobenzenophanes **35-38** with bridges of different length and at different positions of aromatic rings.

Another type of rigid AB-containing macrocycles are so called "light-driven molecular hinges".[191,192] A hinge is a structure with two rigid planes that are connected with each other through an axis. "Molecular hinges" comprise two fused polycyclic systems connected with two -N=N- bridges (Figure 2.5). In the opened state they have *trans,trans*-configuration of the two AB units and in the closed state *cis,cis*-configuration. For an efficient switching, AB isomerization in hinges should take place in a synchronous manner, since hinges cannot exist in the *trans,cis*-state for prolonged periods of time due to its instability. Hinge-like motion is induced with almost simultaneous photochemical isomerization of AB units, but molecular motion is rather restricted due to ring strain in the intermediate *trans,cis*-state. Therefore, isomerization yields strongly depend on the light intensity: only high intensity irradiance allows for almost simultaneous isomerization of both N=N bonds.

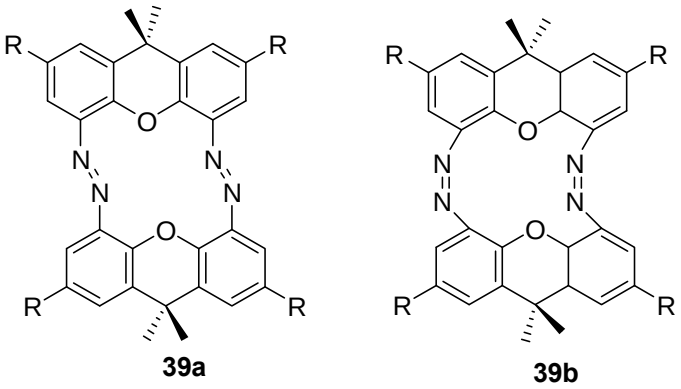
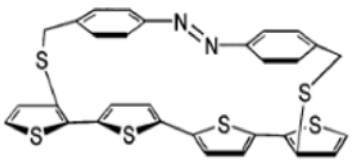


Figure 2.5: Structures of Xanthene-based cyclic AB dimers.

In order to gain control of responsive materials at the molecular level, dynamic molecular actuators are needed. For example, control of bond geometry by conformation distortion may be used to create responsive molecular semiconductors.[193] Using light as a power source for molecular dynamic devices showed great advantages, such as direct accessibility to the active site targeted and the absence of necessity to add foreign chemicals. Stimuli-responsive units can be appended to a π-conjugated system for indirect reversible conformational changes.[194] Electrochemical actuators associated with electrochemical process based on the volume changes of conjugated polymers have been studied extensively, but synthesis of dynamic π-conjugated structures remain scarce. *Marsella et. al.* paved a way into photochemical molecular actuation when tetra[2,3-thienylene] was reported. Covalently attaching a photoactive sensitive group into an oligothiophene at two fixed points allows to control its electrochemical properties by light irradiation, as it was shown on example of 3,3'''-[1,1'-azobis(4-benzylsulfandiyl)]-2,2':5',2'':5'',2'''-quaterthiophene **40** (figure 2.6).[195–197]



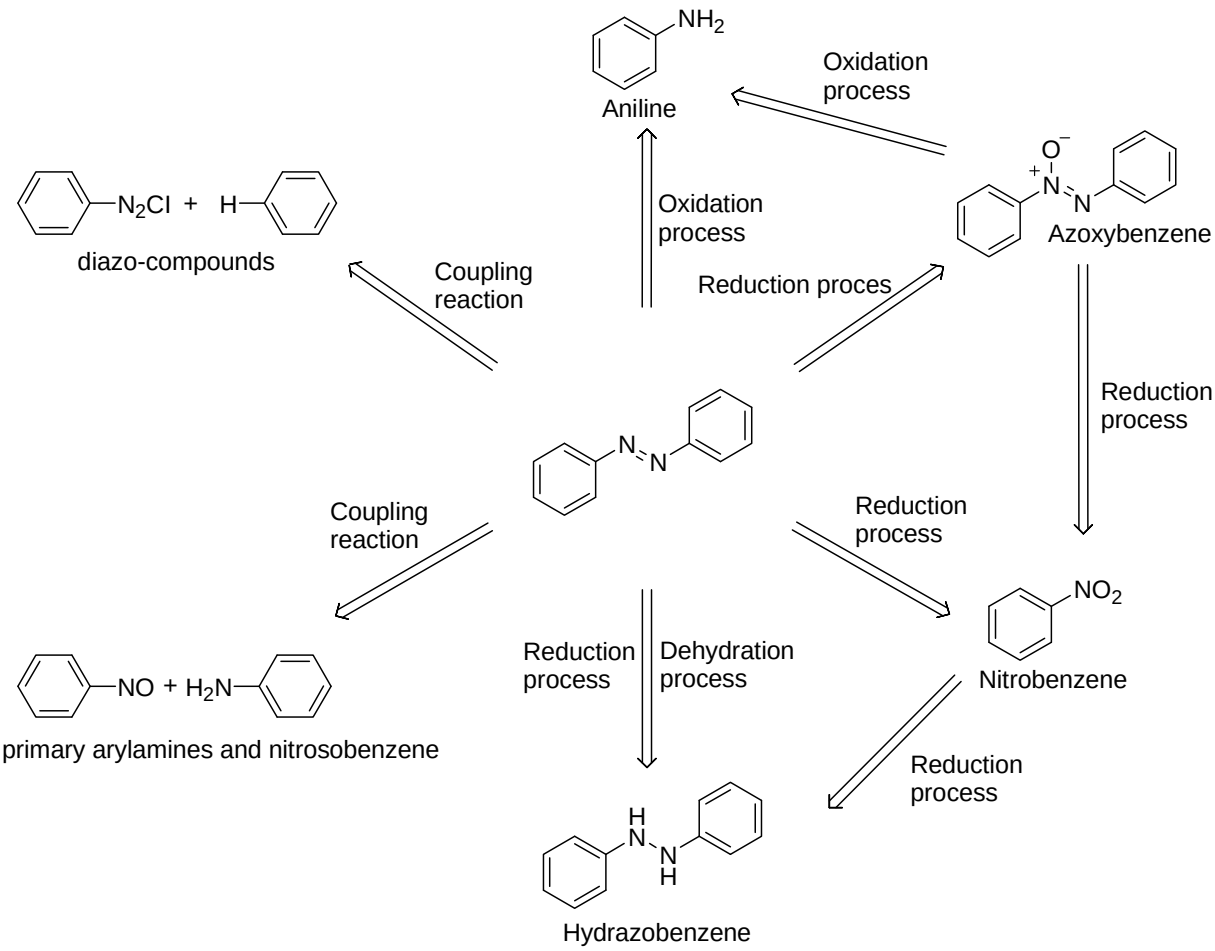
40

Figure 2.6: Structure of thiophene-based **40**.[195]

2.4 Approaches to azobenzene synthesis

Azobenzenes can be prepared using several established methods such as: electrophilic reaction of diazonium salts, reduction of aromatic compounds possessing a nitro group, reduction of azoxybenzene derivatives, coupling of primary arylamines with nitroso

compounds, oxidation of hydrazobenzene derivatives, and oxidation of aromatic primary amines, to mention a few (Scheme 2.2).[198]



Scheme 2.2: Representing a summary pathways towards a preparation of AB.

Selective oxidation of primary aromatic amines is one of the best know methods in synthetic chemistry. Several oxidants have been used as oxidizing agent for aniline,[199] such as: potassium permanganate, mercury compounds (e.g., HgI_2 or HgO), ferrate salts, lead salts, manganese salts, hypervalent iodine derivatives, to prepare symmetrical AB derivatives from primary aromatic amines.[198] Catalytic oxidation by oxygen or air has been the most promising and preferable method applied as an oxidants.[200] A report from *Jiao* and co-workers showed a preparation of azo-compounds using an inexpensive and commercial available copper-catalysed reaction for an aerobic dehydrogenative oxidation in a presence of air or oxygen for coupling of anilines.[201] *Minakata* and co-workers reported excellent result in preparing azo-compounds by dimerization of anilines using organic oxidant[202] and *Qing Lin* reported a convenient preparation of symmetrical AB using oxidant *N*-chlorosuccinamide (NCS).[203] These methods showed yields in the range of 44-97%.

Products of the reaction are dependent on the reaction conditions, type of oxidants being used and nature of aromatic substituents during oxidation process of anilines.[199] Meanwhile, some methods show disadvantages such as the use of toxic oxidants, low yields, long reaction times, and use flammable gases or bio-hazardous reagents (e.g., Hg- or Pb-based) which leads to a search for better pathways for efficient oxidative coupling of anilines to form AB.[204] Some AB derivatives can be prepared by the use of solvent-free reaction using permanganate oxidant.[205]

Dehydrogenation is one of the most common method for a preparation of ABs from hydrazobenzene compounds. *Mihara et. al* reported an easier way and more efficient process which is solvent-free dehydrogenation using commercial available alumina.[206] Recently, a new selective method using polystyrene-supported Au nanoparticles as catalysts for a preparation of hydrazobenzene from nitrobenzene using green chemistry solvents, sustainable and recyclable catalyst and mild reducing conditions has been suggested.[207]

Selective reduction of nitrobenzene can lead to a production of *N*-containing compounds with important industrial applications, such as, hydrazobenzenes, azoxybenzenes, azobenzenes, anilines, nitrosobenzene and hydroxlamines.[208] Generally, nitrobenzene reduction with a suitable reducing agents is one of most applied straightforward methods for direct preparation of ABs. Reduction of nitrobenzenes to azobenzenes is possible with metal-based reducing agents, such as zinc in basic medium or lead with HCO_2H or metal aluminium hydrides, such as $LiAlH_4$. Use of metal (Ru, Pt and Pd) nanoparticles and nanowire in the presence of hydrogen gas is also possible.[209,210] Metal-mediated heterogeneous catalytic transfer hydrogenations have shown much potential due to selectivity, mild conditions, and simple work up of reaction mixtures.[211–213]

Another active research area is a selective reduction of azoxybenzene derivatives to azobenzenes.[214] In industry, azoxybenzene play an important role as an intermediate in several important reactions. Azoxybenzene are normally form as an intermediate during oxidation of aniline and reduction of nitrobenzene as well as in a condensation between hydroxylamine and nitrosobenzene.[215] It can be also used in Wallach rearrangement for a preparation of hydroxyazobenzene.

Preparation of asymmetrical AB derivatives can be performed via Mills reaction using primary arylamines and aromatic compounds with a nitroso group. In starting materials for this reaction, substituents can occupy *para*-, *ortho*-, and *meta*-positions position on aromatic amine and aromatic nitroso derivatives, and can be both of electron-donating or electron-withdrawing nature.[216,217] One another method to prepare azobenzenes is a coupling reaction of diazo-compounds via diazonium salts under either basic or acidic conditions. Reagent attack commonly occur at *para*-position for steric reasons, and this reaction can also tolerate substituents of different nature.[198]

Chapter 3 : Results and Discussion

3.1 Project goals

Synthesis of controllable molecular machines and devices is the area of current scientific interest and active research. Examples of molecular devices with "orthogonal" read and write mode, such as those using optical stimuli that change electronic properties of a molecule, are very scarce. The goal of this project is to look for the approaches to bridge this gap by the preparation and characterisation of the molecules that will contain both redox-switchable[1] and photo-switchable[218] molecular building blocks, and that will have the property to change their electrochemical properties upon influence of optical stimuli. The project focus was the development of switchable molecular systems that may be used as, for example, optically-modulated electronic devices. As initially planned, these systems should comprise two monopyrrolo-tetrathiafulvane (MPTTF, **59**) moieties bridged by one substituted spacer group that should allow or preclude electronic conjugation between two MPTTF groups (Figure 3.1). As such spacers we have considered phenyl, biphenyl, stilbene and azobenzene[219] (AB) moieties. Phenyl group should allow the conjugation between two MPTTF units, because in this case planarity of the system will be maintained, whereas in the case of biphenyl spacer two MPTTF moieties will be decoupled due to the non-planarity of the two phenyl rings around the central C-C bond. The stilbene spacer should allow the conjugation of the appended MPTTF units in its planar *E*-isomeric form, but preclude it in its non-planar *Z*-isomeric form. Finally, azobenzene moiety can exist in two isomeric forms, *E* and *Z*, with the possibility of selective switching between these two forms using light of a certain wavelength, as well as thermally for the case of $Z \rightarrow E$ isomerization. As with stilbenes, conjugation between the two MPTTF moieties should be possible in the case of planar *E*-isomer, but will not be maintained in the case of non-planar *Z*-isomer. The degree of conjugation between the MPTTF moieties can be investigated using electrochemical and spectroscopic methods.

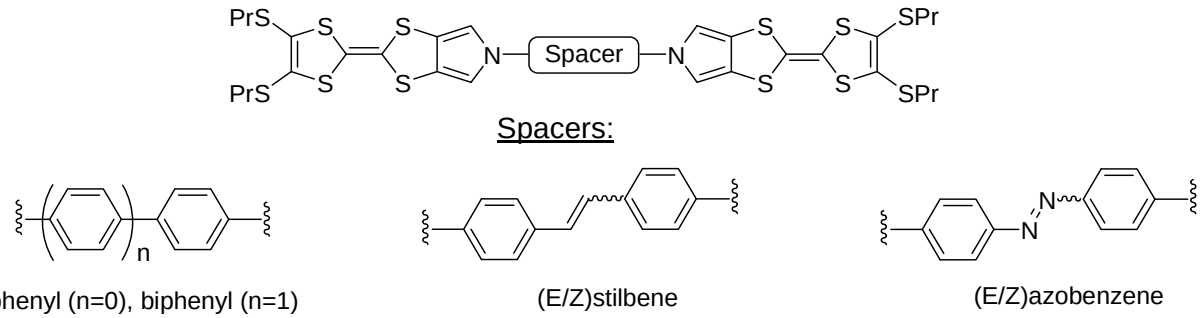


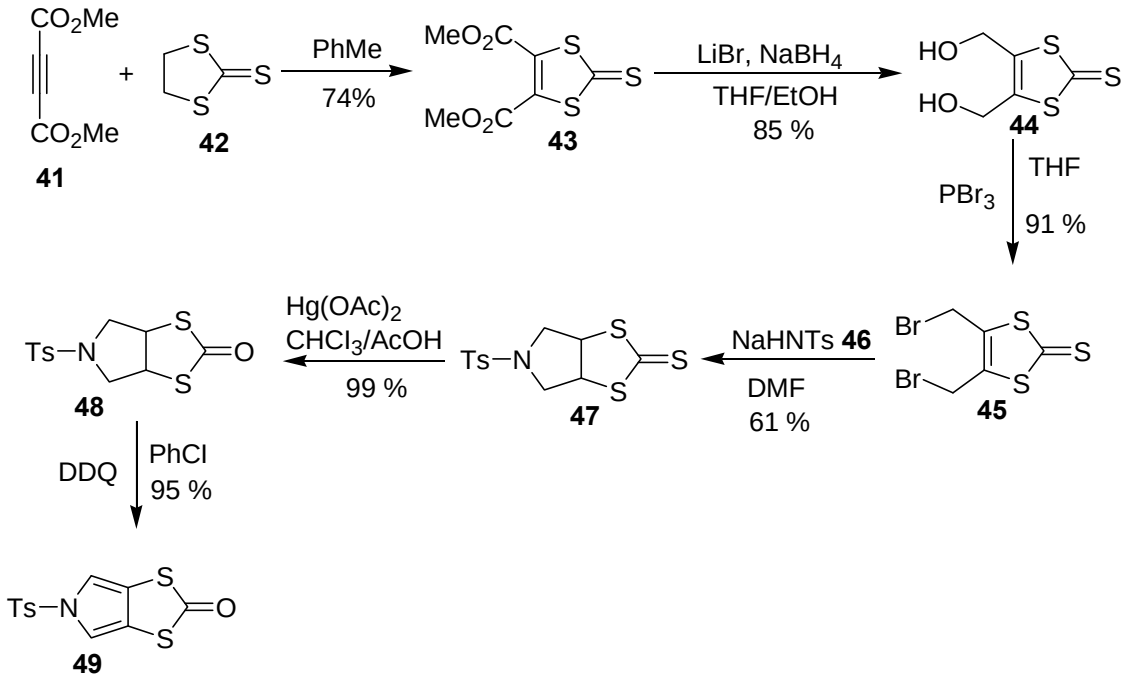
Figure 3.1: Representative structures of MPTTF derivative units linked by spacer groups with variable degree of π-conjugation.

Overall, the project goals were two fold. The first goal was to improve the synthesis of the MPTTF building block. Although at least two general pathways have been know towards its synthesis, both of them suffered from several drawbacks. In particular, the pathway previously used in our group (see below for details) demanded large scale chromatographic separation of one of the intermediates as well as required toxic and environmentally

damaging carbon tetrachloride as a solvent for the radical bromination in another synthetic step. Thus, it was necessary to exploit the possible reaction variations to overcome this difficulty and prepare MPTTF in a sufficient amount for the further studies. The second project goal was to investigate the Ullmann coupling reaction of the MPTTF in order to prepare the target compounds discussed in the paragraph above (Figure 3.1).

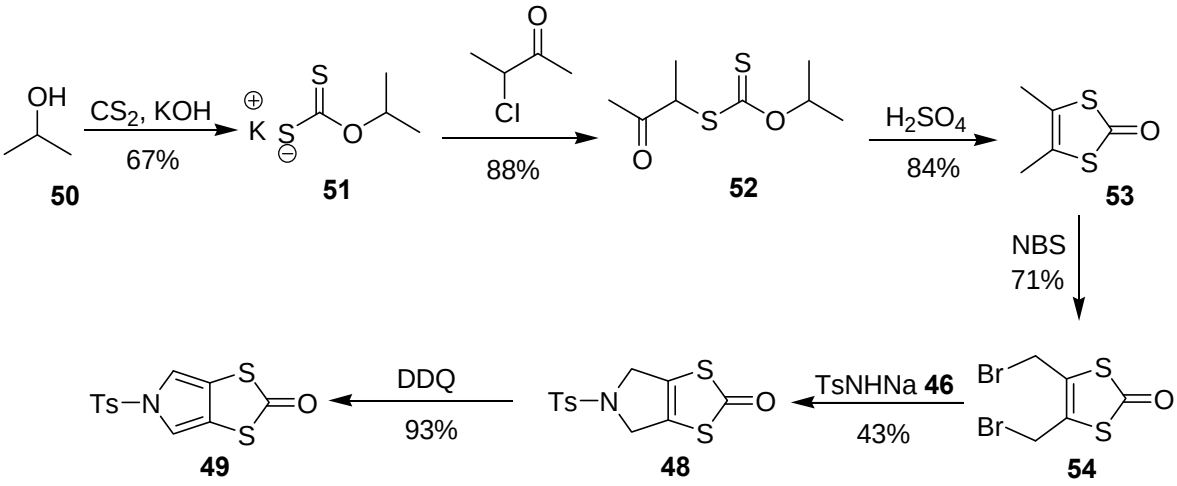
3.2 Preparation of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one, the key intermediate of tetrathiafulvalene

The synthesis of the key intermediate in the MPTTF synthesis 4,5-dimethly-1,3-dithiol-2-one **49** can be performed via two different synthetic pathways, one starting with ethylene trithiocarbonate **41** (Scheme 3.1) and another one with carbon dioxide (CS_2) (Scheme 3.2). 1,3-Dithiol-2-one can be used as a precursor for synthetic route of TTF, related materials and metal dithiolene complexes. Compound **53** can be easily modified and can undergo reaction such as nucleophilic substitution, bromination and substitution. Synthetic pathway gives excellent yields.[23,47,48] *Becher* and his co-workers have developed the first synthesis of pyrrolo-TTF and its derivatives.[36] Recently, the group of *Jeppesen* came up with large scale of the synthesis of *N*-tosyl-4,6-dimethly-(1,3)-dithiolo[4,5-c]pyrrole-2-one **49** (Scheme 3.1) the key intermediate for the synthesis of pyrrolo-TTFs.[2] The further functionalisation of pyrrolo-TTFs have attracted much scientific attention, since they found use as building blocks in various molecular and supramolecular systems.[23,37,47]



Scheme 3.1: Synthesis of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49**, a key intermediate by *Jeppesen et al*.

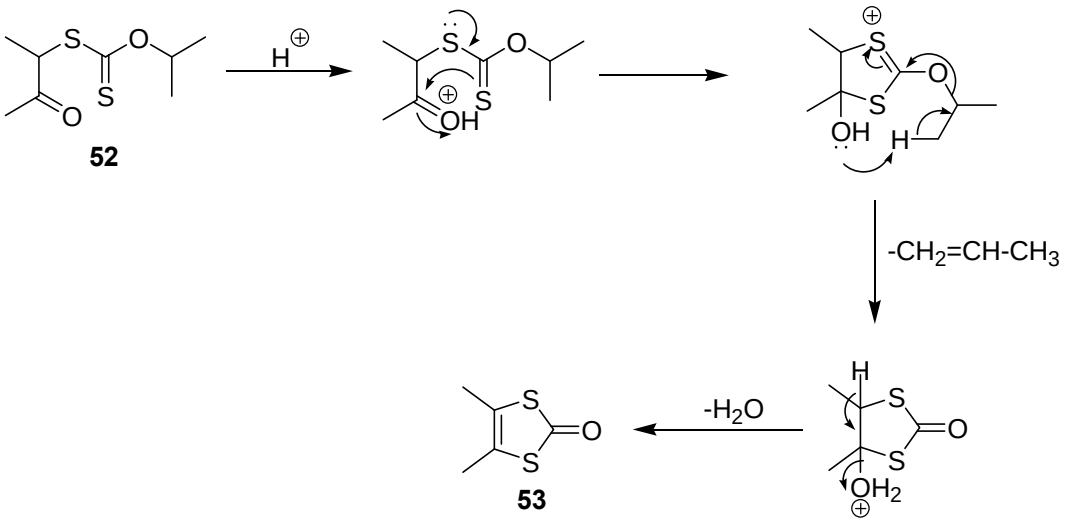
The first phase of my experimental work was aimed at the optimization of the synthesis of two key intermediates for the preparation of MPTTFs, compound **53** and compound **49** (Scheme 3.2). This synthetic pathway, previously used in our research group, differs from the one developed by *Jeppesen* et al. discussed above by the use of very affordable starting materials and avoidance of the use of toxic mercury acetate. The synthesis of compound **53** is commonly performed via a three-step sequence using low cost easily available starting materials: CS_2, 2-propanol, KOH and 3-chlorobutanone. Compound **53** is used as a precursor for the synthesis of TTFs and related materials as well as metal dithiolene complexes.[48,220] Compound **53** shows simple and recognizable NMR spectra because of its simple symmetric structure, and can be further modified by radical halogenation of the methyl groups as well as by transchalcogenation forming the corresponding 4,5-dimethly-1,3-dithiol-2-thione. Compound **49** is a key intermediate for a synthesis of MPTTFs and BPTTFs. After preparation it can be stored for years without decomposition,[48] which makes it one of the most useful building blocks in TTF synthesis. Straightforward accessibility of compound **53** will allow preparation of compound **49** in multigram quantity. In this, work, initial preparation of compound **49** was performed on relatively low gram scale for the optimization of reaction procedures, but it was scaled up in subsequent experiments (Scheme 3.2).



Scheme 3.2: The synthetic pathway for the synthesis of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49**.

Potassium *O*-isopropyl dithiocarbanate **51** was prepared upon reaction of 2-propanol **50** with CS_2 in the presence of KOH. The product was purified by its recrystallization from ethanol. It was noted that using dry KOH leads to the improvement of the yield. Synthesis of compound **52** was performed in the reaction of potassium *O*-isopropyl dithiocarbanate **51** with 3-chloro-2-butanone. Though this reaction was usually performed in acetone, it was discovered that the solventless reaction affords the formation of the target product with the yield of >88%, not compromising its purity, as demonstrated by NMR. Purification of the product was performed by the dilution of the reaction mixture with DCM, filtration of the precipitate and solvent evaporation. Compound **52** was used in the next synthetic step

without further purification. Cyclization of **52** was performed in an acid-catalysed reaction (Scheme 3.3) which afforded 4,5-dimethly-1,3-dithiol-2-one **53** with yields up to 84 %. Again, we tested the reaction with neat solvent-free starting material, and several test reactions were run for the optimization of preparation of compound **53** using different concentrations and ratios of H_2SO_4. Reaction temperature was maintained below 5 °C in all experiments, which is important for successful crystallization of the product directly from the reaction mixture. Work-up was performed by addition of ice-cold water-ice mixture, which lead to almost complete precipitation of the product in the form of large colourless transparent crystals. Filtration followed by drying of the crystals over phosphorus pentoxide afforded pure product without the need for additional purification. When using H_2SO_4 (18.4 M) 67% yield was obtained, whereas slight dilution of the acid to ca. 15 M improved the yield of the reaction to 84%. This improved synthetic procedure afforded the preparation **53** without the need of column chromatography or vacuum distillation, which were used before to obtain **53** in its preform. Physical propertied of **53** (melting pint, NMR) evidenced the high purity of the synthesized product.



Scheme 3.3: Acid-catalyzed mechanism of the ring closure of 4,5-dimethly-1,3-dithiol-2-one **53**.

All three synthetic steps for the preparation of compound **53** were achieved only with recrystallization, evaporation and filtration as purification methods. Avoidance of chromatography allows preparation of compound **53** in scales of up to 100 g.[23] Besides the inexpensive starting material and the convenient purification, which permits easily scale-up, this pathway offers the benefit of avoiding the use of mercury compound for transchalcogenation, as in the pathway previously suggested by *Becher* et al.[47]

4,5-Bis(bromomethly)-1,3-dithiol-2-one **54** was prepared from compound **53** by radical bromination reaction with freshly recrystallized NBS (Table 3.1). NBS was ground before the reaction, which is important due to its relatively low solubility in the reaction mixture. Original

reaction was performed in CCl_4, which is nowadays considered to be a highly toxic ozone-depleting solvent, and its commercial accessibility has also become rather challenging. Due to this fact, we decided to optimize the reaction testing it in other solvents suitable for radical reactions, as well as investigating radical initiators. Thus, in addition to CCl_4, this reaction was also tested in CH_3CN, $CHCl_3$ and DCM. No target product could be isolated when CH_3CN was used as a solvent, the starting material also decomposed. Then reaction was tested in refluxing $CHCl_3$ using AIBN instead of $(BzO)_2$ as a radical initiator, since due to the lower boiling point of $CHCl_3$ we needed to take an initiator with lower activation energy of radical formation. Still the yield almost did not improve. Finally, we discovered that DCM was the best solvent when visible light (300 W incandescent lamp was used as its source) was used as a radical initiator: the yield improved to 71%. DCM is a readily available solvent that is considered to be much more environmentally benign than CCl_4 or $CHCl_3$. The target product of the reaction, the symmetric *bis*-brominated derivative **54**, crystallizes from the reaction mixture, unlike other possible asymmetric and poly-brominated side products. Therefore, the workup of the reaction was relatively easy and constituted the trituration of the product with hot MeOH, which removed more soluble side products, succinimide and traces of the unreacted NBS. This simple purification method afforded the compound **54** in very high purity, as evidenced by its sharp melting point and clean NMR spectra.

Table 3.1: Bromination reaction of 4,5-dimethly-1,3-dithiol-2-one **53** with NBS in different solvents and with different radical initiators.

Entry	Starting material	Radical initiator	Solvent	Temperature (°C)	Time (hrs)	Yield (%)
1	**53**	Bz_2O_2	CCl_4	73 (reflux)	2	39
2	**53**	Bz_2O_2	CH_3CN	80 (reflux)	2	-
3	**53**	AIBN	$CHCl_3$	61 (reflux)	24	43
4	**53**	light	$CHCl_3$	35-40	4	43
5	**53**	light	DCM	40 (reflux)	4	71

TsNHNa **46** protecting group was prepared using sodium metal in ethanol to produce sodium ethoxide (NaOEt), which was then reacted with toluene sulphonamide **60** to give pure finely crystalline product. As next, cyclization reaction of compound **54** with TsNHNa **46** gave 4,6-dihydro-*N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **48**. Two equivalents of the TsNHNa **46** needed to be used for the reaction, the first equivalent performed nucleophilic substitution of one of the bromides, whereas the second equivalent served as a base to deprotonate -NH group in the partially closed intermediate. Tosyl group has been established as the most convenient protecting group for the pyrrol-2-one intermediate in the synthesis of pyrrolo-TTFs, since it proved to be stable in the triethyl phosphite-mediated coupling reaction under harsh conditions.[37] Variations of reaction conditions were attempted by using different solvents, such as DMF and DMSO (strongly polar aprotic solvents are necessary for the dissolution of the starting materials) but no significant influence on reaction yields was noted (Table 3.2). Compound **48** was then further oxidised by reacting with 2 equivalents of DDQ to

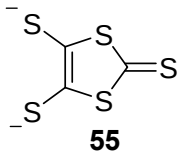
obtain the key TTF precursor *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49** with 93% yield. During this reaction, aromatic pyrrole ring is being formed, which facilitates this oxidation reaction.

Table 3.2: Ring closing reaction of 4,5-Bis(bromomethly)-1,3-dithiol-2-one **54** with TsNHNa **46** in different solvents with formation of 4,6-dihydro-*N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49**. Reaction conditions: 25 °C, 2 h.

Entry	Starting material	Solvent	Yield (%)
1	**54**	DMF	43
2	**54**	DMSO	43

3.3 Preparation of 1,3-dithiole-2-thiones, building blocks for tetrathiafulvalene

1,3-Dithiole-2-thione (DMIT, **55**) play an important role on the preparation of different TTF-derivatives. For easy separation of DMIT it is commonly isolated as zinc chelate in the form of $(Et_4N)_2[Zn(DMIT)_2]$ **56**.[221] In 1927, *Fetkenheuer et al*. prepared DMIT dianion (Figure 3.2) due to failure to prepare tetrathiooxalate. Reduction of CS_2 can be carried out electrochemically and it can procced through a transient tetrathiooxalate intermediate. Easy synthesis of DMIT by the reduction of CS_2 provide a general way to prepare it acyl and alkyl derivatives. Other synthetic strategies have been developed to prepare compounds incorporating the DMIT moiety.[222] DMIT serves as a convenient precursor for various TTF derivatives. Desulfurization or carbeniod coupling can be performed after conversion to the dithiolium salts. In 1964, *Mayer* and co-workers reported a preparation of 1,3-dithiole-2-thiones by cyclization reaction of sodium acetylides with sulphur and CS_2 in liquid ammonia. The yield was, however, very low.[223]

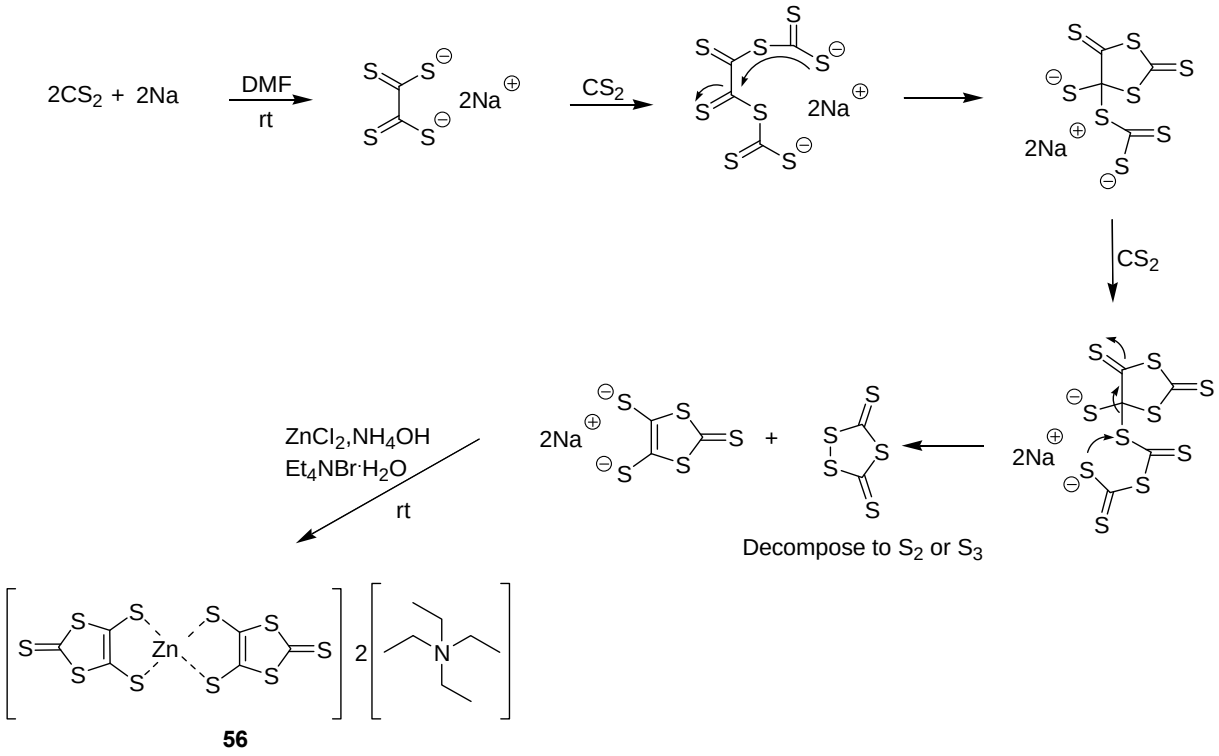


55

Figure 3.2: Structure of 1,3-dithiole-2-thione dianion (DMIT, **55**).

Asymmetric MPTTFs are prepared in a coupling reaction between pyrrolone **49** and differently substituted 1,3-dithiole-2-thiones **57**, which are conveniently prepared from $(Et_4N)_2[Zn(DMIT)_2]$ salt **56.** Stability of $(Et_4N)_2[Zn(DMIT)_2]$ **56** is much higher in comparison with sodium, lithium, and potassium salts, which are all found to be unstable in acidic reaction medium and air/moisture sensitive. Salt **56** can be stored for several months at room temperature without any special precautions. Preparation of 1,3-dithiole-2-thione-4,5-dithiolate can be performed in several ways where reduction of CS_2 by sodium metal (Scheme

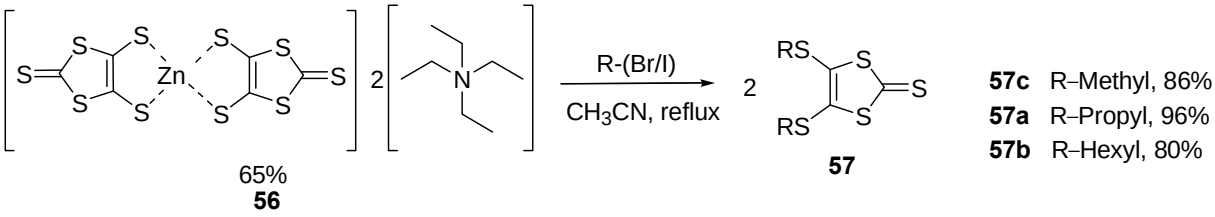
3.4) in dry DMF is the most convenient one.[222,224] DMIT is then isolated as $(Et_4N)_2[Zn(DMIT)_2]$ **56**. *Hoyer* group developed a synthetic approach from commercially available cheap starting materials, which is easily scaled up to ca. 100 g (Scheme 3.4).



Scheme 3.4: Mechanism of formation of $(Et_4N)_2[Zn(DMIT)_2]$ **56.**[26]

$(Et_4N)_2[Zn(DMIT)_2]$ **56** was prepared upon reduction of CS_2 reaction with sodium metal in dry DMF overnight. Afterwards zinc chloride in ammonium hydroxide solution was added followed by the addition tetraethylammonium bromide (Et_4NBr) solution. After that $(Et_4N)_2[Zn(DMIT)_2]$ **56** precipitates from the reaction mixture, is filtered off, washed with ether and dried. Intermediate C_2S_5 is considered to be unstable and likely to decompose to CS_2 and sulphur.[224] Still, significant amounts of malodorous sulphur derivatives form in this reaction, therefore, the reaction residue and filtrates should be disposed with care.

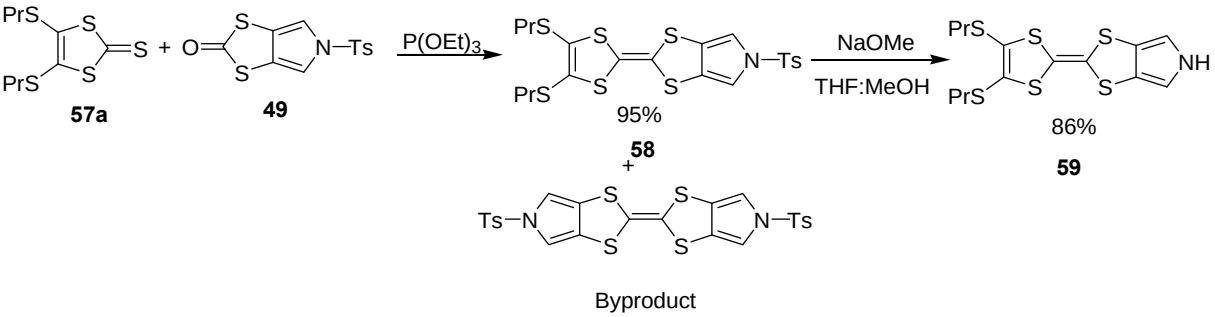
Several differently substituted 1,3-dithiole-2-thiones **57a-c** were prepared upon reaction of $(Et_4N)_2[Zn(DMIT)_2]$ **56** with alkyl halides such as, propyl bromide, hexyl bromide and methyl iodide (Scheme 3.5). Compound **57a** and **57b** were prepared from zincate salt **56** in reactions with propyl bromide or hexyl bromide, correspondingly, under reflux in MeCN. Compound **57c** was also prepared from zincate salt **56** and methyl iodide under reflux in MeCN, crystalline precipitate recrystallized from DCM and petroleum ether (1:1). The use of large-scale flash column chromatography was not necessary, filtration through silica plug of ca. 3 cm was performed to eliminate the minor amounts of polar reaction impurities in compounds **57a** and **57b**.



Scheme 3.5: Synthesis of 1,3-dithiole-2-thiones **57a-c**.

3.4 Preparation of monopyrrolo-tetrathiafulvalene derivative

Cross-coupling of 4,5-bis(propylthio)-1,3-dithiole-2-thione **57a** with compound **49** in neat triethyl phophite afforded the *N*-tosyl-2-(4,5-bis(propylthio)-(1,3)-dithiol-2-ylidene)-(1,3)-dithiolo[4,5-c]pyrrole **58** in 95% yield (Scheme 3.6), whereas the symmetric derivative by-product is formed only in trace amounts. Such good yield of the asymmetric product is achieved by the use of an excess, 2 equivalents ,of 1,3-dithiole-2-thione **57**, which minimizes the self-coupling of compound **49**. After that, tosyl protecting group was removed from tosyl-MPTTF **58** by heating/reflux in a presence of sodium methoxide (NaOMe) excess in a 3:2 mixture of dry THF:MeOH[37,47] under argon, since the non-protected MPTTF **59** is an easily oxidizable compound, affording the target 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole **59** as a crystalline orange powder. Physical properties of the synthesized compound fully corresponded to the previously reported ones, confirming the identity of the product. Thus, the first goal of the project, the optimized synthesis of the MPTTF **59**, was successfully achieved.

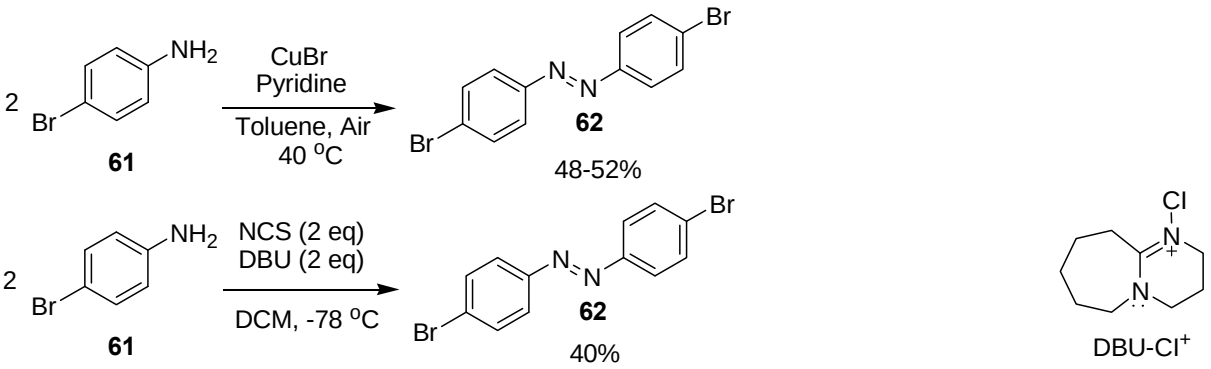


Scheme 3.6: MPTTF **59** derivative synthesis.

3.5 Preparation of azobenzene derivative

4,4'-Dibromoazobenze **62** was prepared using two methods that use commercially available and inexpensive starting materials under mild conditions. First method makes use of 4-bromoaniline **61**, which undergo a self-reaction via oxidation in a presence of 2 equivalents of NCS that react with 2 equivalents of DBU to produce the reactive chloro-DBU intermediate.[203] 4-Bromoaniline **61** react with chloro-DBU specie to give 4,4'-dibromoazobenze **62** in 40% yield. Second method, was a use of air or dioxygen as an oxidant

in the presence of copper(I) catalyst and pyridine. This method offers high yield obtained using air or dioxygen as an oxidant while resulting in high efficiency transformation using pyridine as a copper ligand. Several test reactions were performed and it was observed that longer period of time gives lower yields.[201] A slight modification on both methods for 4,4'-dibromoazobenze **62** purification, a filtration technique was applied to filter off the crystalline product instead of column chromatography.



Scheme 3.7: Synthesis of **62** from **61** via oxidation methods.

3.6 Preparation of monopyrrolo-tetrathiafulvalene derivative conjugates with different spacer groups

S_N2 reactions have proven to show excellent results for a coupling reaction between suitable activated compounds with a pyrrole-*H* to produce *N*-alkylation of MPTTFs. Copper(I)-catalyzed Ullmann-type coupling reaction are used for the *N*-arylation of MPTTFs to prepare the extended conjugate systems.[48] *N*-Arylation reaction can be performed in a presence of rich or deficient electron aromatic derivatives of thio-alkyl or non-substituted MPTTF substrates. The use of Buchwald–Hartwig amination reaction, which uses expensive Pd-based catalyst, has been so far avoided due to the general efficiency of a copper-mediated Ullman-type reaction with inexpensive Cu(I) catalyst.[225] In my project, commercially available spacer groups, such as single phenyl **67** in which central aromatic bridge will maintain either permanent conjugation or permanent decoupling with biphenylene **69** and stilbene based with permanent conjugation **71** have been tested in preparation of MPTTF derivatives using copper-mediated Ullman-type reaction (Figure 3.3).

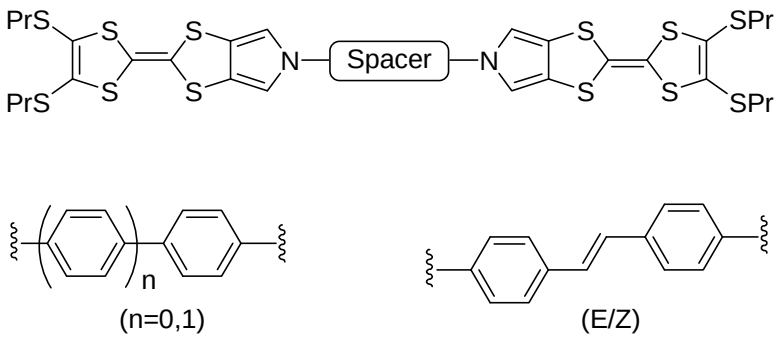
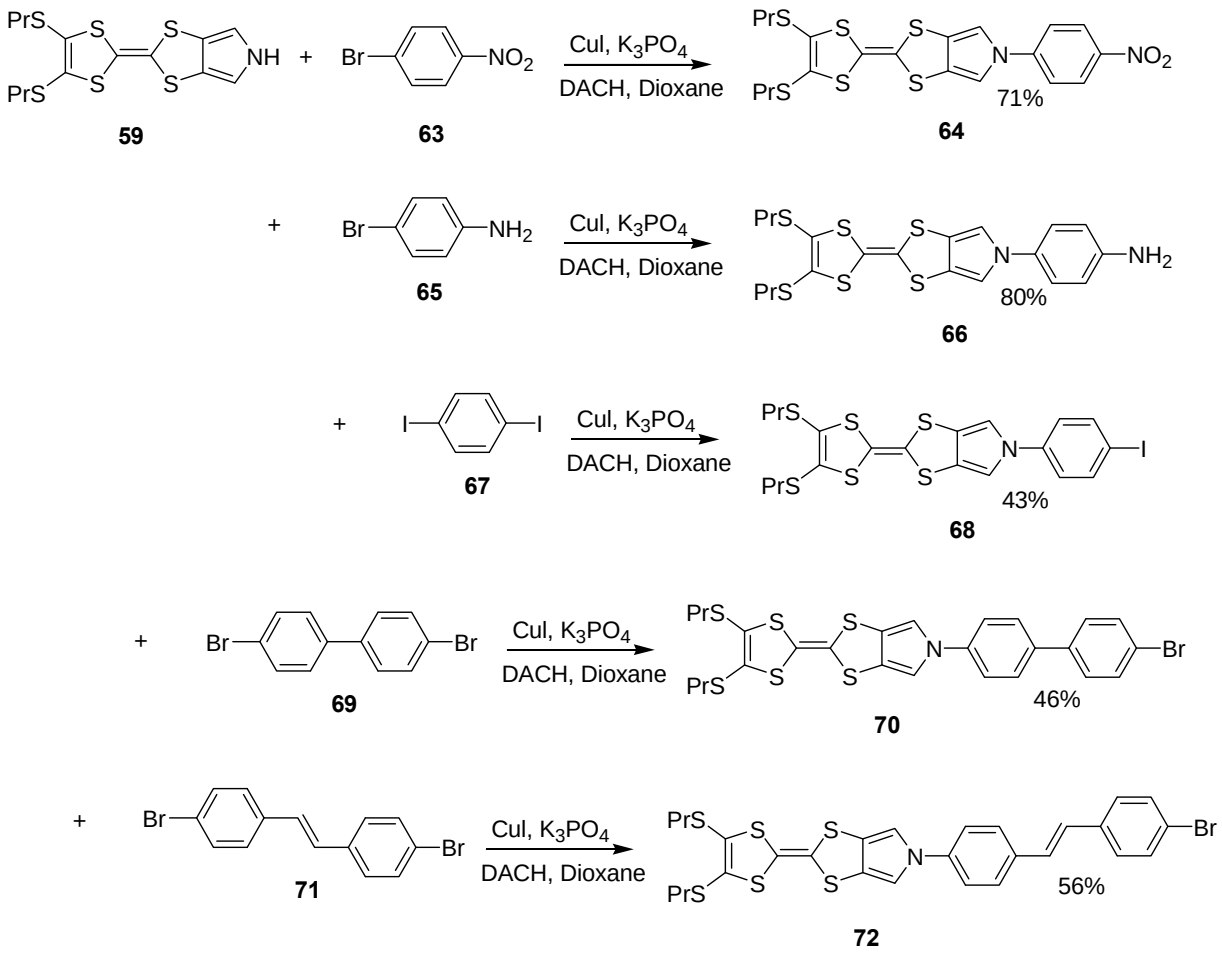


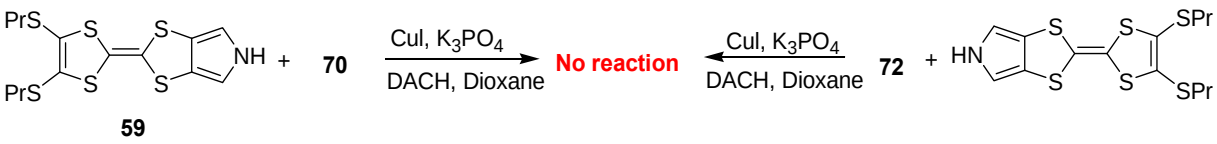
Figure 3.3: Target MPTTFs derivative linked with a spacer group of different span and conjugation.

2-[4,5-Bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-nitro-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **64** was prepared via Ullman-type reaction with copper (I) catalyst using Schlenk tube from 4-bromonitrobenzene **63** and MPTTF **59** derivatives which resulted in 71% yield (Scheme 3.8). 2-[4,5-Bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-analine)-5*H*-1,3-dithiolo[4,5-c]pyrrole **66** was prepared via two methods: Schlenk tube heating and microwave activation,[226] both gave same yield of 80% from 4-bromoanaline **65** and MPTTF **59** derivatives. Compounds **64** and **66** were prepared for preparation of **73**. Using 1,4-diiodobenzene **67** spacer groups with an aim to make permanent conjugation with MPTTF **59** derivatives. Unfortunately mono-phenyl-MPTTF coupling took place instead of the desirable di-phenyl-MPTTF coupling, resulting in 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-iodo-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **68** with 43% yield**.** After an unsuccessful attempt with a phenyl spacer, which should maintain permanent conjugation between two MPTTF units, non-conjugating 4,4'-bromobiphenylbenzene **69** spacer was tried. Unfortunately, mono-biphenylene-MPTTF coupling took place and 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-bromo-biphenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **70** was obtained with a yield of 46%. Increasing the reaction time and use of MPTTF excess did not help to achieve the desired two-fold coupling reaction.



Scheme 3.8: *N*-Arylation using Ullman-type coupling reaction.

A further attempt to obtain the *bis*-MPTTF aromatic derivatives was performed using the reaction between mono-coupling products **70** and **72** and MPTTF **59** under the Ullmann coupling conditions (Scheme 3.9). The idea was that the use of the excess of fresh MPTTF **59** and Cu(I) catalyst would afford the formation of the target *bis*-MPTTF derivative. Unfortunately, these attempts also proved to be unsuccessful.



Scheme 3.9: Synthetic attempts to prepare *bis*-MPTTF products from mono-coupling products **70** and **72**.

Only a few examples of tetrathiafulvalene-azobenzene (TTF-AB, **73**) conjugates have been reported up to date. Two recent papers report on modulation the redox properties of photochromic TTF derivatives by optical isomerization of appended AB chromophores.[144,227]

In both cases, TTF backbone changes it electrochemical properties due to its mechanical distortion induced by an AB moiety in a macrocyclic architecture.

4,4'-Dibromoazobenze **62** it one of the spacer group that was tested with an intention to bridge two MPTTF **59** derivative groups creating MPTF-AB **73** conjugates (Figure 3.4). In the E-configuration of AB moiety, both **59** units will be conjugated with each other through the central planar aromatic AB unit (it is known from X-ray structures that MPTTFs are conjugated with the neighbouring aromatic units, see for example),[225] whereas in the Z-configuration of AB both MPTTFs will be not in conjugation and electronically decoupled from each other. Such change in conjugation of two MPTTF units should lead to the alteration of their electrochemical properties upon photo-switching.[228] Using AB spacer group may allow the preparation of prototypes for electronic memory modules with orthogonal write (optical) and read (electrochemical) modes.

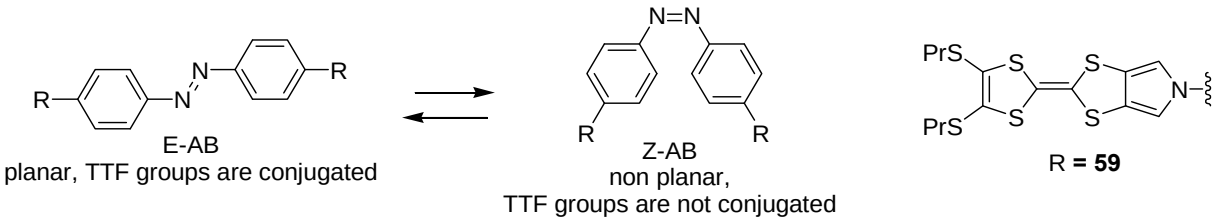
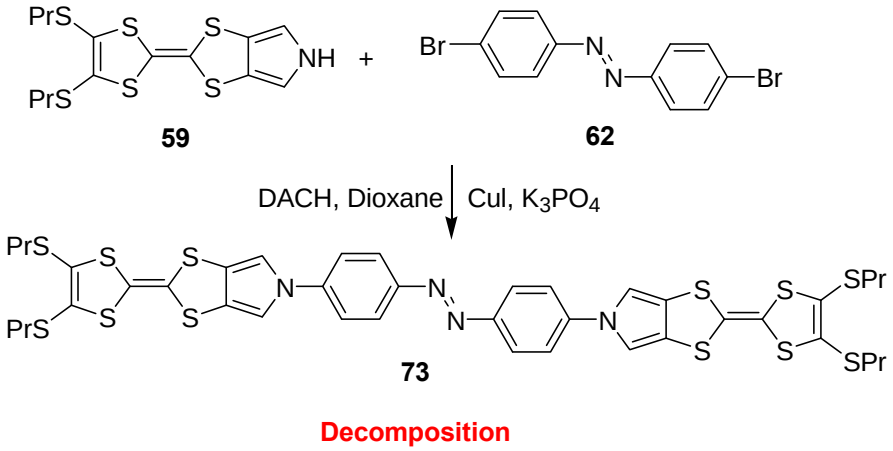


Figure 3.4: Modus operandi of the molecular device.

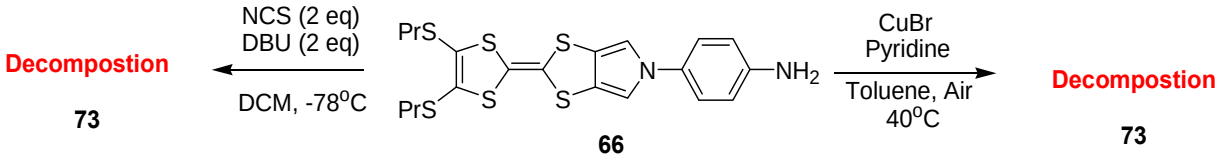
Attempts to prepare MPTTF-AB **73** were unfortunately unsuccessful due to decomposition when using copper-catalysed method coupling method between MPTTF **59** and *bis*-brominated AB **62** (Scheme 3.10).



Scheme 3.10: Copper(I)-catalyzed coupling of MPTTFs **59** with brominated AB **62** derivative.

Other options were considered after the Cu-catalyzed coupling reaction did not produce the target compound. Oxidation reactions under mild conditions were tested since positive

results were obtained with a model compound (Scheme 3.11). Oxidation of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-analine)-5*H*-1,3-dithiolo[4,5-c]pyrrole **66** via air or dioxygen in a presence of CuBr and pyridine was unsuccessful since decomposition was observed during a preparation of **73**. Likely it was due to the electron-rich nature of the MPTTF moiety. Oxidation of **66** with NCS in a presence of DBU was also unsuccessful and decomposition with the formation of non-identifiable product mixture was observed. All three reaction mixtures display an intense red colour, analysis of which indicated the decomposition of the starting materials.



Scheme 3.11: Oxidation of MPTTF-substituted aniline **66** with two different methods.

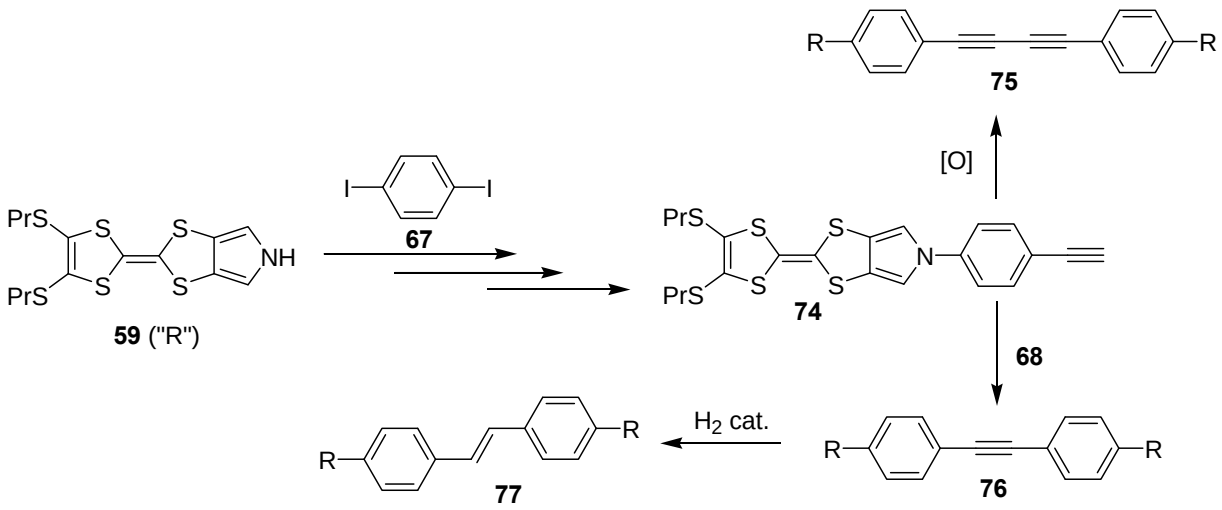
3.7 Conclusions and Outlook

In conclusion, a key precursor *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49** for the synthesis of monopyrrolo-tetrathiafulvalene **59** derivative has been synthesized in six steps. The synthesis of 4,5-dimethly-1,3-dithiol-2-one **53** was optimized to avoid tedious purification that was used before. Cheap reagents and simple workup such as recrystallization, evaporation and filtration allow a multigram-scale synthesis (*ca.* 100 g) of 4,5-dimethly-1,3-dithiol-2-one **53** to be easily achievable. The synthesis of 4,5-bis(bromomethly)-1,3-dithiol-2-one **54** was optimized by replacing highly toxic ozone-depleting solvent CCl_4 with a more environmentaly benign DCM and using light as radical initiator and affording the yield of 71%. Compound **54** was used in the preparation of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49**, the key intermediate in the synthesis of monopyrrolo-tetrathiafulvalene **59**. Large scale column chromatography for 1,3-dithiole-2-thiones **57a-c** was avoided, filtration through silica plug of ca. 3 cm was performed to eliminate the minor amounts of polar reaction impurities. MPTTF derivative **59** was then prepared from compounds **49** and **57a** in a phosphite-mediated coupling and was used in Ullmann-type Cu(I)-catalyzed couplings with different aromatic derivatives. Performed synthetic work is summarized in Scheme 3.12.

Scheme 3.12: Summary of the performed synthetic work.

Unfortunately, the expected two-fold Ullmann coupling reactions with di-iodo and di-brominated aromatic derivatives could not be achieved, instead one-fold couplings with the yields in a range of 43–56% have been observed. Attempts to prepare the bis-MPTTF azobenzne derivatives were also unsuccessful, both using Ullmann coupling to the AB spacer **62**, as well as oxidative coupling of the amino-MPTTF derivative **66**.

Currently we explore the possibility of the preparation of the mono-aromatic MPTTF derivatives followed by their coupling through the middle of the spacer. Ullman-type and Sonogashira reactions are a method of choice for preparing compound **74**, then oxidation can be performed for dimerization compound **75** or coupling with **68** to produce **76**. Compound **76** can be reduced to a stilbene-based derivative **77** (Scheme 3.13).



Scheme 3.13: Possible synthetic routes for the preparation of several aromatic MPTTF derivatives.

Exploration of reduction reactions under mild conditions can be considered an option for the nitro MPTTF derivative **64** with the goal to prepare *bis*-MPTTF azobenzene derivatives.

Chapter 4 : Experimental Part

4.1 Instruments and methods

4.1.1 Reagents and solvents

Reagent and solvents used for reactions, separation, washing, recrystallization, thin-layer chromatography and column chromatography were purchased from Sigma-Aldrich, Glassworld, CC Imelmann, or Promark Chemicals of a reaction grade or higher purity.

Dry solvents and reagents were purified under argon (Ar) as follows:

1,4-Dioxane	Distilled over sodium metal (Na/benzophenone)
Tetrahydrofuran	Distilled over sodium metal (Na/benzophenone)
Triethyl phosphite	Distilled over calcium hidride (CaH_2)

4.1.2 Melting point determination

Melting points of solid products were taken on a Stuart Melting Point 3 (SMP3) apparatus.

4.1.3 Column chromatography

Column chromatography was performed with silica gel 60 (0.063-0.2 mm). Crude mixture was dissolved in a small amount of solvent and transferred into a column, then pure collected fractions were combined and evaporated on a rotary evaporator under low pressure and temperature of ca. 40 °C.

4.1.4 Thin layer chromatography

TLC plates (aluminium) with silica gel 60 F_{254}, 20 x 20 cm, layer thickness 0.2 mm (Merck), were cut into 2.5 x 5 cm stripes. The spots, marks and bands on a TLC-plate were observed using a UV lamp with a wavelength of 254 nm.

4.1.5 Nuclear magnetic resonance spectroscopy

^{1}H NMR and ^{13}C NMR spectra were studied on a Bruker Fourier 300 (300.18 MHz for ^{1}H) and Bruker Avance II 600 (600.28 MHz for ^{1}H and 150.95 for ^{13}C) operating at temperature ca 25 °C with $CDCl_3$ and *d*-acetone used as solvents using an NMR high resolution probe = 5 mm ^{1}H/^{13}C equipped with z gradient coil. Chemical shifts are recorded in parts per million (ppm) downfield from tetramethylsilane (TMS) with the solvent's signals at δ_H 7.26 ppm and δ_C 77.16 ppm for chloroform-*d* and δ_H 2.09 ppm and δ_C 29.82 ppm for *d*-acetone playing the role of internal reference. Coupling constants (J) are reported in Hz for peak multiplets. The abbreviations s, d t, q and m stand for singlet, doublet, triplet, and multplet, respectively. Commonly, a water peak can be seen at δ_H 1.56 ppm for the spectra measured in chloroform-*d* and δ_H 2.85 ppm for the spectra measured in *d*-acetone.[229] Some trace impurities in chloroform-*d* can be seen at δ_H 1.27 ppm and δ_H 0.90-0.86 ppm and belong to residual long chain alkane-based grease.

4.1.6 Purification techniques and equipment

Filtration was performed using glass sinter funnels, evaporations was performed using a rotary evaporation under reduced pressure and recrystallizations was performed using a heating mantle and then cooling to room temperature and/or about 0 °C in a freezer. Degassing reaction mixture was performed using Schlenk line by freezing the reaction mixture with liquid nitrogen, evacuating under oil pump vacuum, thawing under vacuum, and then filling with an inert gas; repeated two or three times. Closed vessel reactions were performed using thick-walled Schlenk tubes and microwave tubes.

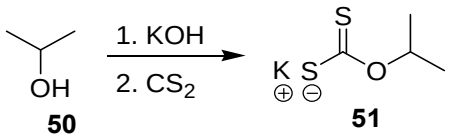
4.1.7 Identification of previously reported compounds

Identify and purity of previously reported compounds was established based on their ^{1}H NMR spectra, melting points and R_f values. In all the cases there was almost a perfect match of the measured quantities/spectra with the previously reported or measured ones, and no additional identification methods were required. In a few cases, low quality ^{13}C NMR spectra were taken to for the ultimate confirmation of the compound identity based on chemical shifts of several intense bands. High quality ^{13}C NMR spectra were measured only for the previously unreported compounds.

4.2 Experimental procedures

4.2.1 Synthesis of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one

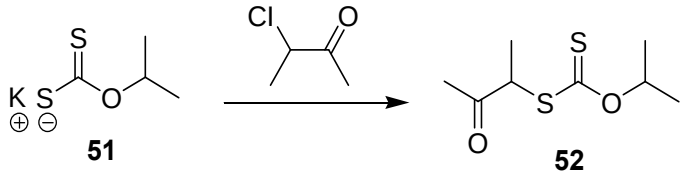
4.2.1.1 The synthesis of potassium *O*-isoproply dithiocarbonate (51)[230]



KOH (11.2 g, 0.20 mol, 1 eq.) was dissolved in 200 mL of isopropanol (**50**) and stirred constantly at room temperature. The CS_2 (15.2 g, 0.20 mol, 12 mL, 1 eq.) was slowly added drop wise and the reaction mixture was allowed to stir for 1 hour under inert atmosphere. Excess ether was then added into the reaction mixture and the precipitate was collected by filtration. The precipitate was then recrystallized from ethanol (*ca.* 200 mL) and gave pure crystals of potassium *O*-isoproply dithiocarbonate (**51**) (23.3 g, 0.134 mol, 67%) as pale-yellow needles.

Melting point: 233–236 °C (decomp.).

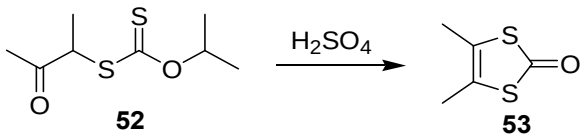
4.2.1.2 The synthesis of *O*-isoproply-*S*-3-oxobutan-2-yl dithiocarbonate (52)[231]



Potassium *O*-isoproply dithiocarbanate (**51**) (21.7 g, 0.124 mol, 1 eq.) was mixed with 3-chloro-2-butanone (13.3 g, 0.124 mol, 12.6 mL, 1 eq.) which was added drop wise. The reaction mixture was allowed to stir overnight constantly. DCM (50 mL) was added, precipitate was filtered through celite, and filtrate concentrated on a rotary evaporator. The evaporation gave pure *O*-isoproply-*S*-3-oxobutan-2-yl dithiocarbonate (**52**) (22.6 g, 0.110 mol, 88%) as a light-yellow oil.

^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 5.76-5.67 (m, 1H, -CH), 4.36 (q, *J* = 7.2 Hz, 1H, -SCH), 2.30 (s, 3H, -CH_3), 1.45 (d, *J* = 7.2 Hz, 3H, -CH_3), 1.38 (d, *J* = 6.2 Hz, 6H, 2x -CH_3).

4.2.1.3 The synthesis of 4,5-dimethyl-1,3-dithiol-2-one (53),[231] general procedure



O-isoproply-*S*-3-oxobutan-2-yl dithiocarbonate (**53**) (1 eq.) was added into chilled to <5 °C H_2SO_4 while stirred within a period of 30 minutes. The reaction mixture was kept under the temperature of <5 °C for 2 hours while constantly stirred. The reaction mixture turned to dark red after a while, and crystals started to form. The ice-cold water was added into the mixture, stirred for 30 minutes, and the colourless precipitate was collected by filtration, and washed with cold water until the pH of the water was around 7.

4.2.1.3.1 The synthesis of 4,5-dimethyl-1,3-dithiol-2-one (53), procedure 1

O-isoproply-*S*-3-oxobutan-2-yl dithiocarbonate (**52**) (1.51 g, 7.32 mmol, 1 eq.) was added drop wise into chilled to <5 °C H_2SO_4 (18.4 M, 8 mL). Purification by means of filtration yielded pure crystals of 4,5-dimethyl-1,3-dithiol-2-one (**53**) (0.720 g, 4.92 mmol, 67%) were obtained as white needles.

Melting point: 46–48 °C; R_f (DCM) = 0.74; ^{1}H NMR(δ) (300.18 MHz, Chloroform-*d*): 2.15 (s, 6H, 2x -CH_3).

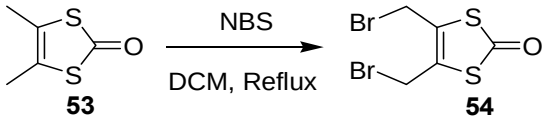
4.2.1.3.2 The synthesis of 4,5-dimethyl-1,3-dithiol-2-one (53), procedure 2

O-isoproply-*S*-3-oxobutan-2-yl dithiocarbonate (**52**) (2.97 g, 14.4 mmol, 1 eq.) was added drop wise into chilled to <5 °C H_2SO_4 (15 M, 10 mL). Purification by means of filtration yielded pure crystals of 4,5-dimethyl-1,3-dithiol-2-one (**53**) (1.36 g, 9.29 mmol, 65%) were obtained as white needles. Physical properties are identical to the product obtained in Procedure 1.

4.2.1.3.3 The synthesis of 4,5-dimethyl-1,3-dithiol-2-one (53), procedure 3

O-isoproply-*S*-3-oxobutan-2-yl dithiocarbonate (**52**) (22.6 g, 0.110 mol, 1 eq.) was added potion wise with first half drop wise into chilled to <5 °C H_2SO_4 (15 M, 60.00 mL) while stirred within a period of 30 minutes and another half after 30 minutes. The reaction mixture was allowed to stir for 1 hour. Purification by means of filtration yielded pure crystals of 4,5-dimethyl-1,3-dithiol-2-one (**53**) (13.4 g, 0.0916 mol, 84%) were obtained as white needles. Physical properties are identical to the product obtained in Procedure 1.

4.2.1.4 The synthesis of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (54),[232] general procedure



53 **54**

4,5-Dimethyl-1,3-dithiol-2-one (**53**) (1 eq.) and finely ground crystals of freshly recrystallized NBS (2.1 eq.) were refluxed as a suspension in a solvent and stirred constantly. During the reaction precipitate of succinimide gradually formed. The reaction mixture was then evaporated to dryness and cold methanol was added to dissolve succinimide and reaction side products, whereas the target dibromide remained undissolved. The product was then additionally triturated with a small portion of methanol.

Note: 10 g of NBS can be recrystallized from ~100 mL of water and then dried over P_2O_5 under high vacuum in a dessicator.

4.2.1.4.1 The synthesis of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (54), procedure 1

4,5-Dimethyl-1,3-dithiol-2-one (**53**) (1.61 g, 11.0 mmol, 1 eq.), ground crystals of freshly recrystallized NBS (4.63 g, 26.0 mmol, 2.4 eq.) and $(BzO)_2$ (0.4845 g, 2 mmol, 0.18 eq.) were refluxed in CCl_4 (10 mL) while stirred constantly for a period of 2 hours. Purification by means of filtration yielded finely white crystals of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (**54**) (1.29 g, 4.24 mol, 39%).

Melting point: 155–158 °C; R_f (DCM) = 0.70; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 4.40 (s, 4H, 2x Br*CH*$_2$).

4.2.1.4.2 The synthesis of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (54), procedure 2

4,5-Dimethyl-1,3-dithiol-2-one (**53**) (0.677 g, 4.63 mmol, 1 eq.), ground crystals of freshly recrystallized NBS (1.78 g, 9.99 mmol, 2.2 eq.) and AIBN (0.0410 g, 0.25 mmol, 0.05 eq.) were refluxed in $CHCl_3$ (10 mL) while stirred constantly for overnight. Purification by means of filtration yielded finely white crystals of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (**54**) (0.604 g, 1.99 mol, 43%). Physical properties are identical to the product obtained in Procedure 1.

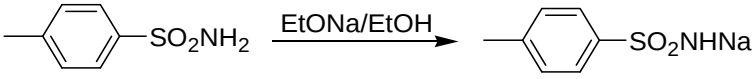
4.2.1.4.3 The synthesis of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (54), procedure 3

4,5-Dimethyl-1,3-dithiol-2-one (**53**) (0.699 g, 4.78 mmol, 1 eq.) and ground crystals of freshly recrystallized NBS (1.78 g, 9.99 mmol, 2.2 eq.) were refluxed in $CHCl_3$ (10 mL) while irradiated with light and stirred constantly for a period of 4 hours. Purification by means of filtration yielded finely white crystals of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (**54**) (0.623 g, 2.05 mol, 43%). Physical properties are identical to the product obtained in Procedure 1.

4.2.1.4.4 The synthesis of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (54), procedure 4

4,5-Dimethyl-1,3-dithiol-2-one (**53**) (15.1 g, 0.103 mol, 1 eq) and ground crystals of freshly recrystallized NBS (38.5 g, 0.216 mol, 2.1 eq) were refluxed in DCM (120 mL) while irradiated with light and stirred constantly for a period of 4 hours. Purification by means of filtration yielded finely creamy crystals of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (**54**) (22.3 g, 0.0734 mol, 71%). Physical properties are identical to the product obtained in Procedure 1.

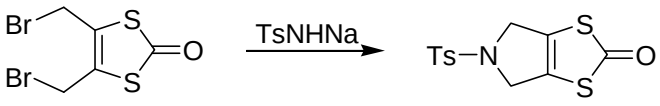
4.2.1.5 The synthesis of toluene sulfonamide monosodium salt (46)



60 **46**

Sodium metal (3.6 g, 0.157 mol, 1 eq.) was washed with hexane and added portion wise to absolute ethanol (*ca.* 200 mL) while stirred and was refluxed until all sodium dissolved. After cooling down to room temperature, toluene sulfonamide (26.9 g, 0.157 mol, 1 eq.) was added to the reaction mixture and refluxed for 1 hour under inert atmosphere. The reaction mixture was left in the fridge for overnight, then the precipitate was filtered off, washed with absolute ethanol (50 mL). Purification by means of filtration yielded finely crystalline white powder of toluene sulphonamide monosodium salt (TsNHNa) (**46**) (28.1 g, 0.145 mol, 93%). Melting point: > 300 °C.

4.2.1.6 The synthesis of 4,6-dihydro-*N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one (48)[51]

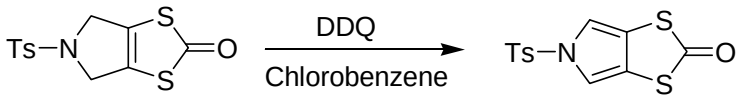


54 **48**

4,5-bis(bromomethyl)-1,3-dithiol-2-one (**54**) (10.9 g, 0.0359 mol, 1 eq.) was dissolved in DMF (80 mL) and cooled to 0-5 °C under inert atmosphere for 10 minutes. Finely crystalline of TsNHNa (13.9 g, 0.0719 mol, 2 eq.) was added and stirred at same conditions for 10 minutes. The reaction mixture was allowed to stand for 1 hour. The reaction mixture was then poured into saturated sodium chloride solution (100 mL), and precipitate was collected by filtration, washed with water (200 mL) and dried under vacuum. The precipitate was dissolved in DCM and the undissolved portion filtered off. The solution was purified by column chromatography in DCM over silica gel 5 cm to yield pure white/creamy powder of 4,6-dihydro-*N*-tosyl-1,3-dithiol[4,5-c]pyrrol-2-one (**48**) (4.86 g, 0.0155 mol, 43%).

Melting point: 177–178.5 °C; R_f (DCM) = 0.56; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*) 7.75 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.36 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 4.49 (s, 4H, Py-*H*), 2.45 (s, 3H, -CH_3).

4.2.1.7 The synthesis of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one (49)[2]



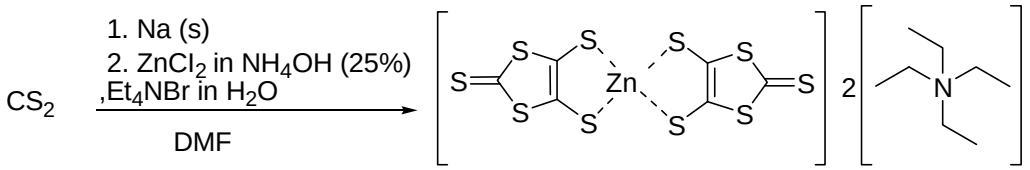
48 **49**

4,6-dihydro-*N*-tosyl-1,3-dithiol[4,5-c]pyrrol-2-one (**48**) (4.22 g, 13.5 mmol, 1 eq.) and DDQ (3.37 g, 14.6 mol, 1.1 eq.) in chlorobenzene (80 mL) were refluxed overnight. The solvent was removed in vacuo and residue purified by column chromatography in DCM over silica gel (10 cm) to yield pure white powder of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one (**49**) (3.91 g, 12.6 mol, 93%).

Melting point: 183–184.5 °C; R_f (DCM) = 0.67; ^{1}H NMR (δ) (300.18 MHz, Acetone-d_6): 7.92 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.63 (s, 2H, Py-*H*), 7.48 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 2.42 (s, 3H, -CH_3).

4.2.2 Synthesis of 1,3-dithiole-2-thiones

4.2.2.1 The synthesis of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol)zincate $(Et_4N)_2[Zn(DMIT)_2]$ (56)[224]

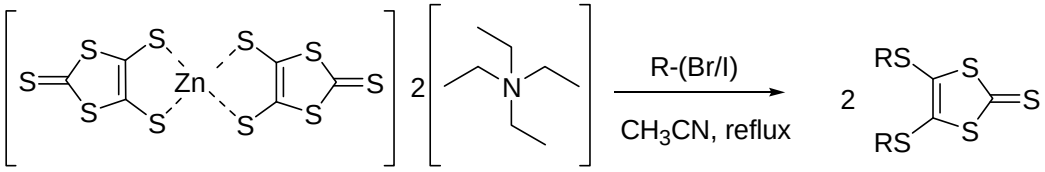


56

Dry DMF (48 mL) was degassed by bubbling of argon through it for about 20 minutes, CS_2 (30.4 g, 0.399 mol, 24 mL, 4 eq.) was added and the reaction mixture kept under argon upon being cooled to 0-5°C. Sodium metal (1.45 g, 0.0631 mol, 2 eq.) was weighed in finely cut pieces under hexane and added gradually into the reaction mixture while continuously stirred at 0-5°C. The intense blood red mixture was allowed to stir for overnight. A zinc chloride solution [$ZnCl_2$ (2.13 g, 0.0156 mol, 2 eq.) in NH_4OH, 46 mL] was slowly added while destroying small residues of unreacted sodium, and after 15 min it was followed by Et_4NBr solution (6.62 g, 0.0205 mol, 2 eq. in H_2O, 50 mL). A reaction mixture was stirred overnight and precipitate was collected by filtration, washed with isopropanol and ether (1:1) to afford pure red powder of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol) zincate salt $(Et_4N)_2[Zn(DMIT)_2]$ (**56)** (12.2 g, 0.0166 mol, 65%).

Melting point: 206–209 °C.

4.2.2.2 The synthesis of 1,3-dithiole-2-thiones (57),[233] general procedure



56 **57**

$(Et_4N)_2[Zn(DMIT)_2]$ (1 eq.) was suspended in CH_3CN, added alkyl halide (~5 eq.) and the reaction mixture was refluxed. The mixture was cooled to room temperature and solvent was removed to dryness. When non-volatile alkyl bromides where used, the residue was left under high vacuum to remove the unreacted alkyl bromide. The residue was dissolved in DCM, precipitate was filtered off through celite and filtrate was concentrated to ca. 30 mL and treated with activated charcoal overnight. The solution was then filtered through a plug of silica and concentrated under vacuum.

4.2.2.2.1 The synthesis of 4,5-bis(propylthio)-1,3-dithiole-2-thione (57a)

$(Et_4N)_2[Zn(DMIT)_2]$ (4.02 g, 5.48 mmol, 1 eq.) was suspended in CH_3CN (45 mL), added propyl bromide (4.19 g, 34.1 mmol, 3.1 mL, 6.2 eq.) and the reaction mixture was refluxed for 3 hours. Purification by means of filtration through silica (ca. 3 cm) yielded dark yellow oil of 4,5-bis(propylthio)-1,3-dithiole-2-thione (**57a**) (3.02 g, 10.7 mmol, 98%).

R_f (DCM) = 0.57; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 2.86 (t, *J* = 7.6 Hz, 4H, -SCH_2-), 1.77-1.64 (m, 4H, -CH_2-), 1.04 (t, *J* = 7.3 Hz, 6H, 2x -CH_3).

4.2.2.2.2 The synthesis of 4,5-bis(hexylthio)-1,3-dithiole-2-thione (57b)

$(Et_4N)_2[Zn(DMIT)_2]$ (11.6 g, 15.8 mmol, 1 eq.) was suspended in CH_3CN (45 mL), added hexyl bromide (13.1 g, 79.4 mmol, 11.14 mL, 5 eq.) and the reaction mixture was refluxed for 3 hours. Purification by means of filtration through silica (ca. 3 cm) yielded dark yellow oil of 4,5-bis(hexylthio)-1,3-dithiole-2-thione (**57b**) (9.05 g, 24.7 mmol, 78%).

R_f (DCM) = 0.81; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 2.88 (t, *J* = 7.0 Hz, 4H, -SCH_2-), 1.67 (p, *J* = 8.2 Hz, 4H, -CH_2-), 1.49-1.38 (m, 4H, -CH_2-), 1.34-1.27 (m, 8H, -CH_2-), 0.91 (t, *J* =7.0 Hz, 6H, 2x -CH_3).

4.2.2.2.3 The synthesis of 4,5-bis(methylthio)-1,3-dithiole-2-thione (57c)

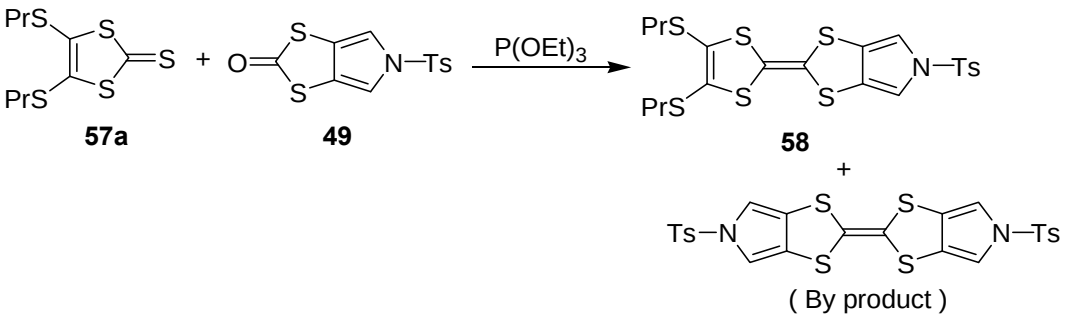
$(Et_4N)_2[Zn(DMIT)_2]$ (6.17 g, 8.41 mmol, 1 eq.) was suspended in CH_3CN (45 mL), added methyl iodide (6.00 g, 42.3 mmol, 2.63 mL, 5 eq.) and the reaction mixture was refluxed for 3 hours. Precipitate was filtrated through silica (ca. 3 cm) and crystalline powder was

recrystallized from DCM and petroleum ether (1:1) to yield pure yellow needle crystals of 4,5-bis(methylthio)-1,3-dithiole-2-thione (**57c**) (3.33 g, 14.7 mmol, 87%).

Melting point: 101–103 °C; R_f (DCM) = 0.79; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 2.51 (s, 6H, 2x -SCH_3).

4.2.3 Synthesis of monopyrrolo-tetrathiafulvalene derivative

4.2.3.1 The synthesis of N-tosyl monopyrrolo-tetrathiafulvalene derivative (58)[2]

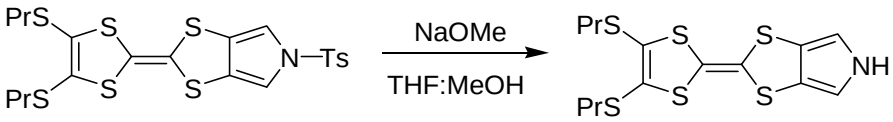


57a **49** **58** (By product)

N-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one (**49**) (3.00 g, 9.63 mmol, 1 eq.) and 4,5-bis(propylthio)-1,3-dithiole-2-thione (**57a**) (2.73 g, 9.66 mmol, 1 eq.) were suspended in distilled triethyl phosphite (30 mL) and refluxed up to 130 °C while stirred. Then the first potion of 4,5-bis(propylthio)-1,3-dithiole-2-thione (**57a**) (1.36 g, 4.81 mmol, 0.5 eq.) was added and stirred for 10 minutes, afterwards the third portion (1.34 g, 4.74 mmol, 0.5 eq.) was added and refluxed for additional 3 hrs. The reaction mixture was cooled to room temperature and diluted with methanol (50 mL). After allowing the mixture to stand for 3 days in a freezer, Precipitate was filtered, washed with methanol, and dried under vacuum. Residue was dissolved in DCM and un-dissolved precipitate by-product was filtered off. Purification by means of filtration yielded yellow powder of *N*-tosyl-2-(4,5-bis(propylthio)-(1,3)-dithiol-2-ylidene)-(1,3)-dithiolo[4,5-c]pyrrole (**58**) (4.97 g, 9.10 mmol, 95%).

Melting point: 118.5–119.5 °C; R_f (DCM) = 0.74; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 7.74 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.32 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.94 (s, 2H, Py-*H*), 2.79 (t, *J* =7.6 Hz, 4H, -SCH_2-), 2.43 (s, 3H, -CH_3), 1,73-1,59 (sext, 4H, -CH_2-), 1.02 (t, *J* =7.3 Hz, 6H,2x-CH_3).

4.2.3.2 The synthesis of monopyrrolo-tetrathiafulvalene derivative (59)[2]



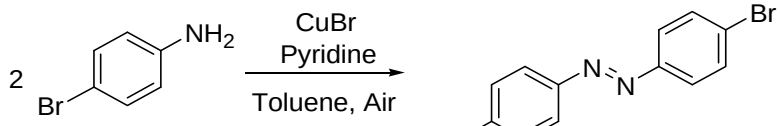
58 **59**

Suspension of *N*-tosyl-2-(4,5-bis(propylthio)-(1,3)-dithiol-2-ylidene)-(1,3)-dithiolo[4,5-c]pyrrole (**58**) (4.00 g, 7.33 mmol, 1 eq.) in dry THF-MeOH (3:2) (60 mL) mixture and sodium methoxide (NaOMe) (3.96 g, 73.3 mmol, 3.6 M, 10 eq.) was placed in a flask equipped with a reflux condenser. The mixture was degassed by a freeze-pump-thaw cycle, and the reaction apparatus was filled with an inert gas. Then the reaction mixture was refluxed for 30 minutes, cooled to room temperature, and concentrated to dryness. Residue was purified by column chromatography in DCM and hexane (7:3) over silica (10 cm) to yield pure orange powder of 2-[4,5-Bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (**59**) (2.46 g, 6.28 mmol, 86%).

Melting point: 89 °C; R_f (DCM/hexane) = 0.67; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 8.18 (s, 1H, -NH), 6.62 (d, *J* = 2.7 Hz, 2H, Py-*H*), 2.82 (t, *J* =7.6 Hz, 4H, -SCH_2-), 1.75-1.60 (sext, 4H, -CH_2-), 1.03 (t, *J* =7.3 Hz, 6H, 2x-CH_3).

4.2.4 Synthesis of azobenzene derivatives

4.2.4.1 The synthesis of 4,4'-dibromoazobenzene (62)[201]

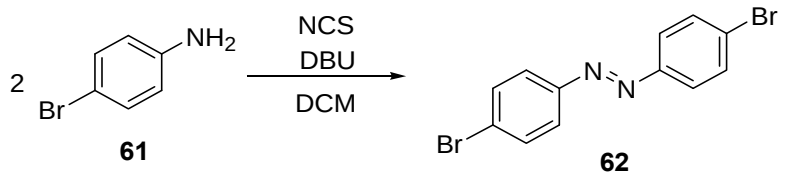


61 **62**

4-Bromoaniline (**61**) (0.257 g, 1.49 mmol, 2 eq.), CuBr (0.0104 g, 0.0725 mmol, 0.05 eq.) and pyridine (1 mL) were mixed in toluene (5 mL) under air 1 atm. The reaction mixture was heated to 40 ℃ under air for 3 days. After cooling down to room temperature and concentrated to dryness, the residue was dissolved in DCM and allowed to stand on a freezer for overnight. Purification by means of filtration and trituration with hexane yielded light orange crystals of 4,4'-dibromoazobenzene (**62**) (0.133 g, 0.394 mmol, 52%).

Melting point: 207–209 °C; R_f (DCM/hexane, 7:3) = 0.74; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 7.81 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 7.67 (d, *J* = 8.4 Hz, 4H, Ar-*H*).

4.2.4.2 The synthesis of 4,4'-dibromoazobenzene (62)[203]



4-Bromoaniline (**61**) (0.100 g, 0.581 mmol, 2 eq.) dissolved in DCM (15 mL) was added DBU (0.177g, 1.16 mmol, 0.18 mL, 2 eq.). The solution was stirred at room temperature for 5 min before being cooled down to −78 °C. NCS (0.155 g, 1.16 mmol, 2 eq.) was added as a solid to the reaction mixture. The orange solution was stirred for 10 min at −78 °C before quenching by addition of a saturated bicarbonate solution. The organic layer was separated with DCM, washed sequentially with water (50 mL) and hydrochloric acid (1 M, 50 mL), dried over anhydrous sodium sulfate, and concentrated to dryness in vacuo. Purification by means of filtration and trituration with hexane yielded light orange crystals of 4,4'-dibromoazobenzene (**62**) (0.0398 g, 0.117 mmol, 40%).

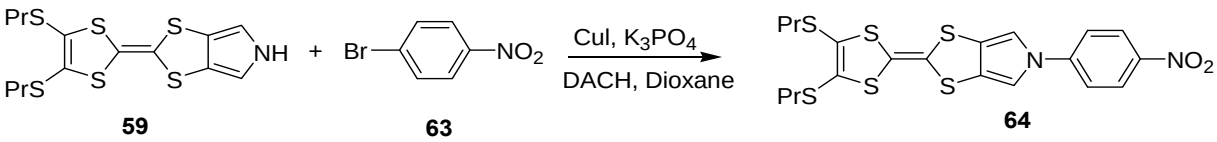
Melting point: 207–209 °C; R_f (DCM/hexane, 7:3) = 0.74; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 7.81 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 7.67 (d, *J* = 8.4 Hz, 4H, Ar-*H*).

4.2.5 Synthesis of monopyrrolo-tetrathiafulvalene conjugates

4.2.5.1 The synthesis of monopyrrolo-tetrathiafulvalene conjugates via Ullmann-type coupling reaction, general procedure

A thick walled Schlenk tube was charged with 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole MPTTF **59** and halogenated benzene, or azo-benzene, or stilbene derivative, copper(I) iodide (CuI), (+/-)-trans-1,2-diaminocyclohexane (DACH), tripotassium phosphate (K_3PO_4) and dry dioxane. The reaction mixture was degassed three times by freeze-pump-thaw cycles under liquid nitrogen, the Schlenk tube was filled with argon, tightly sealed, and stirred at 110- 115 °C for 2-4 days. The reaction mixture was transferred to another flask and evaporated to dryness. Residue was dissolved in DCM, filtered through a plug of celite, and evaporated to dryness. The crude products were triturated with alkane solvent to remove the unreacted aromatic starting material and then purified by column chromatography on silica gel.

4.2.5.1.1 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-nitro-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole (64)[225]

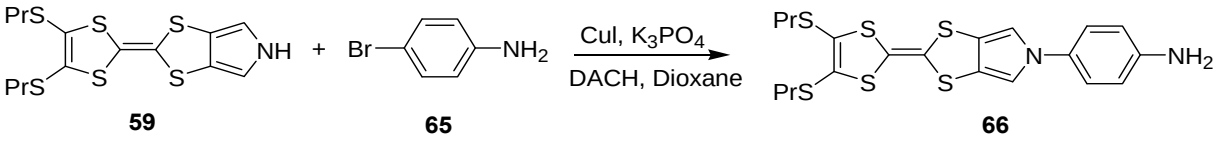


59 **63** **64**

Schlenk tube was charged with 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (**59**) (0.0550 g, 0.140 mmol, 1 eq.), 4-Bromonitrobenzene (**63**) (0,0560 g, 0.277 mmol, 2 eq.), CuI (0.0160 g, 0.0840 mmol, 0.6 eq.), DACH (7.5 μL), K_3PO_4 (0.110 g, 0.518 mmol, 3.7 eq.), dry dioxane (4 mL), and stirred at 115 °C for 2 days. The crude reaction mixture after solvent evaporation was triturated with *n*-hexane. The residue was purified by column chromatography in DCM and hexane (8:2) over silica (10 cm) to yield pure deep red crystals of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-nitro-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole (**57**) (0.0512 g, 0.0998 mmol, 71%).

Melting point: 239.5 °C; R_f (DCM/hexane) = 0.71; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 8.32 (d, *J* = 9.1 Hz, 2H, Ar-*H*), 7.43 (d, *J* = 9.1 Hz, 2H, Ar-*H*), 7.00 (s, 2H, Py-*H*), 2.83 (t, *J* =7.2 Hz, 4H, -SCH_2-), 1.76-1.63 (m, 4H, -CH_2-), 1.04 (t, *J* =7.3 Hz, 6H, 2x-CH_3).

4.2.5.1.2 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-analine)-5*H*-1,3-dithiolo[4,5-c]pyrrole (66)[2]

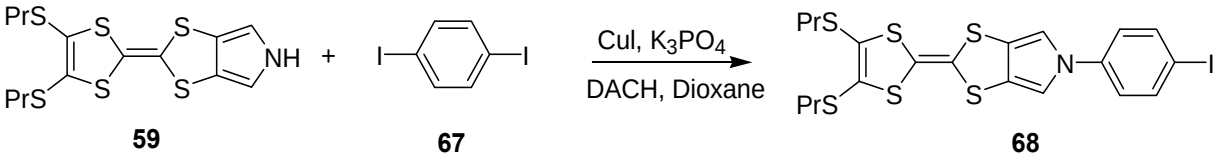


59 **65** **66**

Schlenk tube was charged with 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (**59**) (0.110 g, 0.281 mmol, 1 eq.), 4-bromoanaline (**65**) (0.0966 g, 0.562 mmol, 2 eq.), CuI (0.0642 g, 0.337 mmol, 1.2 eq.), DACH (0.085 mL), K_3PO_4 (0.179, 0.842 mmol, 3 eq.), dry dioxane (5 mL) and stirred at 115 °C for 3-4 days. The crude reaction mixture after solvent evaporation was purified by column chromatography in DCM and hexane (8:2) over silica (10 cm) to yield pure yellow solid of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-analine)-5*H*-1,3-dithiolo[4,5-c]pyrrole (**66**) (0.109 g, 0.226 mmol, 80%).

Melting point: -117.5°C; R_f (DCM/hexane) = 0.37; ^{1}H NMR (δ) (300.18 MHz, Chloroform-*d*): 7.11 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.77 (s, 2H, Py-*H*), 6.71 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 2.82 (t, *J* =7.7 Hz, 4H, -SCH_2-), 2.76-1.62 (m, 4H, -CH_2-), 1.03 (t, *J* =7.3 Hz, 6H, 2x-CH_3).

4.2.5.1.3 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-iodo-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole (68)



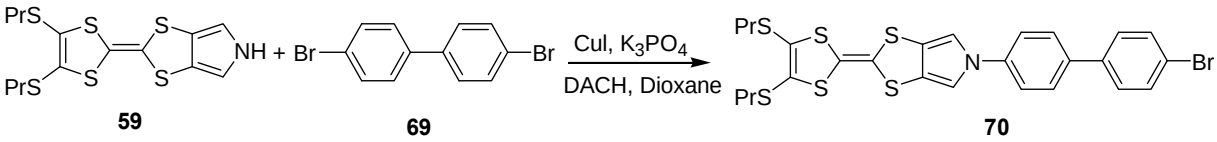
59 **67** **68**

Schlenk tube was charged with 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (**59**) (0.100 g, 0.256 mmol, 1 eq.), 1,4-diiodobenzene (**67**) (0.175 g, 0.532 mmol, 1.7 eq.), CuI (0.0298, 0.156 mmol, 0.5 eq.), DACH (7.5 μL), K_3PO_4 (0.134 g, 0.625 mmol, 3 eq.), dry dioxane (5 mL), and stirred at 115 °C for 3 days. The crude reaction mixture after solvent evaporation was triturated with pentane. The residue was purified by column chromatography in DCM and hexane (8:2) over silica (10 cm) to yield pure yellow solid of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-iodo-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole (**68**) (0.0649 g, 0.109 mmol, 43%).

Melting point: 158-159°C; R_f (DCM/hexane) = 0.80; ^{1}H NMR (δ) (600.28 MHz, Chloroform-*d*): 7.75 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.09 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.87 (s, 2H, Py-*H*), 2.84 (t, *J* =7.2 Hz, 4H, -SCH_2-), 1.74-1.67 (m, 4H, -CH_2-), 1.05 (t, *J* =7.3 Hz, 6H, 2x-CH_3); ^{13}C NMR (δ) (150.95 MHz, Chloroform-*d*): 139.86, 138.77, 127.55, 122.99, 121.62, 110.53, 89.72, 38.27, 23.16, 13.18.

Note: Two resonances for the quaternary carbons of the central TTF double bond are missing for ^{13}C (normally are expected to be around 118-112 ppm). This is common for TTF spectra, since these quaternary carbons have very long relaxation times and, therefore, very low intensity.

4.2.5.1.4 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-Bromo-biphenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole (70)



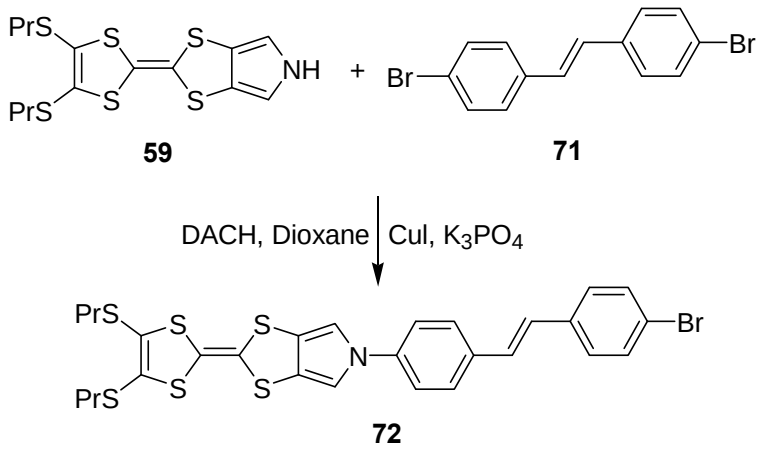
59 **69** **70**

Schlenk tube charged with 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (**59**) (0.138 g, 0.353 mmol, 2.2 eq.), 4,4'-bromobiphenylbenzene (**69**) (0.0523 g, 0.160 mmol, 1 eq.), CuI (0.0153 g, 0.0802 mmol, 0.5 eq.), DACH (7.5 μL), K_3PO_4 (0.102 g, 0.481 mmol, 3 eq.), dry dioxane (5 mL), and stirred at 115 °C for 2 days. The crude reaction mixture after solvent evaporation was triturated with pentane. The residue was purified by flash column chromatography in DCM and hexane (8:2) over silica (10 cm) to yield pure pale-yellow

solid of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-bromo-biphenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole (**70**) (0.0478 g, 0.0768 mmol, 46%).

Melting point: 208-210.5°C; R_f (DCM/hexane) = 0.91; ^{1}H NMR (δ) (600.28 MHz, Chloroform-*d*): 7.67 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.62 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.49 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.40 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 6.96 (s, 2H, Py-*H*), 2.84 (t, *J* =7.3 Hz, 4H, -SCH_2-), 1.74-1.67 (m, 4H, -CH_2-), 1.05 (t, *J* =7.3 Hz, 6H, 2x-CH_3). ; ^{13}C NMR (δ) (150.95 MHz, Chloroform-*d*): 139.95, 139.39, 139.02, 131.55, 128.93, 128.38, 127.55, 126.92, 122.42, 120.20, 118.86, 112.26, 110.81, 38.27, 23.17, 13.19.

4.2.5.1.5 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-Bromo-*trans*-stilbene)-5*H*-1,3-dithiolo[4,5-c]pyrrole (72)



Schlenk tube was charged with 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (**59**) (0.0946 g, 0.242 mmol, 1.6 eq.), 4,4'-dibromo-*trans*-stilbene (**71**) (0.0511 g, 0.151 mmol, 1 eq.), CuI (0.0141 g, 0.0740 mmol, 0.5 eq.), DACH (7.5 μL), K_3PO_4 (0.0942 g, 0.444 mmol, 2.9 eq.), dry dioxane (5 mL), and stirred at 115 °C for 3 days. The crude reaction mixture after solvent was purified by column chromatography in DCM and hexane (8:2) over silica (10 cm) to yield light yellow solid of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-bromo-*trans*-stilbene)-5*H*-1,3-dithiolo[4,5-c]pyrrole (**72**) (0.0554 g, 0.0854 mmol, 56%).

Melting point: 176-178°C; R_f (DCM/hexane) = 0.77; ^{1}H NMR (δ) (600.28 MHz, Chloroform-*d*): 7.57 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.51 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.40 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.32 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.10 (d, *J* = 16.3 Hz, 1H, CH), 7.04 (d, *J* = 16.3 Hz, 2H, CH), 6.94 (s, 2H, Py-*H*), 2.84 (t, *J* =7.2 Hz, 4H, -SCH_2-), 1.74-1.67 (m, 4H, -CH_2-), 1.05 (t, *J* =7.3 Hz, 6H, 2x-CH_3). ; ^{13}C NMR (δ) (150.95 MHz, Chloroform-*d*): 139.48, 136.04, 134.83, 131.87, 128.06, 127.98, 127.84, 127.68, 127.55, 122.59, 121.55, 119.97, 118.71, 112.32, 110.62, 38.26, 23.16, 13.19.

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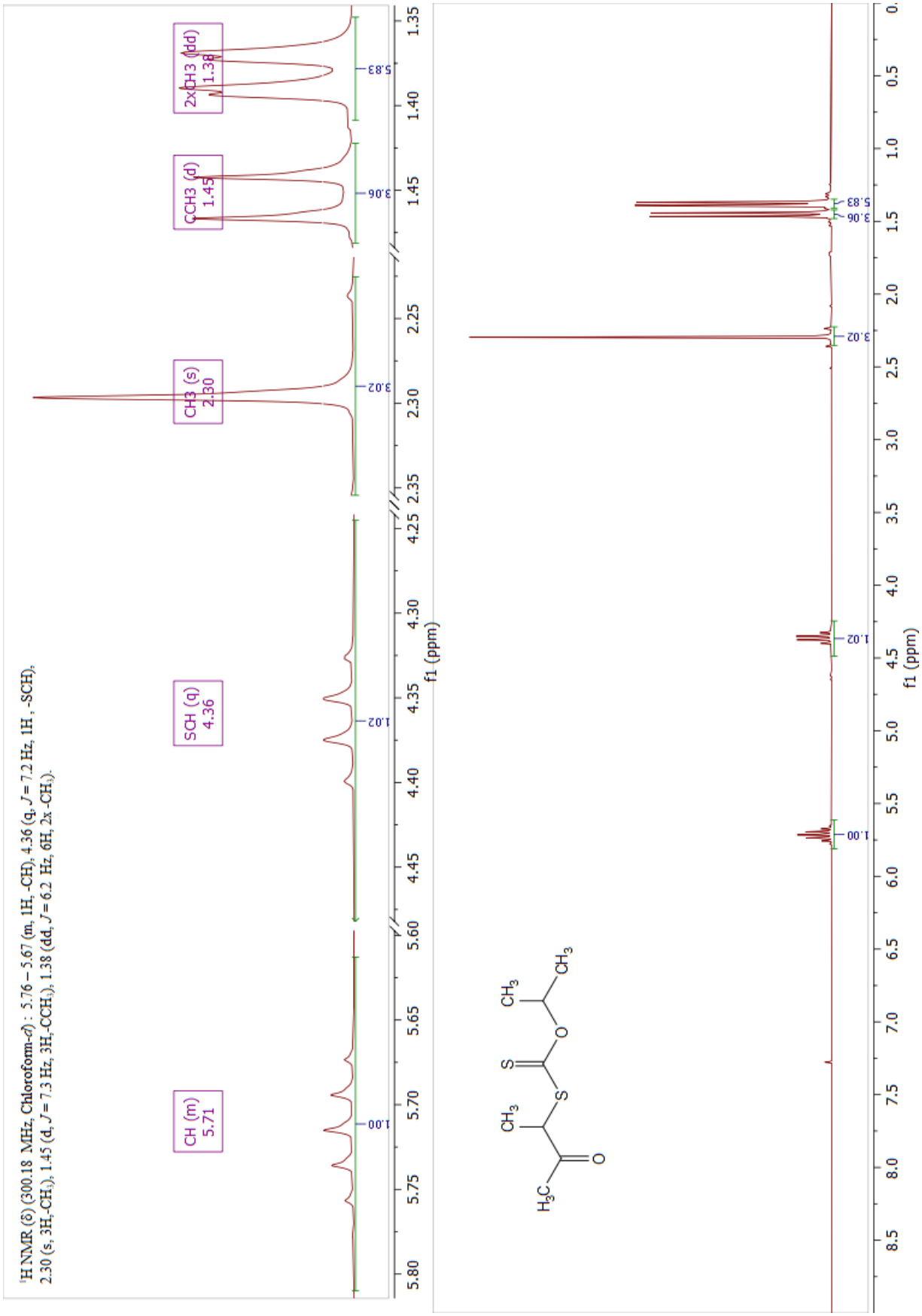
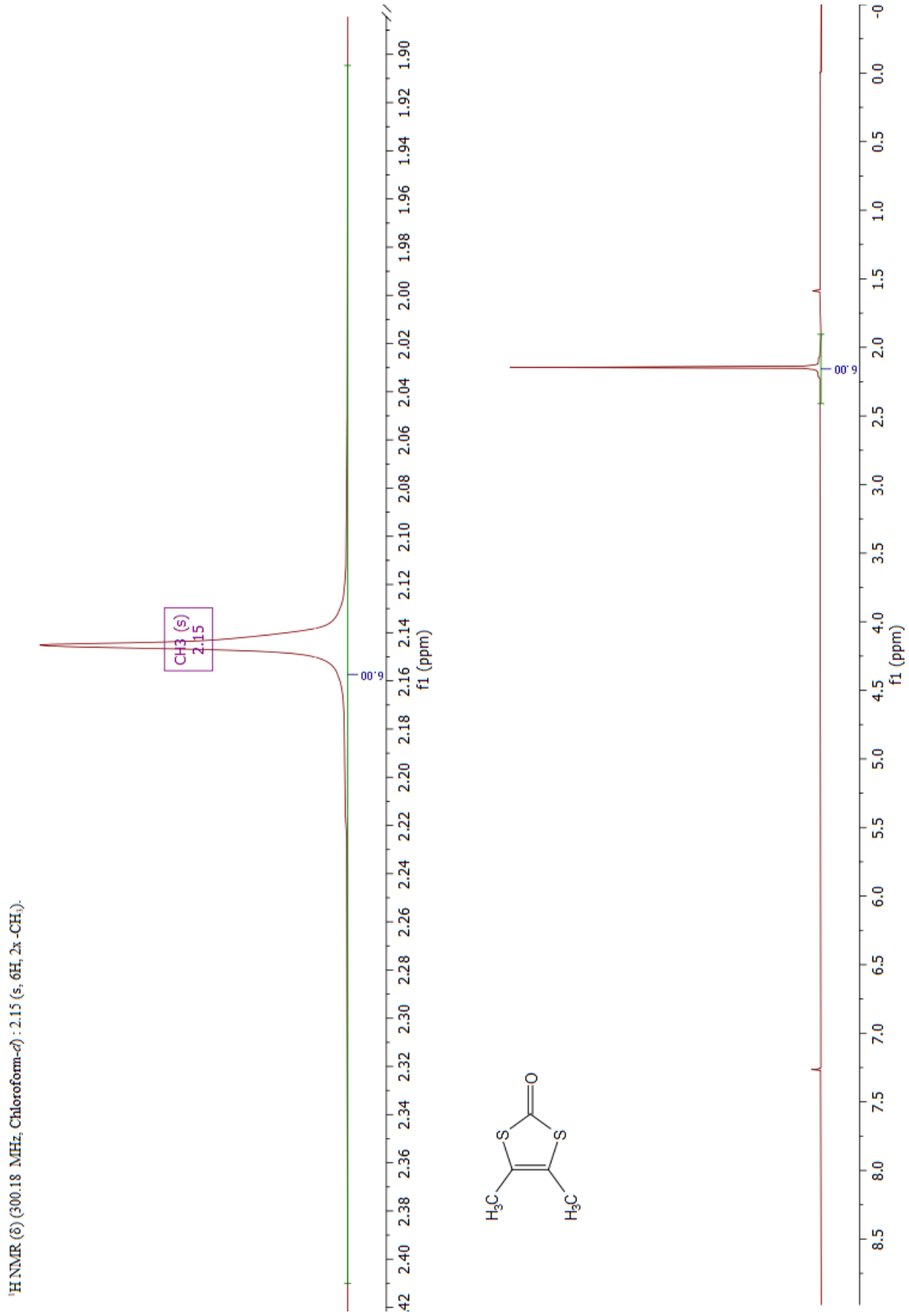
Appendix

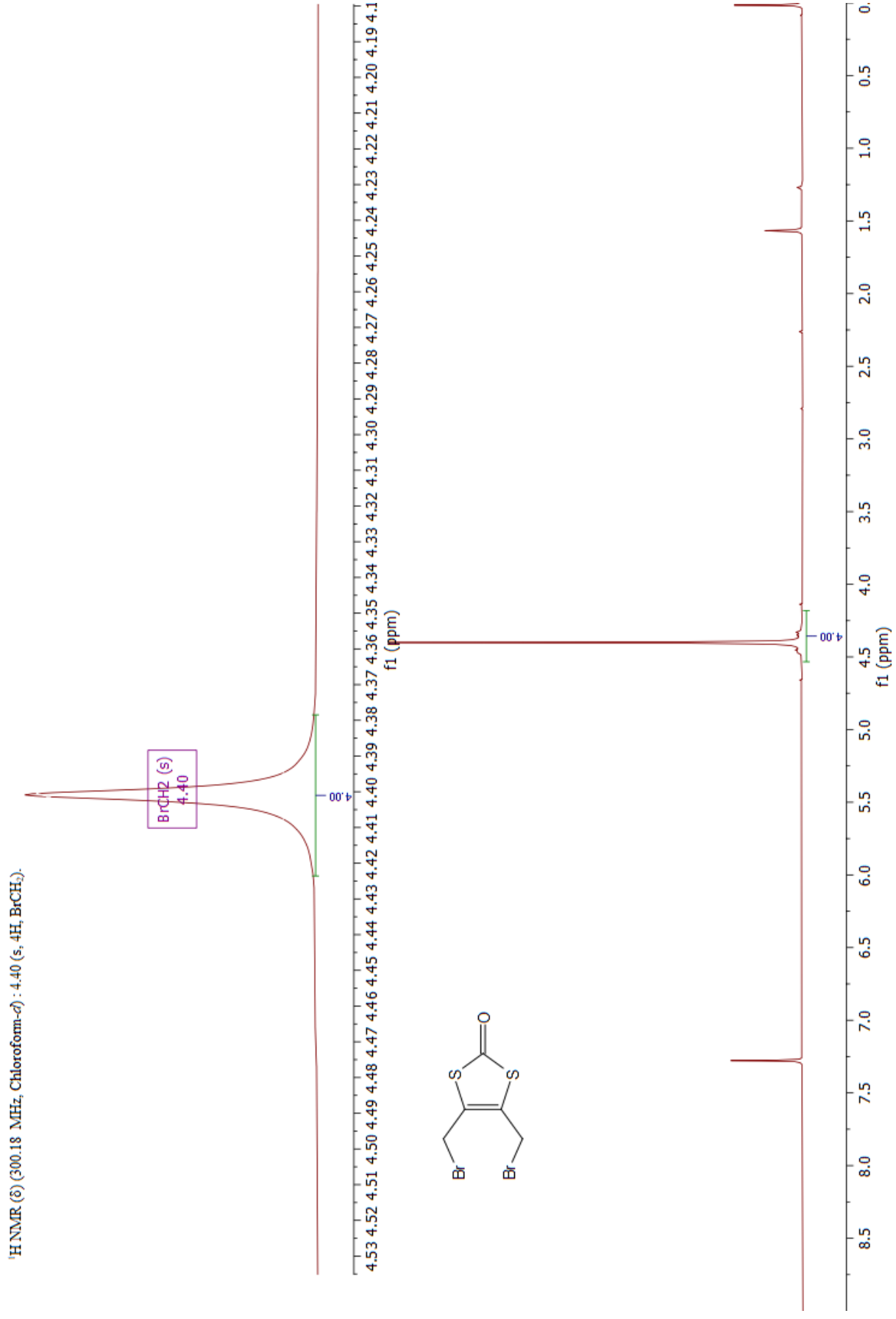
^{1}H NMR and ^{13}C NMR Spectra



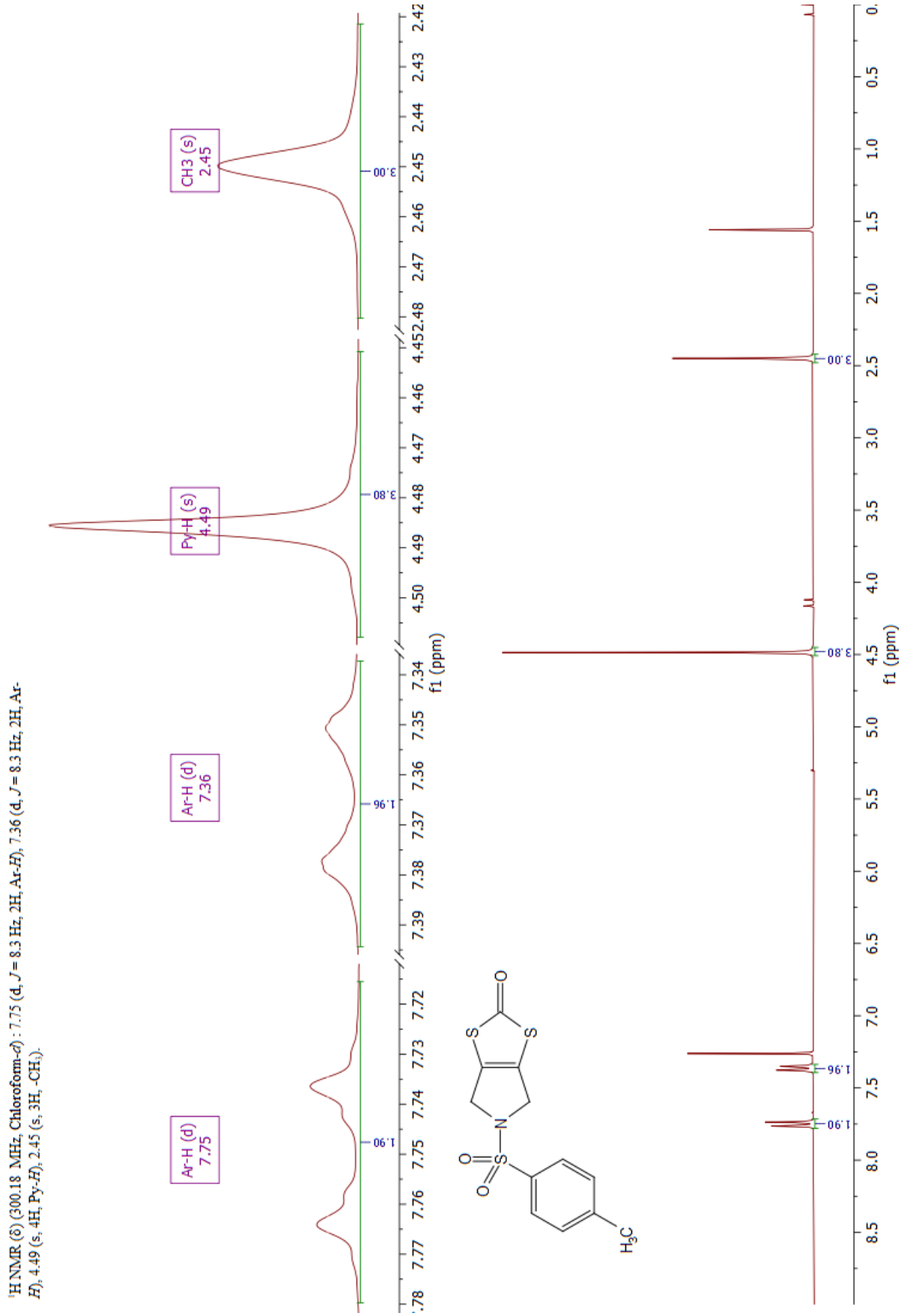
^{1}H NMR (300.18 MHz, Chloroform-*d*)) spectrum of *O*-isopropyl-S-3-oxobutan-2-yl dithiocarbonate **52**



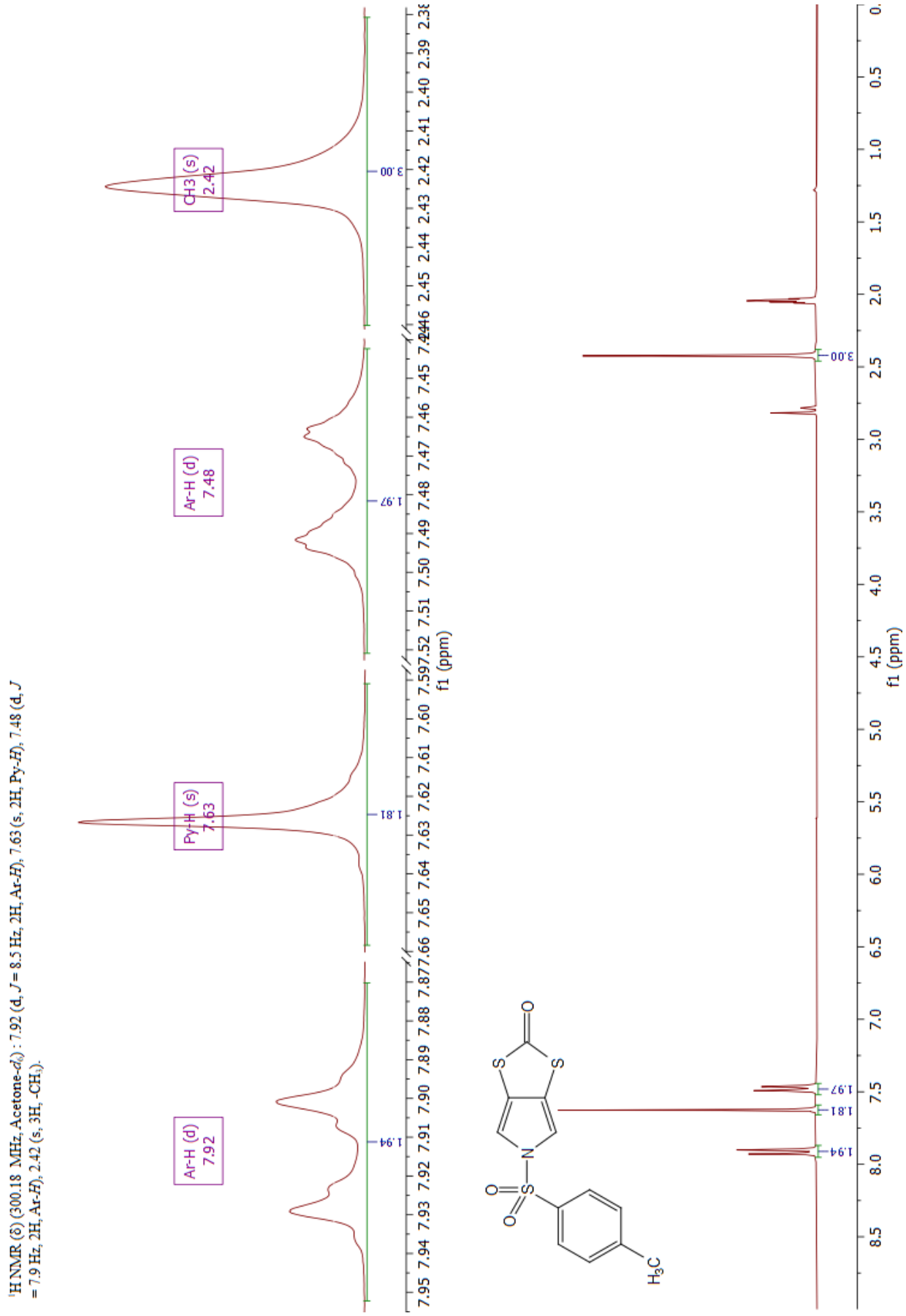
[1]H NMR (300.18 MHz, Chloroform-*d*)) spectrum of 4,5-dimethyl-1,3-dithiol-2-one **53**



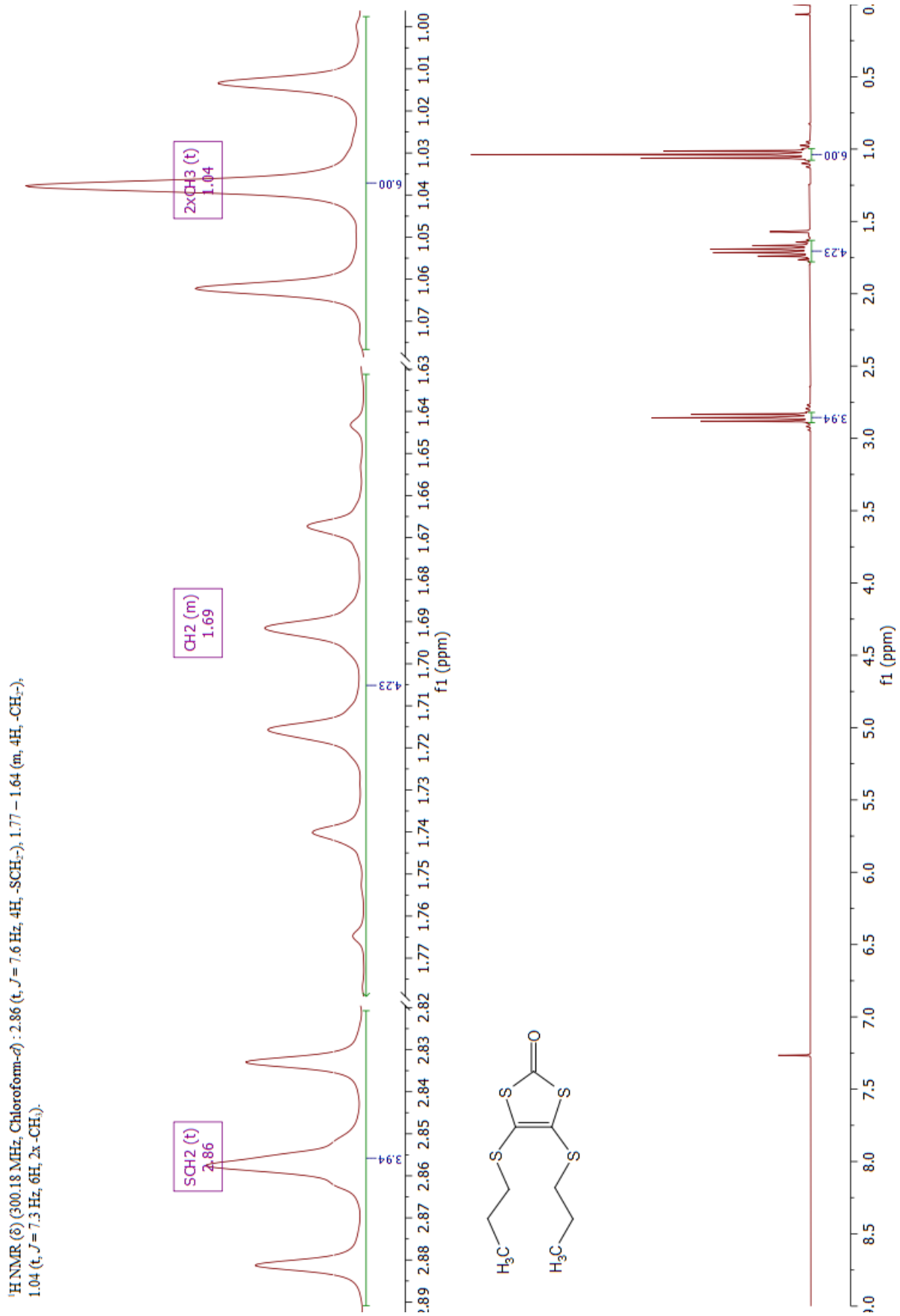
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of 4,5-bis(bromomethyl)-1,3-dithiol-2-one **54**



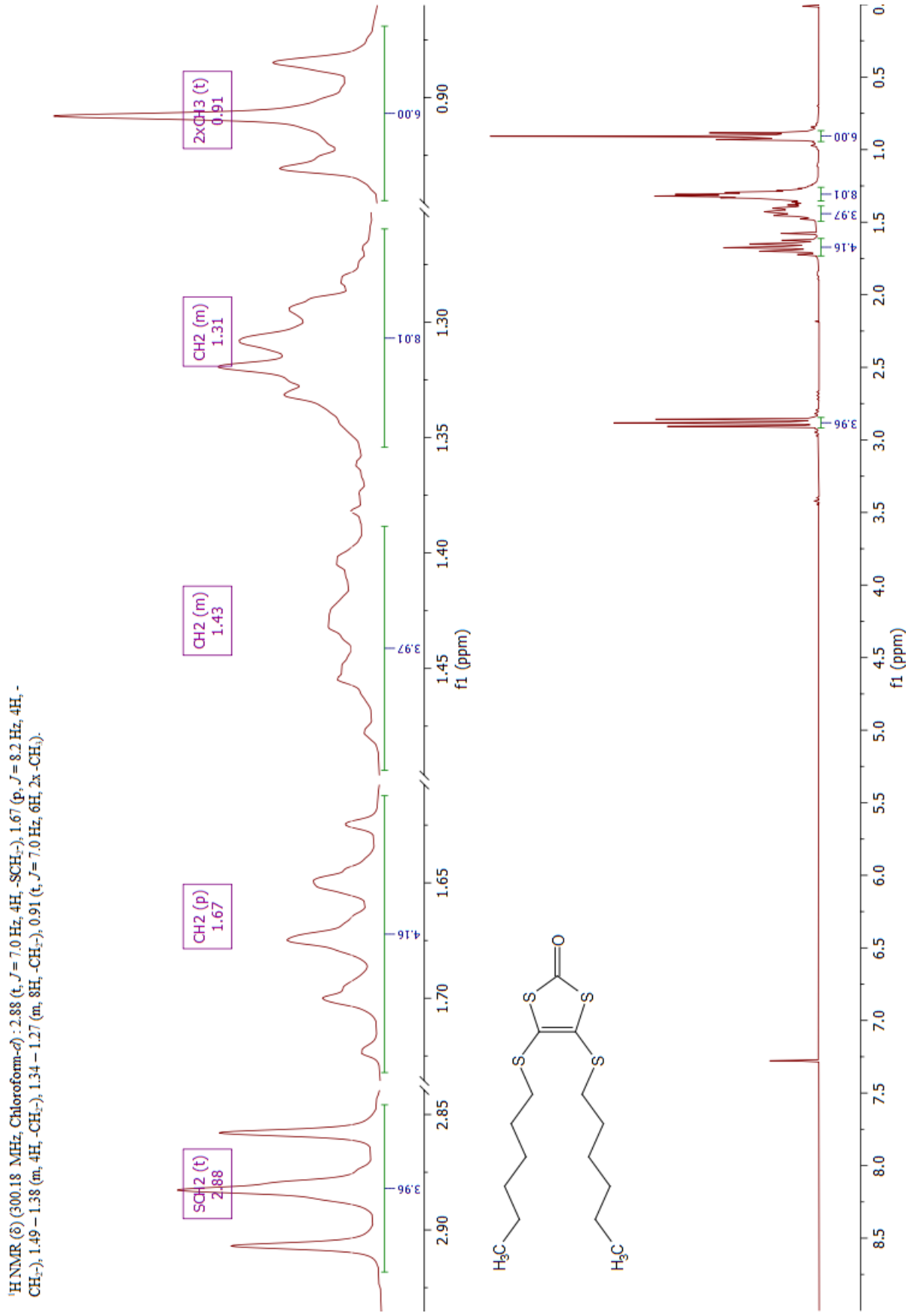
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of 4,6-dihydro-*N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **48**



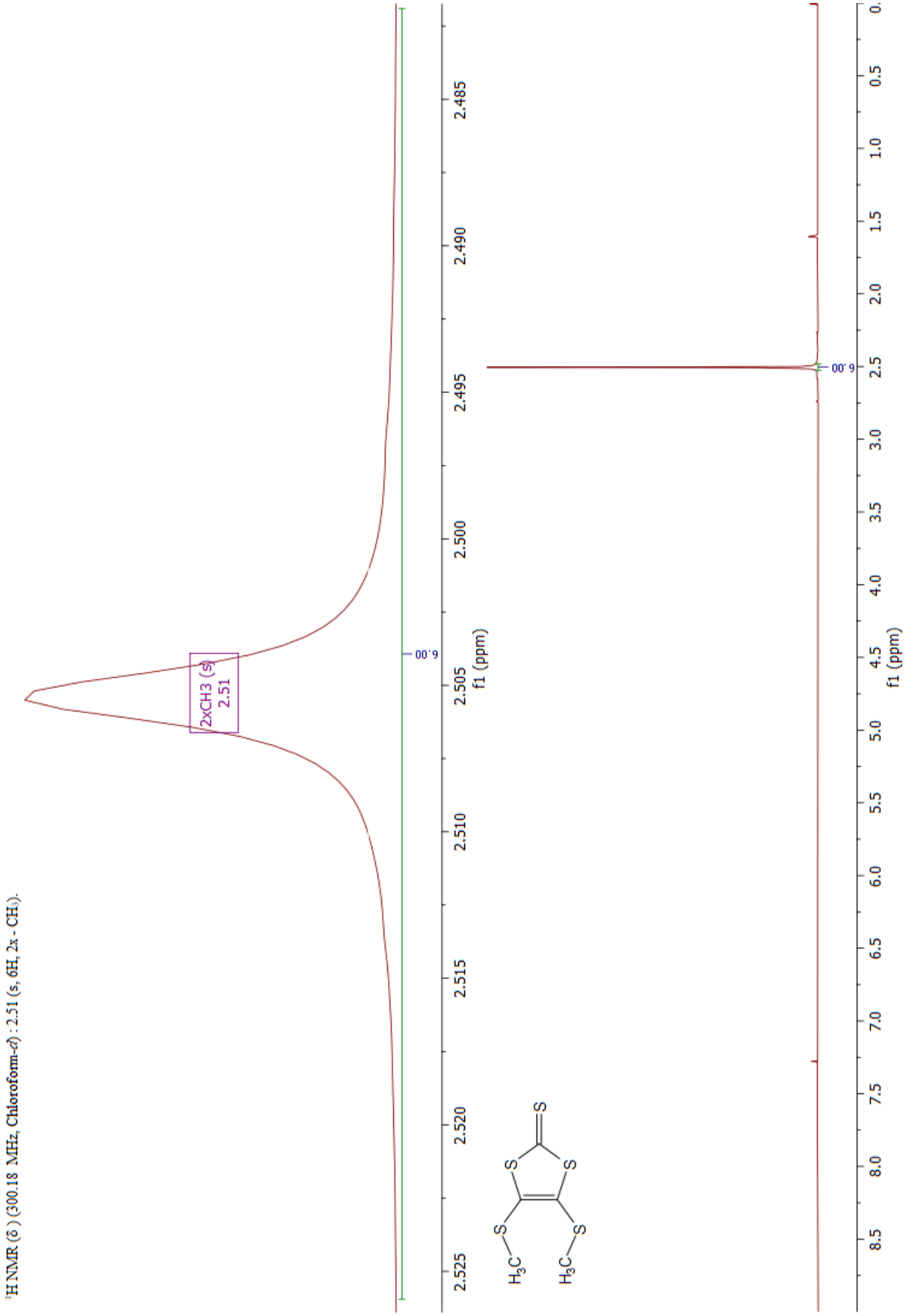
^{1}H NMR (300.18 MHz, Acetone-d_6) spectrum of *N*-tosyl-1,3-dithiolo[4,5-c]pyrrol-2-one **49**



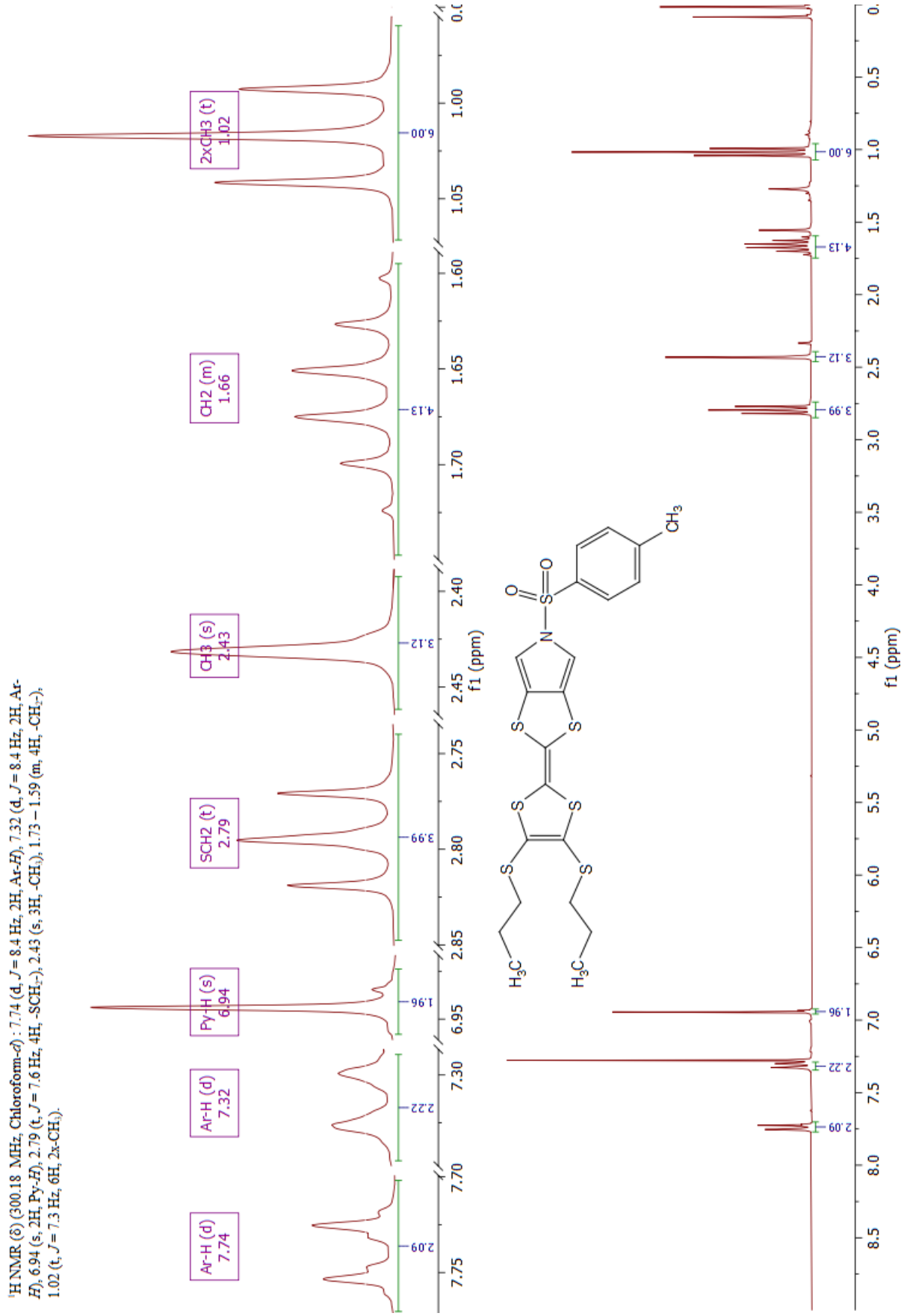
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of 4,5-bis(propylthio)-1,3-dithiole-2-thione **57a**



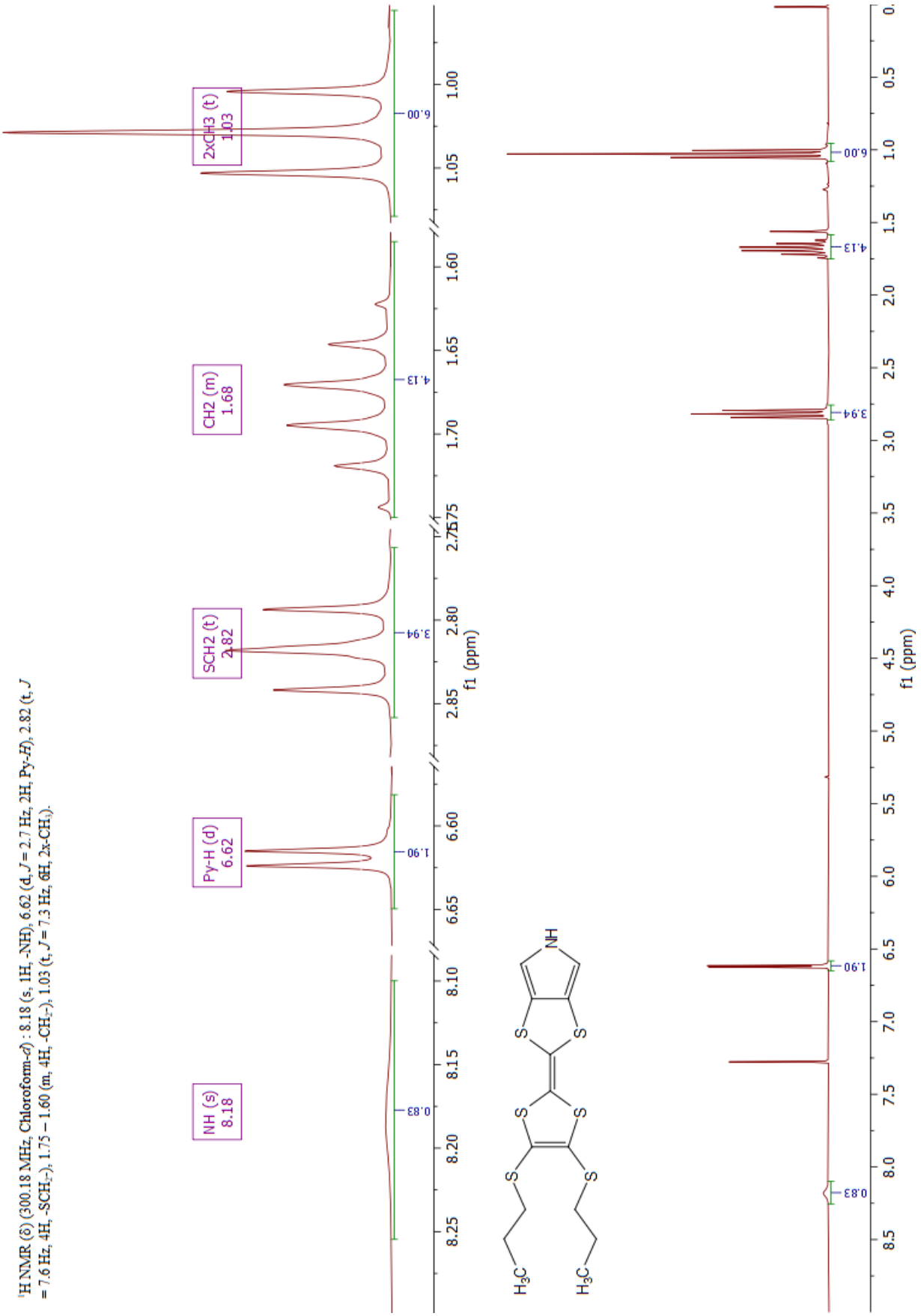
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of 4,5-bis(hexylthio)-1,3-dithiole-2-thione **57b**



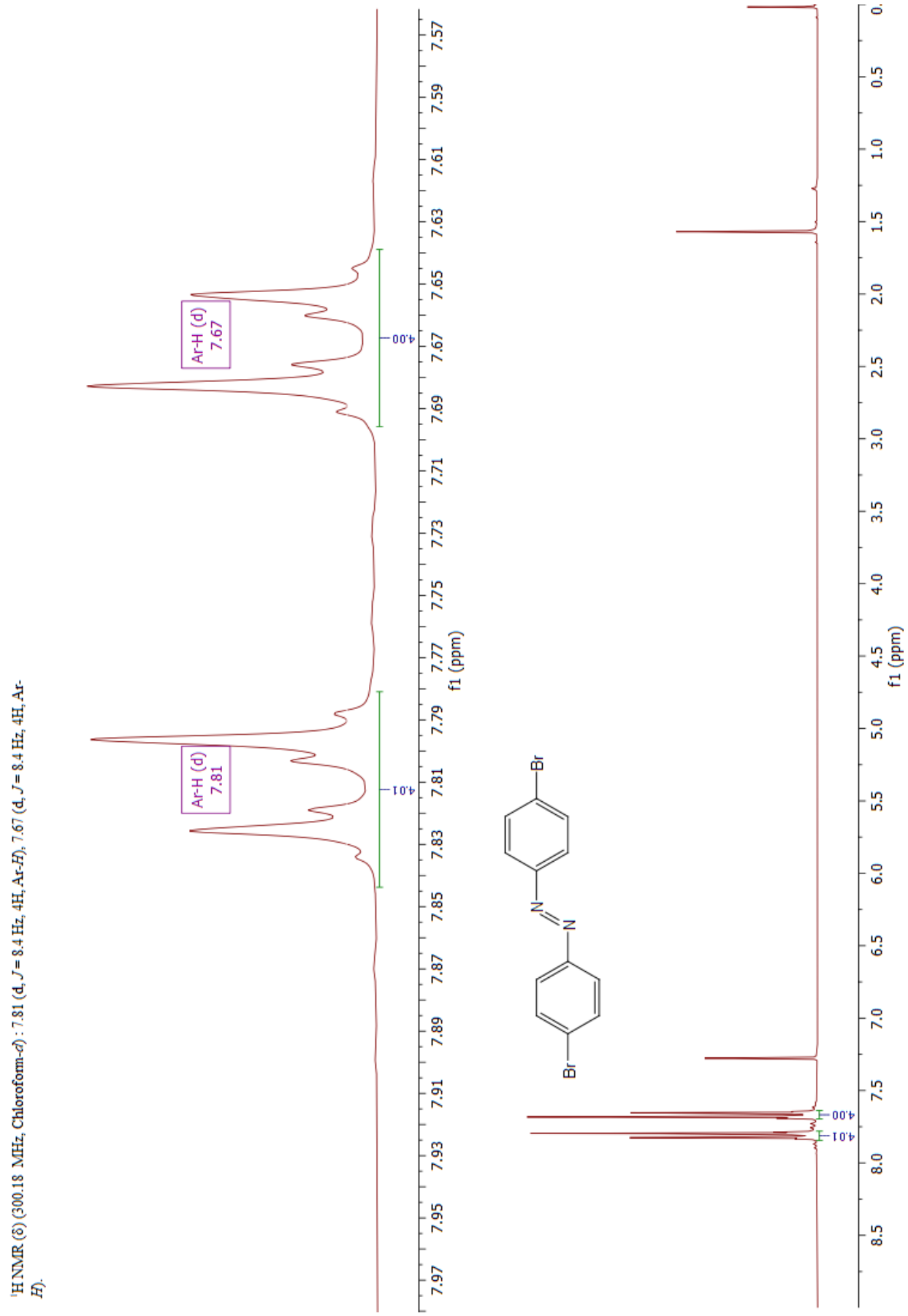
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of 4,5-bis(methylthio)-1,3-dithiole-2-thione **57c**



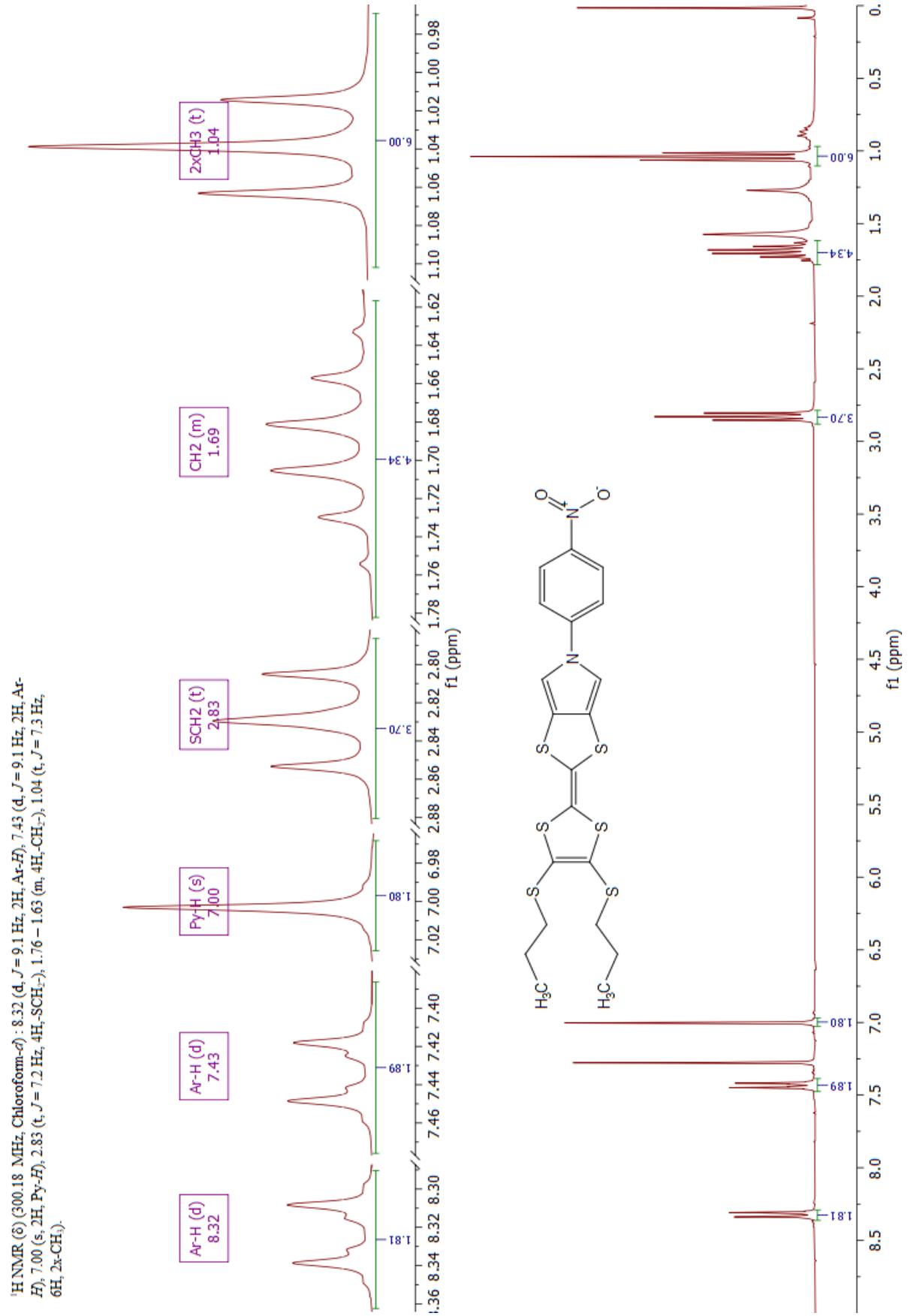
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of *N*-tosyl-2-(4,5-bis(propylthio)-(1,3)-dithiol-2-ylidene)-(1,3)-dithiolo[4,5-c]pyrrole **58**



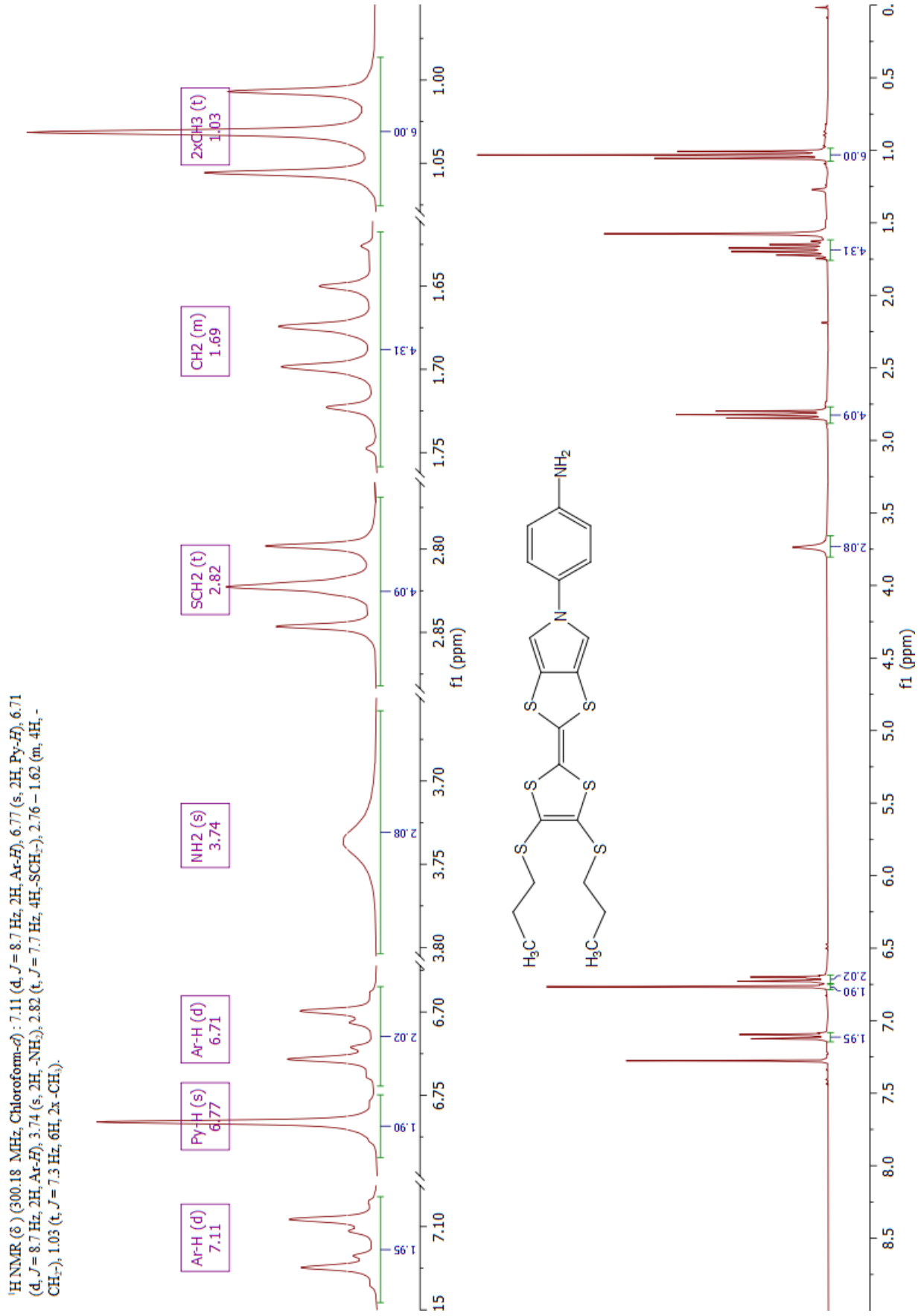
[1]H NMR (300.18 MHz, Chloroform-*d*) spectrum of 2-[4,5-Bis(propylthio)-1,3-dithiol-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole **59**



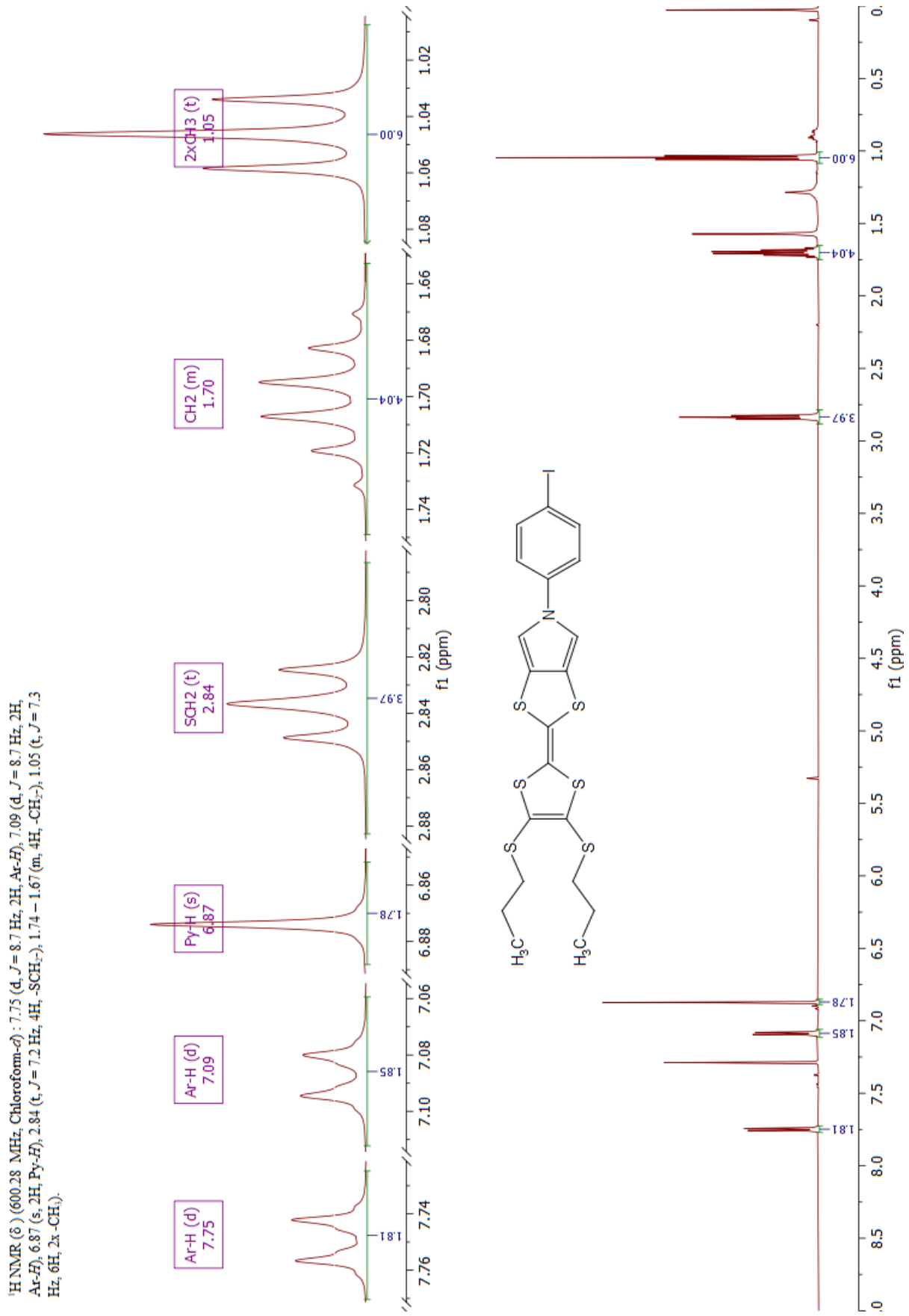
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of 4,4'-dibromoazobenzene **62**



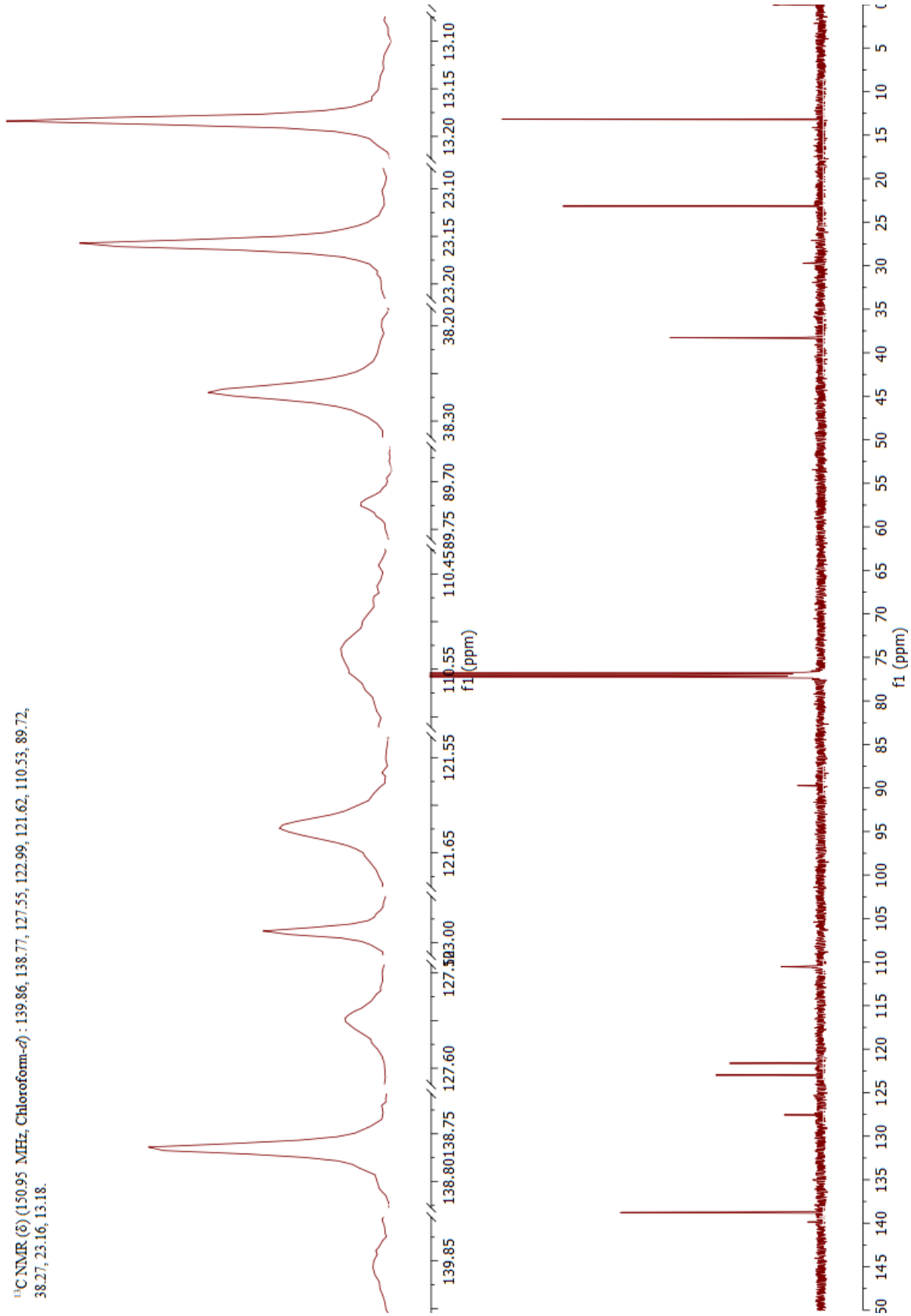
^{1}H NMR (300.18 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-nitro-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **64**



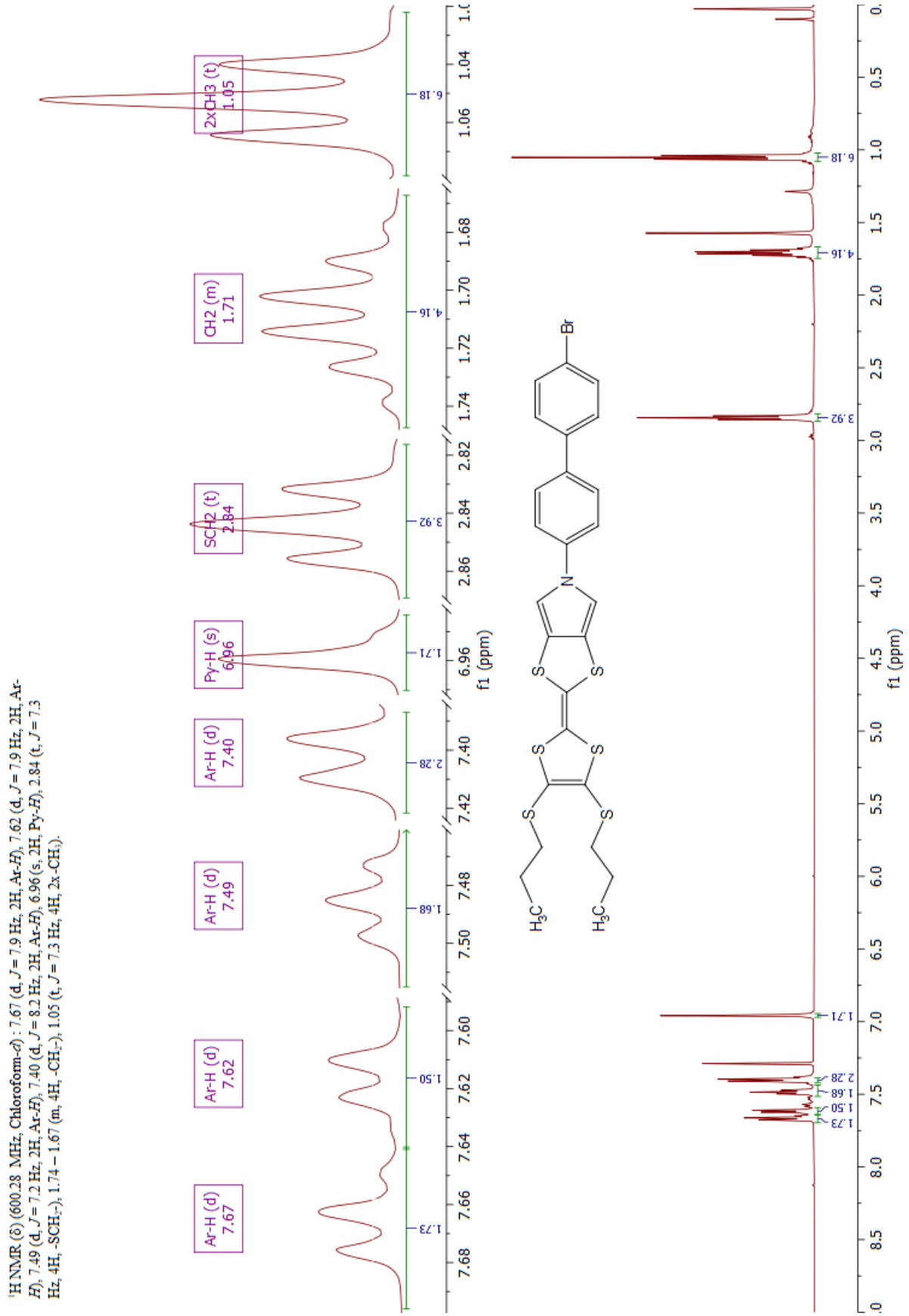
[1]H NMR (300.18 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-analine)-5*H*-1,3-dithiolo[4,5-c]pyrrole **66**



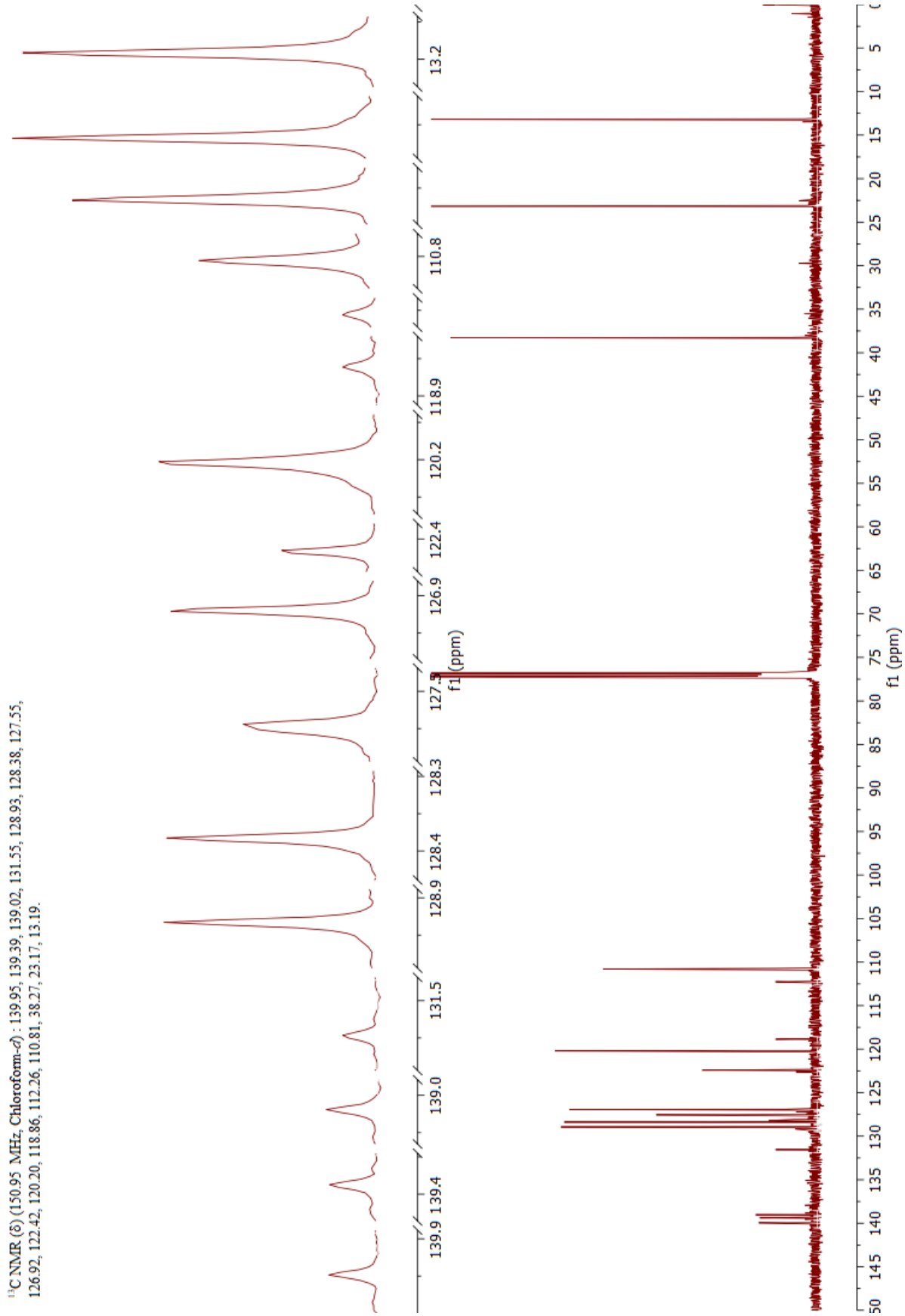
^{1}H NMR (600.28 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-iodo-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **68**



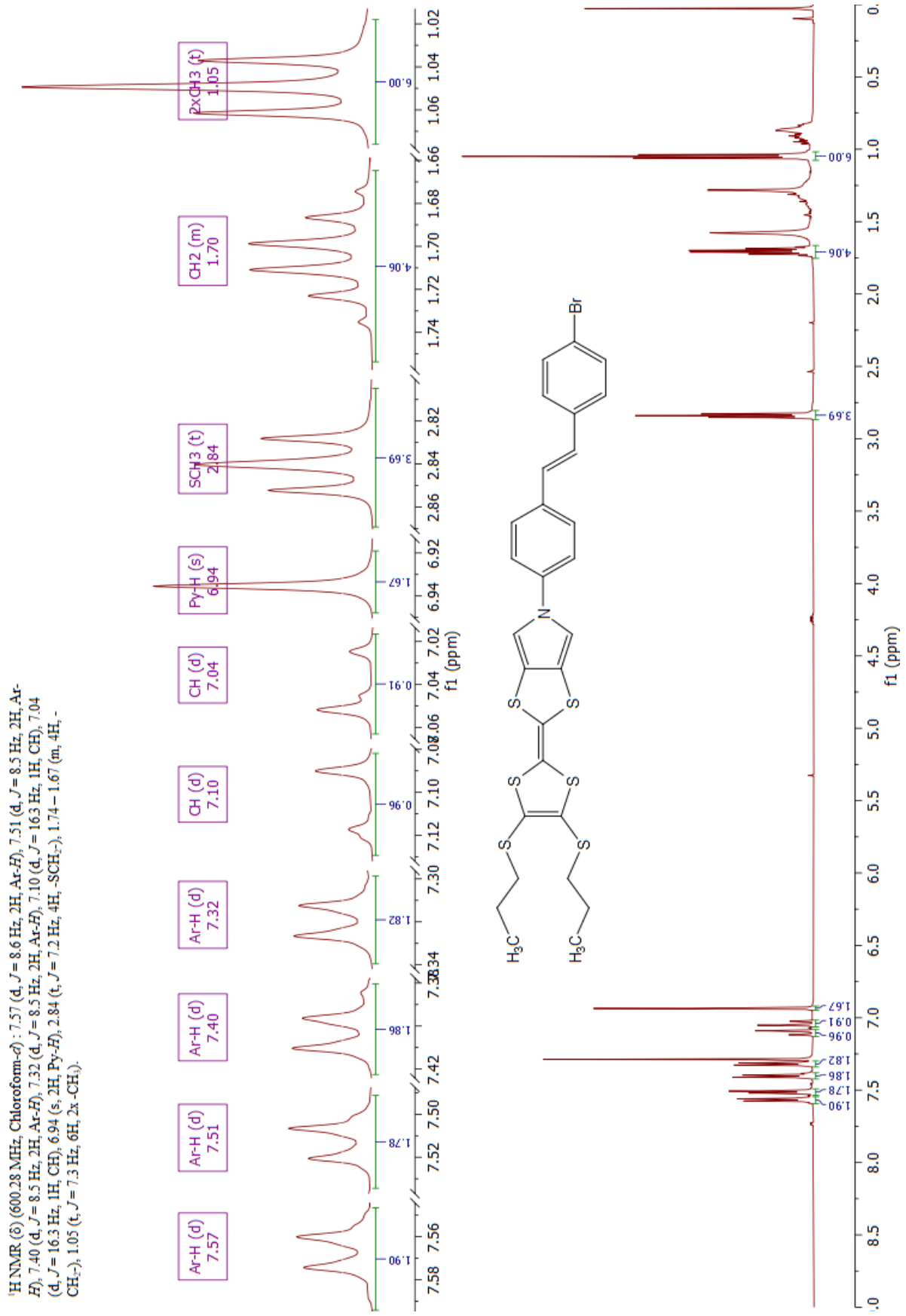
^{13}C NMR (150.95 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-iodo-phenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **68**



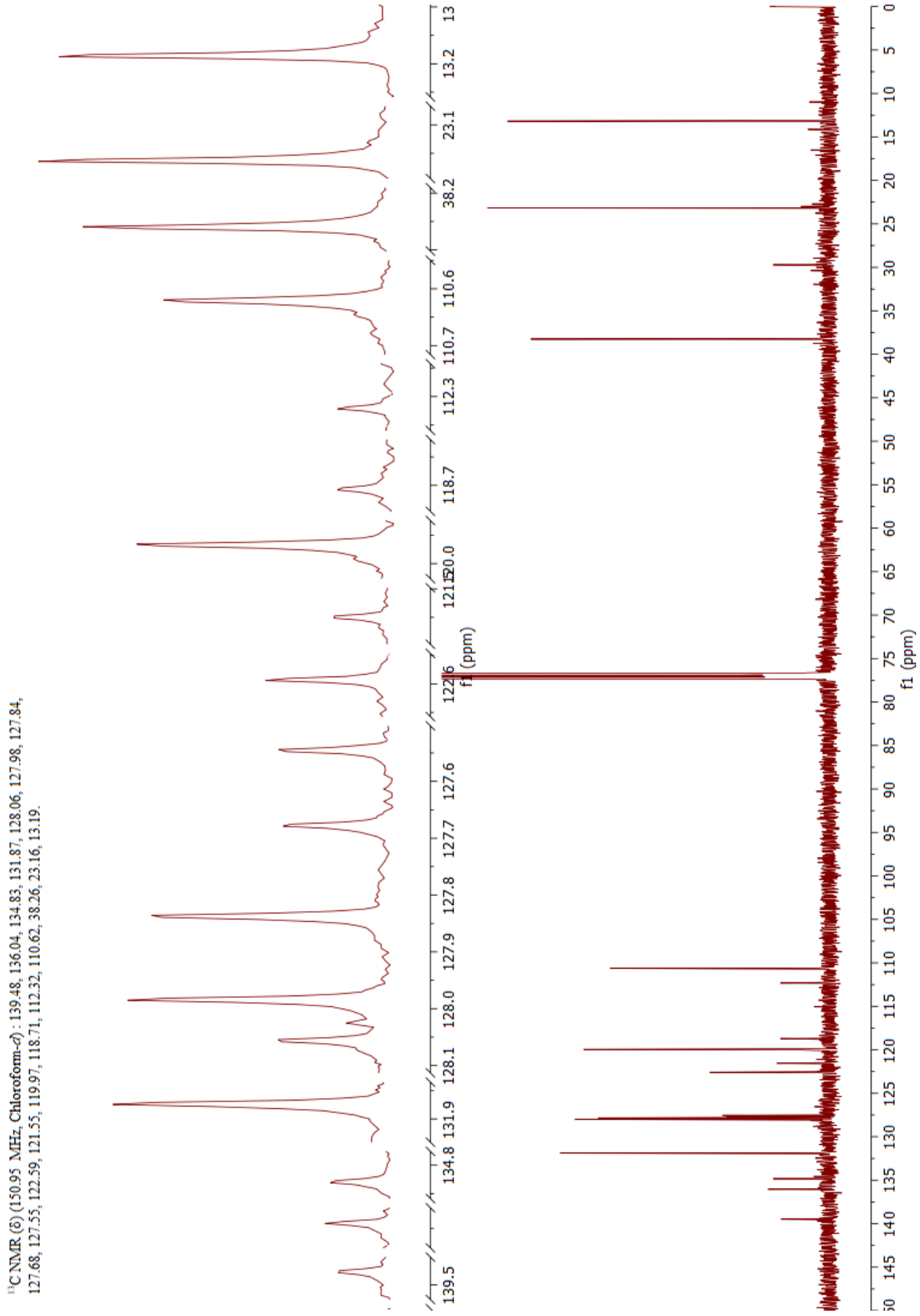
^{1}H NMR (600.18 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-Bromo-biphenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **70**



^{13}C NMR (150.95 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-Bromo-biphenyl)-5*H*-1,3-dithiolo[4,5-c]pyrrole **70**



^{1}H NMR (600.28 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-bromo-*trans*-stilbene)-5*H*-1,3-dithiolo[4,5-c]pyrrole **72**



^{13}C NMR (150.95 MHz, Chloroform-*d*) spectrum of 2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-bromo-*trans*-stilbene)-5*H*-1,3-dithiolo[4,5-c]pyrrole **72**