UNIVERSITÄT ROSTOCK

Synthetic Studies of Benzodithiophenes, Benzodithiazoles, Benzopyranones and Chemoselective Palladium(0)-Catalyzed Cross Coupling Reactions of Brominated Naphthalenes, Benzothiophenes and Naphthaquinones

Dissertation

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Dedication

To those who have sincere contributions to humanity.

"Auch aus Steinen, die in den Weg gelegt werden, kann man Schönes bauen"

Johann Wolfgang von Goethe

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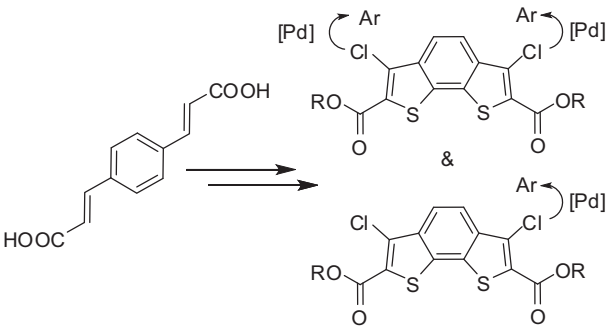
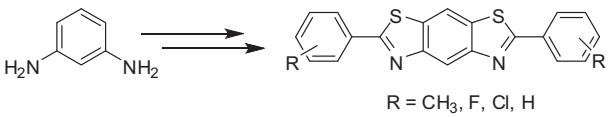
MAIN CONTENTS

Synthesis of benzo[1,2-*b*;5,6-*b*']dithiophenes and their subsequent desymmetrization



An overview of the synthesis of benzo[1,2-*b*;5,6-*b*']dithiophenes and structure revision through subsequent desymmetrization is given.

Synthesis of benzodithiazoles using *N*-benzyl DABCO tribromide (organo ammonium tribromide OATB) through oxidative cyclization of thiobenzanilides



The synthesis of new benzodithiazole derivatives through oxidative cyclization using *N*-benzyl DABCO tribromide has been discussed. This method is not only highly efficient but also simple and convenient to give high yields in all cases. New interesting heterocyclic frames were synthesized efficiently.

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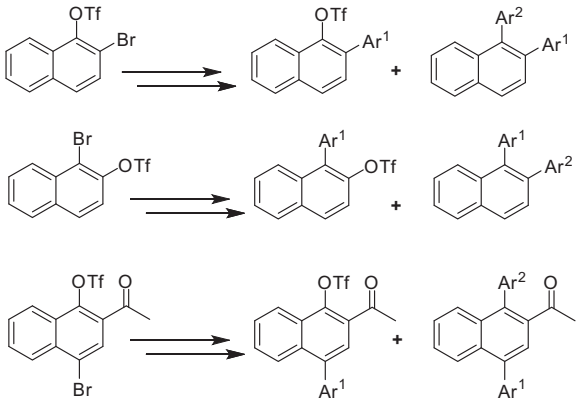
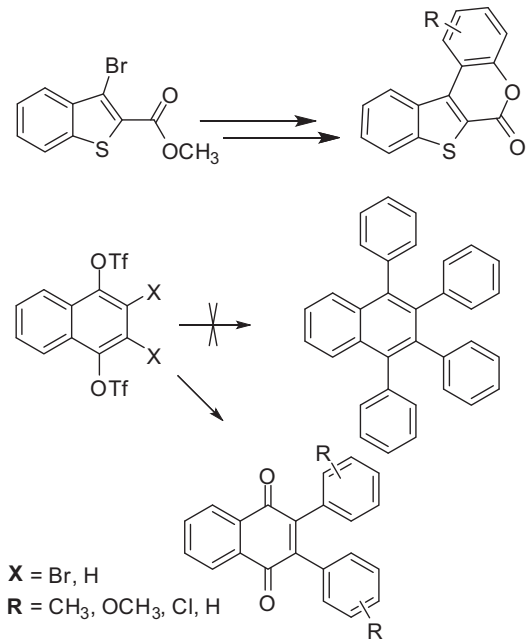
Synthesis of arylated naphthalenes through chemoselective Suzuki-Miyaura cross coupling reactions (Br versus OTf)



In this chapter, the steric and electronic effects on chemoselective Suzuki-Miyaura coupling reactions has been described. It was concluded that the first attack was always observed at brominated carbon C-Br while C-OTf was attacked later on. All reactions proceed with excellent selectivity

CHAPTER 4 Page 44 - 52

Synthesis of heteroaryl-fused benzopyranone analogues and arylated naphthaquinones via palladium-catalysed Suzuki-Miyaura coupling reactions



Functionalized benzopyranone analogues and arylated naphthaquinones were prepared by palladium-catalysed Suzuki-Miyaura coupling reactions. The products are not readily available by other methods. Optimization of the reaction conditions, to obtain better yields and to lower the loading of catalyst, were studied as well.

DETAILED CONTENTS

1. Synthesis of benzo[1,2-*b*;5,6-*b*']dithiophenes and their subsequent desymmetrization

1.1 Introduction

Benzo[*b*]thiophenes show a wide range of pharmacological activities, such as estrogen receptor modulating activity, tubulin binding activity, activity as MRP1, angiogenesis and thrombin inhibitors, antiinflammatory activity, and antifungal activity.[1] More complex, annulated thiophene derivatives often contain a low singlet-triplet energy gap and are important core structures of magnetic and electronic materials,[2] such as organic ferromagnets, conductors, transistors, photovoltaic cells and organic light-emitting diodes (OLEDs).[3] Therefore, the synthesis and properties of rigid benzothiophene-fused aromatic compounds has been extensively studied in recent years.

The molecular structure and their mechanism of formation are of substantial biological and industrial importance. Miura and coworkers have recently reported the synthesis of various 3,7-diarylbenzo[1,2-*b*;4,5-*b*']dithiophenes[4] by twofold Suzuki-Miyaura and Sonogashira cross coupling reactions of 3,7-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophenes. The basic known methodology, the cyclization of thionyl chloride with cinnamic acids to give benzophenones, was first reported by Krubsack and Higa.[7a] The latter compounds were first prepared by Ried[5] and Karminski-Zamola[6] and their coworkers by cyclization of 1,4-phenylenediacrylic acid with thionyl chloride and subsequent addition of a nucleophile. Herein, in this chapter, a number of new experimental data has been presented related to the unambiguous structural evidences that several of the earlier reported structures, 3,7-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophenes (**2'**), are wrong and that, by contrast, 3,8-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophenes (**2**) are formed (Figure 1). As a consequence, the structures of numerous arylated dithiophenes prepared by cross coupling reactions of the parent chlorinated derivatives have to be revised as well.

1.2 Results and discussion

In 1980, Ried and Oremek reported [5] that the reaction of 1,4-phenylenediacrylic acid with thionyl chloride, in the presence of catalytic amounts of pyridine, afforded the diacid dichloride **A'** as a reactive intermediate which was subsequently trapped with methanol as a nucleophile to give the 3,7-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophene **2'** (Scheme 2). In their

original report,[5] Ried and coworkers characterized their product by ^{1}H NMR, IR and MS spectroscopy and by elemental analysis (Scheme 1). It has been theorized that, alternatively, the isomeric 3,7-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene **2** could have been formed. But they decided that isomer **2'** is more likely based on analysis of the IR bands in the fingerprint region because more reliable methods were not available at that time. As the possible resulting benzodithiophene cores show molecular symmetry, they have chemically equivalent protons at the benzene ring which can not be differentiated by NMR techniques.

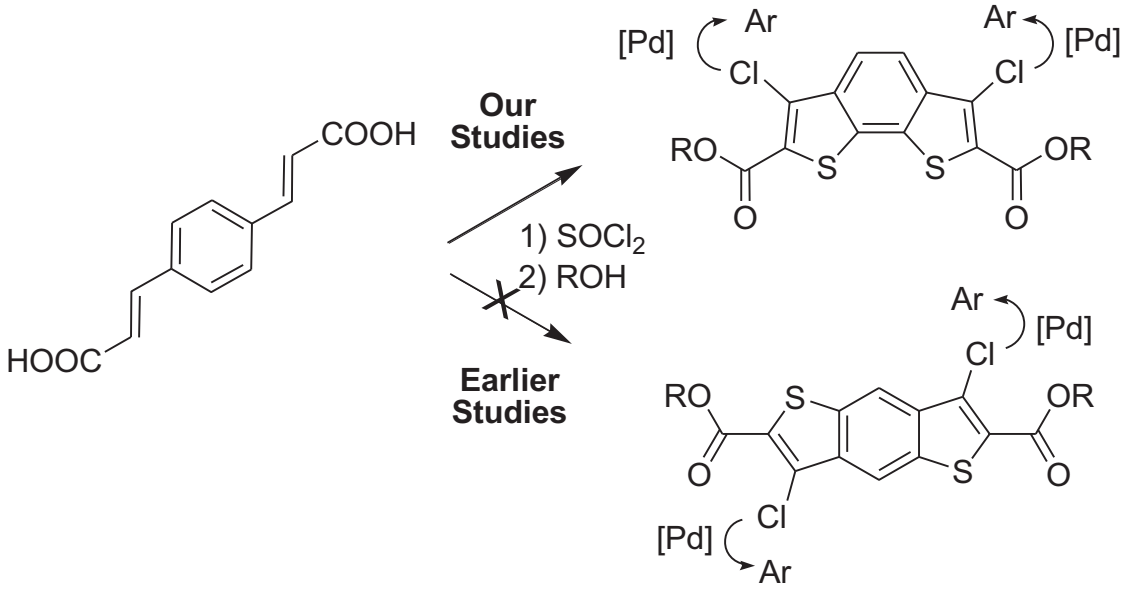
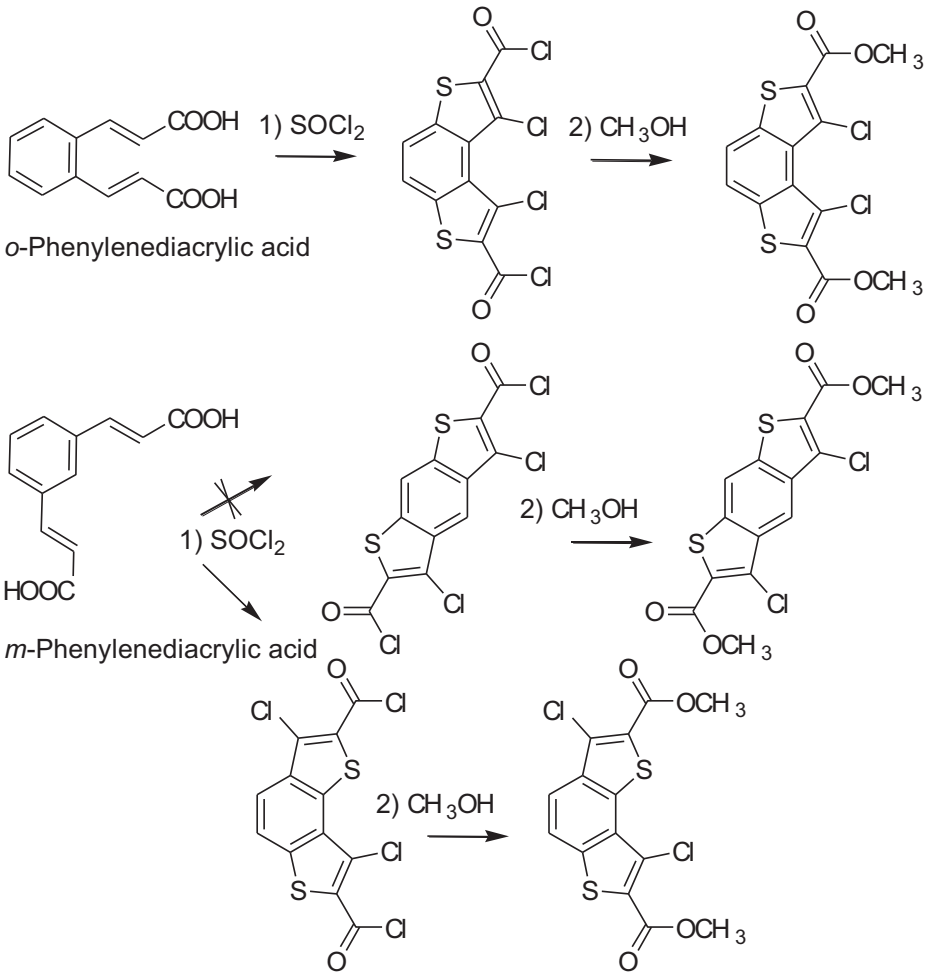


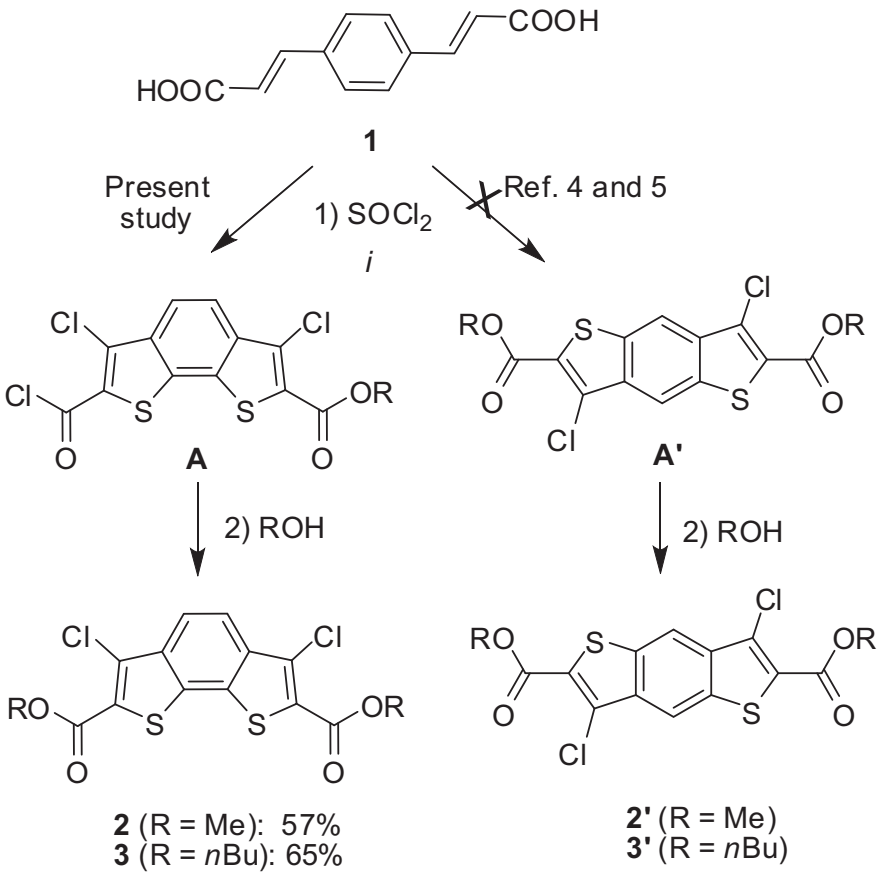
Figure 1. Our synthetic approach

In 1995, Karminski-Zamola referred to the original report of 1980 and reported the employment of anilines as the nucleophile and formation of 3,7-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophene diamides. In 2009, Miura used *n*-butanol as the nucleophile and reported the synthesis of diester **3'** (Scheme 2).[4a] This product was transformed into various symmetrical diarylated 3,7-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophenes by twofold Suzuki-Miyaura cross-coupling reactions of the chloride groups. None of all these structures reported were unambigiously confirmed by X-ray crystal structure analyses or detailed NMR studies.



Scheme 1. Cyclization pattern of *o*-, *m*-, *p*-phenylenediacrylic acids

We have found that the reaction of 1,4-phenylenediacrylic acid with thionyl chloride (5h, 140 °C), in the presence of catalytic amounts of pyridine, and subsequent addition of methanol (2h, reflux), following the conditions reported by Ried,[5] afforded a yellow crystalline solid. To our surprise, an X-ray crystal structure analysis revealed that the product was dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene **2** instead of the expected isomeric 3,7-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophene **2'** (Scheme 2, Figure 1).



Scheme 2. Synthesis of **2** and **3**; *i*,1) $SOCl_2$, pyridine, 5 h, 140 °C; 2) ROH, 2 h, reflux

Phenylenediacrylic acids (*o*-, *m*- and *p*-isomers) cyclize with thionyl chloride to furnish their relative esters (Scheme 1).[5] We reinvestigated the previous work of Ried and Miura and their coworkers.

To confirm that product **2'** does not simply represent a by-product which crystallized in the presence of **2**, special attention was given to the work-up procedure. The NMR data of the crystals were identical with the rest of the material. The moderate isolated yield of **2** (57 %) can be explained by losses during the chromatographic purification. The isomeric product **2'** was not formed which was confirmed by NMR measurements of the crude product (before chromatographic purification).

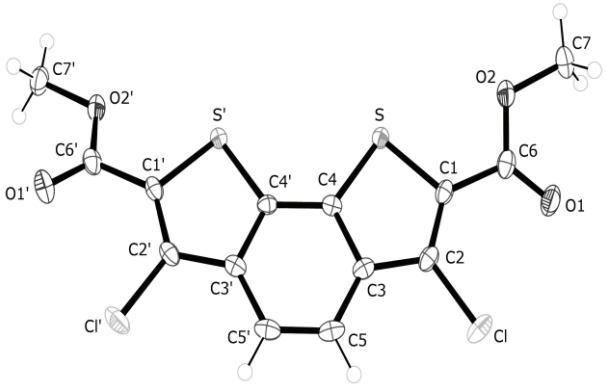


Figure 1. Ortep plot of **2**

Di(butyl)ester **3'** was also synthesized, repeating the same method which was reported by Miura in 2009.[4] The cyclization of 1,4-phenylenediacrylic acid with $SOCl_2$ and subsequent reaction with *n*-butanol (instead of methanol) again afforded a yellow solid. The structure, which was unambiguously confirmed by X-ray crystal structure analysis, turned out to be 3,8-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene **3** instead of 3,7-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophene **3'** (Figure 2).

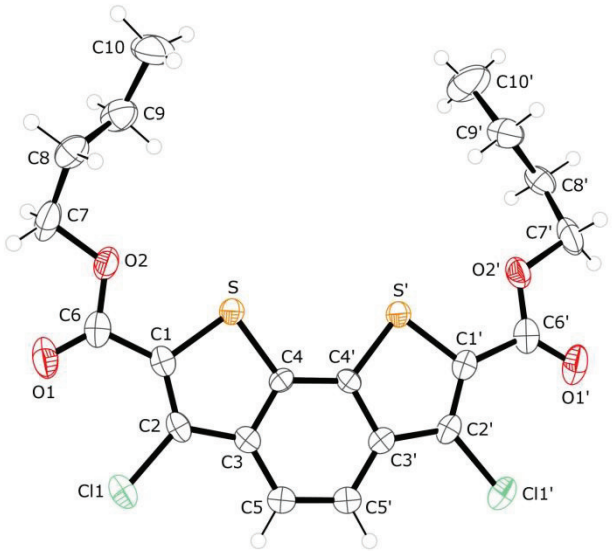


Figure 2. Ortep plot of **3**

Because of the importance of these finding, we aimed to get additional structural proofs by NMR through desymmetrization of parent substrates. The NMR data of our product were identical with those reported by Miura and coworkers. [9] Due to the symmetrical structures of both dithiophenes **3** and **3'**, similar NMR data are expected and the exact structural elucidation by NMR is not possible. These chemically equivalent protons will resonate at the same chemical shift. The aromatic protons H_a appear as a singlet with the integration of two

protons. However, this observation is compatible with both isomers **3** and **3'**, since no coupling between the two aromatic protons H_a is expected (the protons are chemically and magnetically equivalent) (Figure 3). The practical assessment of molecular symmetry can not be decided through simple NMR values.

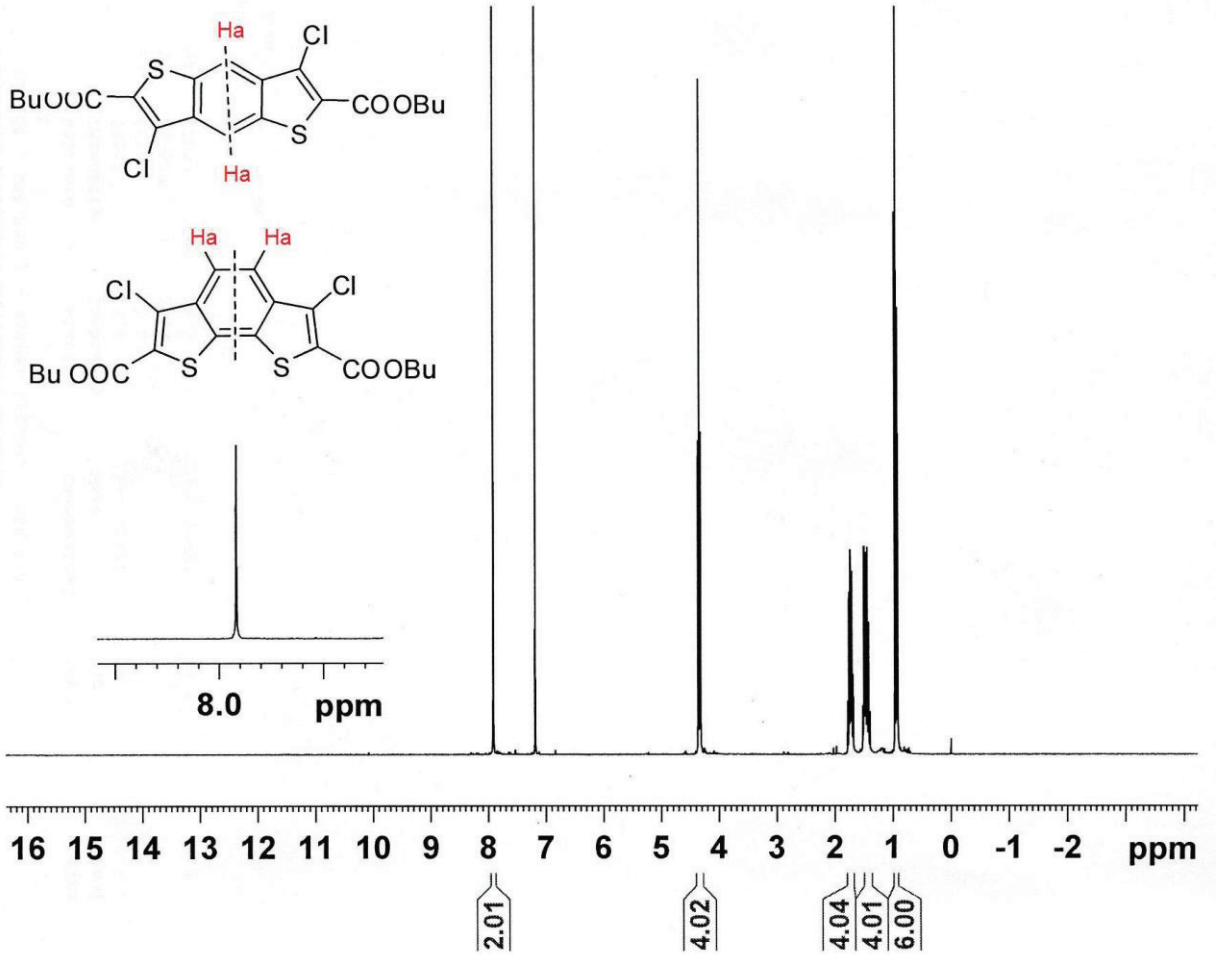
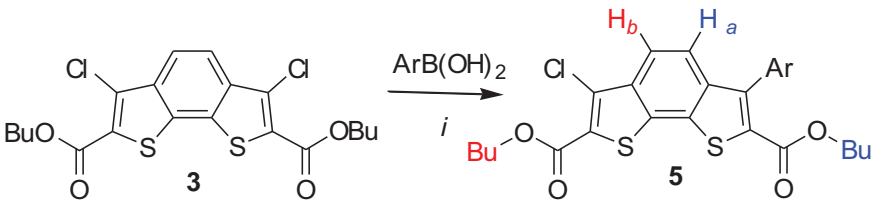


Figure 3. ^{1}H NMR spectrum of compound **3** in $CDCl_3$ at 300 MHz

The desymmetrization approach was explored under the optimized reaction conditions (Scheme 3). The symmetrical substrate **3** gave rise to the desymmetrized products (unsymmetrical derivatives **5a-c**). These findings provide a clear basis to decide about the structure of the parent substrate independently, even if not any X-ray structure would be available. The mono-Suzuki-Miyaura cross-coupling reaction of **3** with 1.2 equiv of arylboronic acids **4a-c** afforded the 3-aryl-8-chlorobenzo[1,2-*b*;5,6-*b*']dithiophenes **5a-c** in very good yields (Scheme 2, Table 1).[8] The best yields were obtained when $Pd(PPh_3)_4$ (mol %) and K_3PO_4 (1.5 equiv.) were used as the catalyst and base, respectively. The reactions were carried out in dioxane (120 °C, 4h). The arylboronic acids were chosen in the sense that

their ^{1}H NMR signals would not disturb the structure elucidation of the aromatic core structure (vide infra).



Scheme 3. Synthesis of **5a-c**. *Conditions: i*, **3** (1.0 equiv.), $ArB(OH)_2$ (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (2.0 equiv.), dioxane, 120 °C, 4h

Table 1. Synthesis of **5a-c**

4	Ar	% (**5**)[a]
a	2-MeO-5-FC_6H_3	82
b	2-MeO-5-ClC_6H_3	87
c	2-(MeO)C_6H_4	90

[a] Yields of isolated compounds

Inspection of the ^{1}H NMR spectra of **5a-c** clearly showed that the two aromatic protons H_a and H_b are, as expected, chemically and magnetically different and resonate as characteristic dublets at approx. δ = 7.74 and 7.36 ppm with coupling constants of about 8.8 Hz (Figure 4). These results are only compatible with the structures of 3-aryl-7-chlorobenzo[1,2-*b*;5,6-*b*']dithiophenes **5a-c**, but not with the corresponding isomeric 3-aryl-7-chlorobenzo[1,2-*b*;4,5-*b*']dithiophenes. In the latter case, no significant coupling is possible for the aromatic protons H_a and H_b. As a consequence, the NMR experiments of **5a-c** clearly confirm the structure of dichlorodithiophene **3** as well, as no change of the aromatic core can be expected during the coupling reactions.

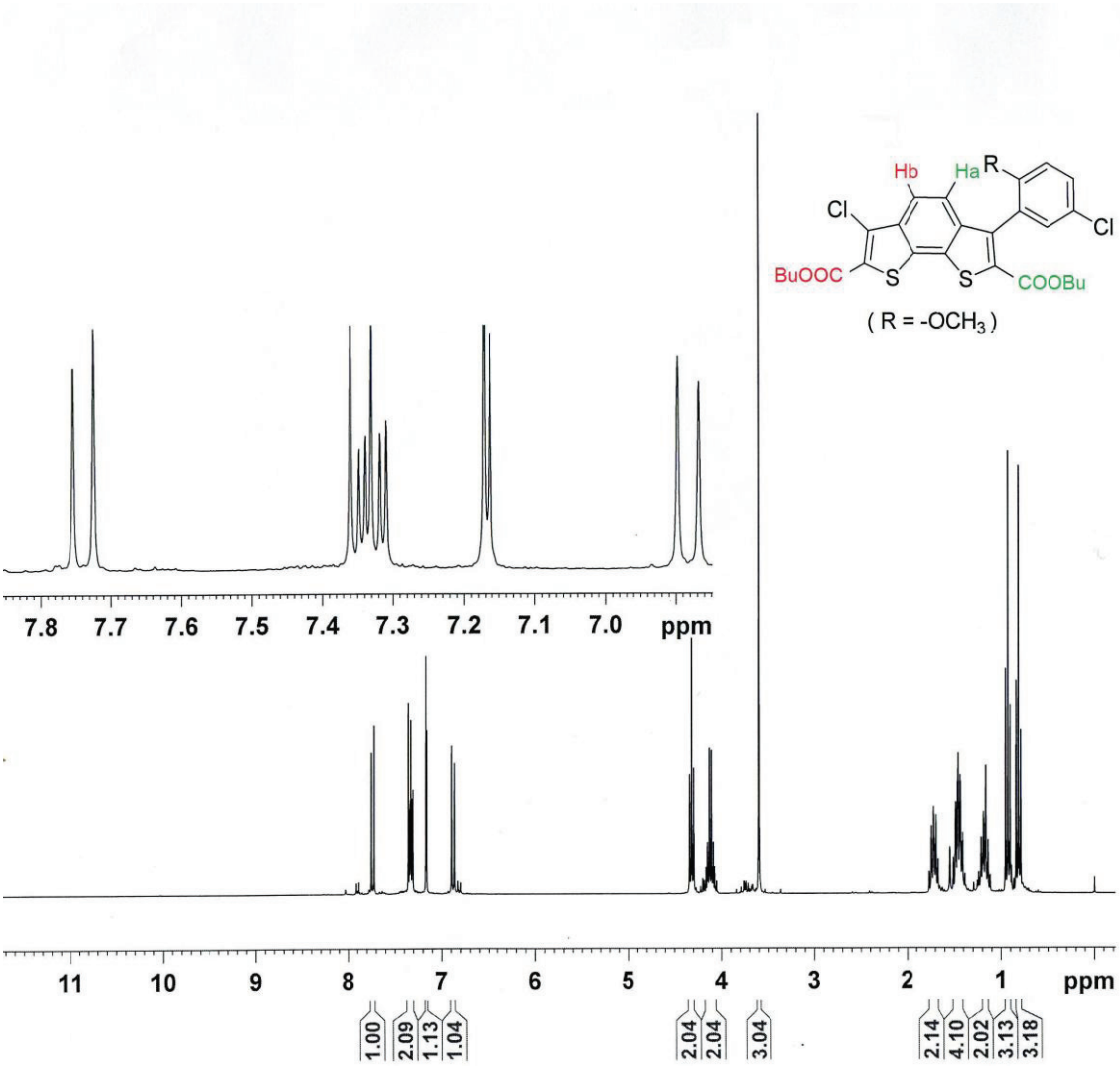
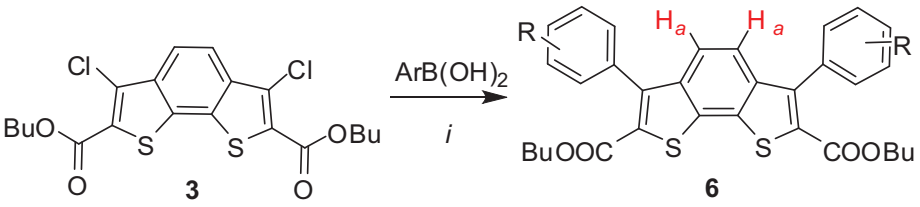


Figure 4. ^{1}H NMR Spectrum of **5b** in $CDCl_3$ at 300 MHz

Moreover, additional structural informations were obtained by the effective diarylation of dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene moiety **3** (Scheme 4, Table 2). The diarylation coupling reactions initially failed using $Pd(PPh_3)_4$ (5 mol %) as catalyst, but successfully worked out adding biaryl monophosphine ligand SPhos (**L**) (10 mol %) which has been recently developed by Buchwald and coworkers. [4b] SPhos is an organophosphorus compound derived from biphenyl. Its palladium complexes exhibit high activity for Suzuki coupling reactions involving aryl chlorides, which are less or unreactive with other palladium complexes. These ligands have convenient handling characteristics, since they are air-stable (Figure 5). The bis(butoxycarbonyl)dichlorobenzo[b]dithiophene **3** was employed as a platform for the Suzuki-Miyaura cross coupling reaction, using palladium catalyst $Pd(PPh_3)_4$ (5 mol %) along with Buchwald ligand SPhos (10 mol %), for a facile preparation of diarylbenzodithiophenes (Scheme 4). The resulting diarylated benzo[1,2-*b*;5,6-

b']dithiophenes again have a symmetrical core where both the equivalent protons H_a can not be differentiated to give separate chemical shift values.



Scheme 4. Synthesis of **6b,c**. *Conditions: i*, **3** (1.0 equiv.), $ArB(OH)_2$ (2.5 equiv.), $Pd(PPh_3)_4$ (5mol %), SPhos ligand (10 mol %), K_3PO_4 (4.0 equiv.), dioxane, 120-130 °C, 6-8h

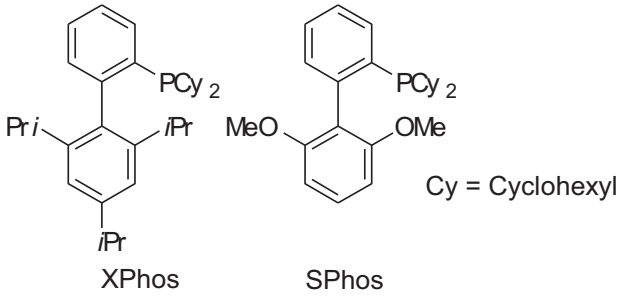


Figure 5. Buchwald ligands [4b]

The resulting diarylated benzodithiophene products **6b,c** are again symmetrical where identical NMR data are expected and a clear structural differentiation by NMR is not possible. The aromatic protons H_a appear as a singlet with the integration of two protons. However, this observation is compatible with both parent isomers **3** and **3'**, since no coupling between the two aromatic protons H_a is expected (the protons are chemically and magnetically equivalent) (Figure 6).

Table 2. Synthesis of **6b,c**

4	Ar	% (**6**)[a]
b	2-MeO-5-ClC_6H_3	62
c	2-MeO-5-C_6H_4	74

[a] Yields of isolated compounds

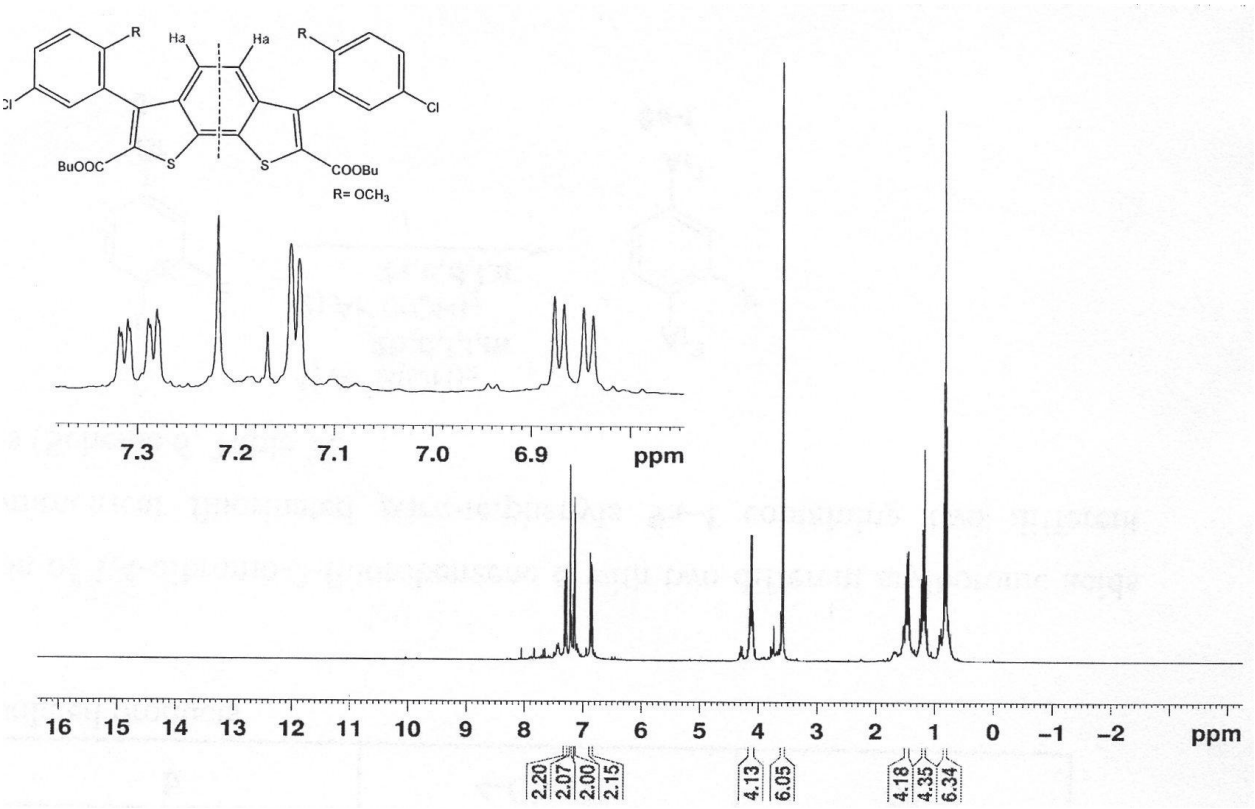


Figure 6. ^{1}H NMR Spectrum of **5b** in $CDCl_3$ at 300 MHz

Due to the striking difference between our results and those reported earlier, the cyclization reaction of 1,4-phenylenediacrylic acid with thionyl chloride, pyridine and methanol or *n*-butanol was repeated five times under the original conditions and always the same result was observed (formation of **2** and **3** as the main products, respectively). The reaction was also carried out in the absence of pyridine, but no significant change of the product distribution was observed.

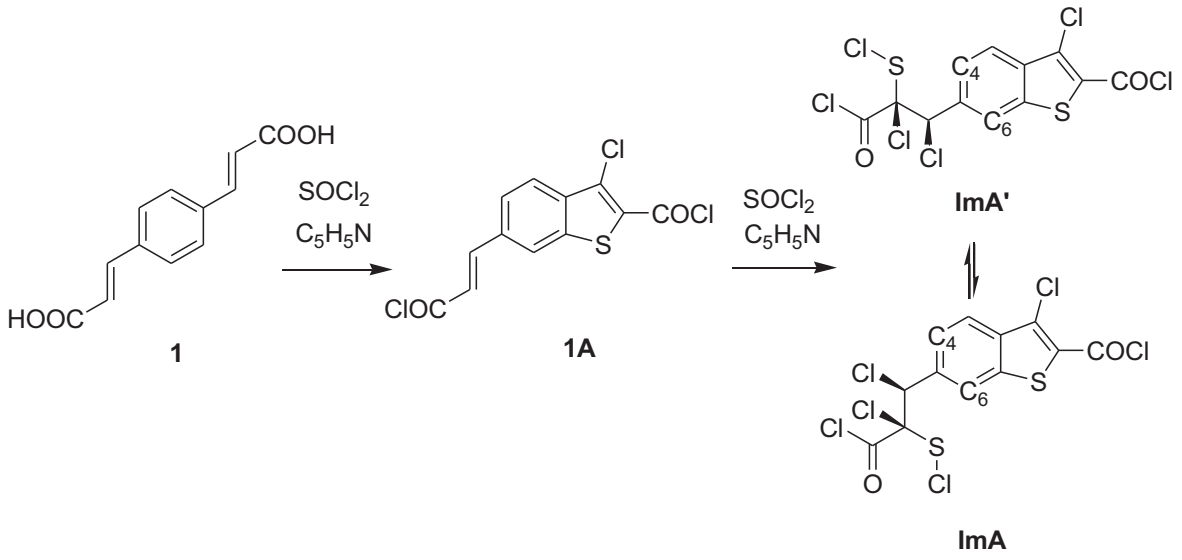
Looking at the literature that after the first publication of Krubsack nobody has investigated the real mechanism of this cyclization. Actually, Krubsack reported that the cyclization is not regio-selective, thus, an investigation on the actual mechanism of this regio-cyclization to

rationalize the formation of the more hindered benzo[b]dithiophenes was carried out on further computational basis.

Computations

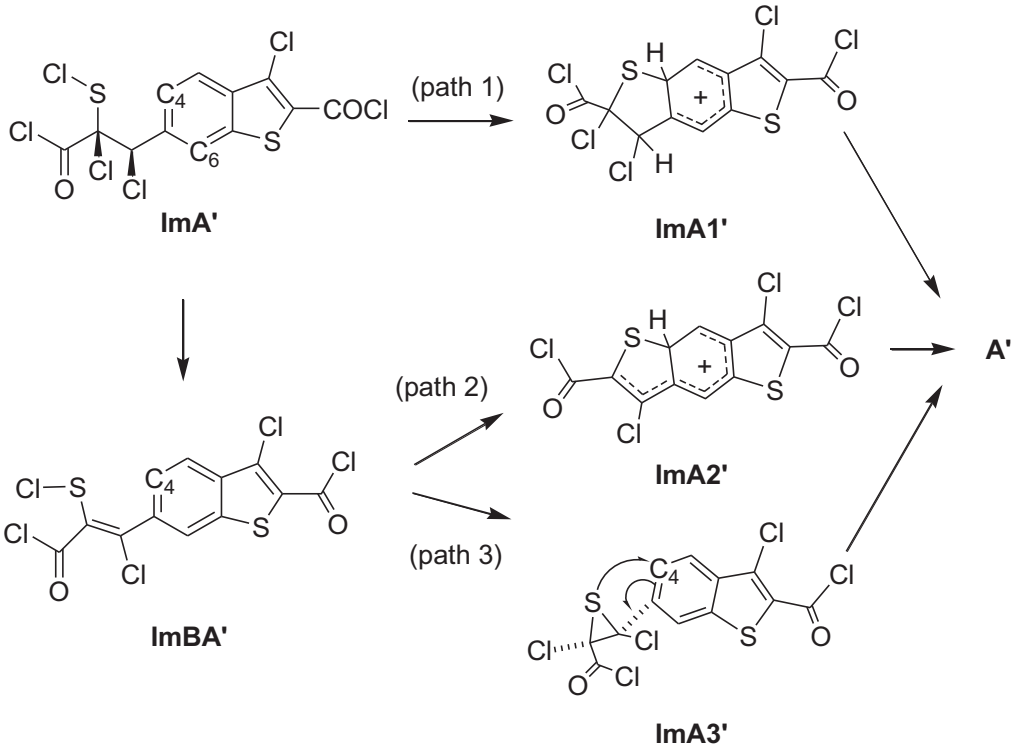
To get some rationalization of the observed selectivity in favour of 3,6-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene **A** instead of 3,7-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophene **A'** (Scheme 5), the cyclization of **1** with thionyl chloride was studied by Density Functional Theory calculations (DFT) at the B3LYP level of theory using a 6-31G* basis set. The DFT calculations show that isomer **A** is thermodynamically more stable than isomer **A'** (by 5.5 kJ/mol, Table 3). However, the thermodynamic stability is unlikely to be the reason for the selectivity of the reaction because the reaction is irreversible. Therefore, possible mechanistic intermediates were studied by DFT calculations. The calculations were carried out for analogues of the mechanistic intermediates suggested by Krubsack *et al.* for the reaction of *trans*-cinnamic acid with thionyl chloride.

We assumed that the two cyclization reactions of diacrylate **1** occur sequentially and not at the same time. Thus, the first cyclization of **1** with thionyl chloride afforded the planar intermediate **1A** which reacts with a second equivalent of thionyl chloride to give the rotamers **ImA** and **ImA'** (Scheme 6). In principle, two diastereomers can be formed for each rotamer. However, only one diastereomer was considered because the energetic difference between the two diastereomers is low.

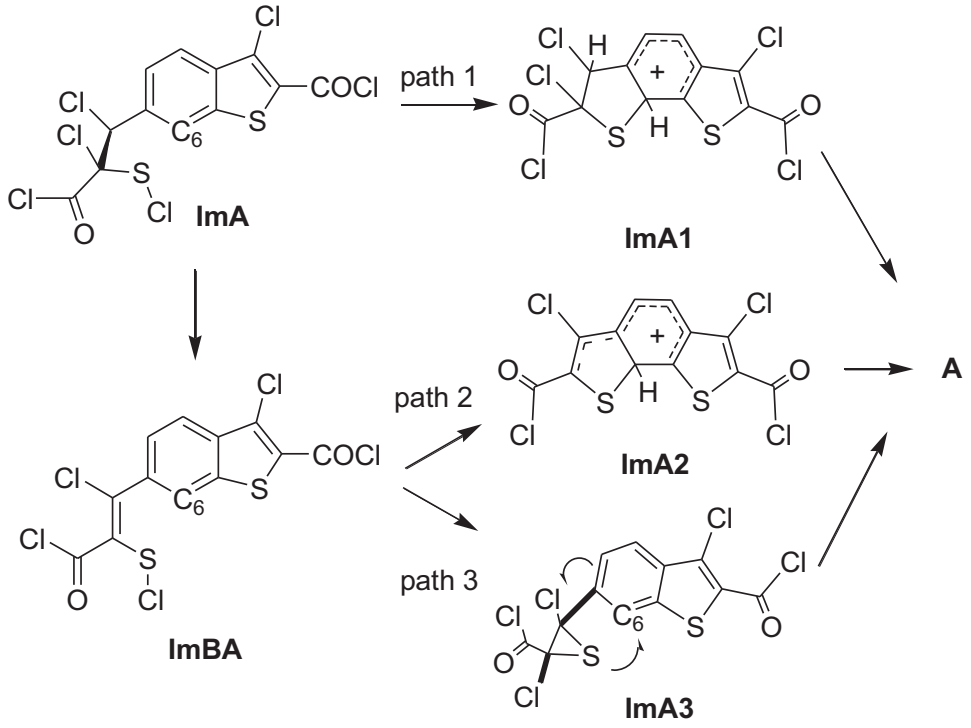


Scheme 5. Formation of **ImA** and **ImA'**

In analogy to the mechanistic studies of Krubsack *et al.* for *trans*-cinnamic acid, three possible paths for the transformation of **ImA** and **ImA'** to **A** and **A'** can be proposed, respectively (Schemes 6 and 7). This includes a direct electrophilic substitution (path 1), or electrophilic substitution via intermediate **ImBA** which could be formed by 1,2-elimination of hydrogen chloride (path 2), or rearrangement of intermediate **ImBA** to episulfide **ImA3** (path 3).



Scheme 6. Proposed mechanism for the formation of 3,8-dichlorobenzo[1,2-*b*;4,5-*b*']dithiophene **A'**



Scheme 7. Proposed mechanism for the formation of 3,8-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene **A**.

The energies of the open-chained intermediates **ImA**, **ImBA**, **ImA3** were compared with the energies of their rotamers **ImA'**, **ImBA'**, **ImA3'**, respectively. In general, the rotamers, in which the aromatic carbon atom C-6 is more close to the sulfur atom, are slightly energetically favoured (by 0.8 kJ/mol - 2.1 kJ/mol). In addition, position 6 of the arene moiety has a higher electron density as compared to position 4. Based on these calculations, the sulfur atom of the S-Cl moiety is expected to preferentially attack at carbon C-6 (Table 3). In addition, we computed the energies of the cationic cyclic intermediates **ImA1**, **ImA1'**, **ImA2** and **ImA2'** (Table 4). Interestingly, intermediate **ImA1** is considerably more stable than **ImA1'** (by 16.15 kJ mol^{-1}). Likewise, **ImA2** is more stable than **ImA2'** (by 12.63 kJ mol^{-1}). The calculations rationalize the fact that isomer **A** instead of **A'** is formed.

Table 3. Energies of the optimized structures, the energy differences between the conformers, natural (NBO) charges and distances (S-C) of **ImA**, **ImA'**, **ImBA**, **ImBA'**, **ImA3, ImA3'** calculated at the B3LYP/6-31G* level for optimized structures.

Intermediate		**ImA**	**ImA'**	**ImBA**	**ImBA'**	**ImA3**	**ImA3'**
Energy / a.u.		-4167.66135	4167.66105	-3706.85652	-3706.85603	-3706.85263	-3706.85185
ΔE /kJ mol^{-1}		-0.785129		-1.28786		-2.06798	
Charge /a.u.	**C6**	-0.21715	-0.19980	-0.19426	-0.19107	-0.20603	-0.18995
	C4	-0.20714	-0.22368	-0.19969	-0.20087	-0.19660	-0.20846
	S	0.33445	0.33571	0.33339	0.33321	0.31805	0.32131
r (S-C) / Å	**C6**	3.33400	3.89695	3.24921	4.33132	3.20363	4.13341
	C4	3.87239	3.31937	4.35374	3.26222	4.17400	3.22313

Table 4. Energies of the optimized structures, the energy differences between the conformers of **ImA1, ImA1', ImA2, ImA2', A** and **A'** calculated at the B3LYP/6-31G* level for optimized structures.

Intermediate	**ImA1**	**ImA1'**	**ImA2**	**ImA2'**	**A**	**A'**
Energy / a.u.	-3707.16569	-3707.15954	-3246.38173	-3246.37692	-3246.10058	-3246.09848
ΔE /kJ mol^{-1}	-16.15168		-12.6282		-5.5161	

1.3 Conclusion

Our findings are of particular importance for the future extension of work related to benzodithiophenes. The misinterpretation of the structures of many benzo[1,2-*b*;5,6-*b*']dithiophenes by several authors is presumambly based on the fact that all of them relied on previously published reports without providing an independent unambiguous structural proof, such as an X-ray crystal structure analysis, 2D NMR or preparation of unsymmetrical derivatives. Our structural assignments are based on X-ray crystal structure analyses of the parent chlorinated dithiophenes and on NMR spectroscopic studies of unsymmetrical derivatives which were prepared for the first time. In addition, our desymmetrization approach can be explored under the optimized reaction, an absolute approach for structure and symmetry confirmation of such molecules. These findings provide clear basis to decide the symmery independently either if no any X-rays structure Would be available. The formation of benzo[b]thiophenes starting from 3-phenylpropanoic acid with thionyl chloride and a small amount of pyridine was also mechanistically discussed by Krubsack et al. in 1975.7a Based on his investigations we carried out quantum chemical calculations for several possible mechanistic intermediates. The calculations support the experimental findings and indicate that the formation of 3,6-dichlorobenzo[1,2-b;5,6-b']dithiophenes is considerably more favored than the formation of 3,7-dichlorobenzo[1,2-b;4,5-b']dithiophenes. Our results are, of course, also important for the future design of related molecules and materials.

2. Synthesis of benzodithiazoles using *N*-benzyl DABCO tribromide (organic ammonium tribromide OATB) through oxidative cyclization of thiobenzanilides

2.1 Introduction

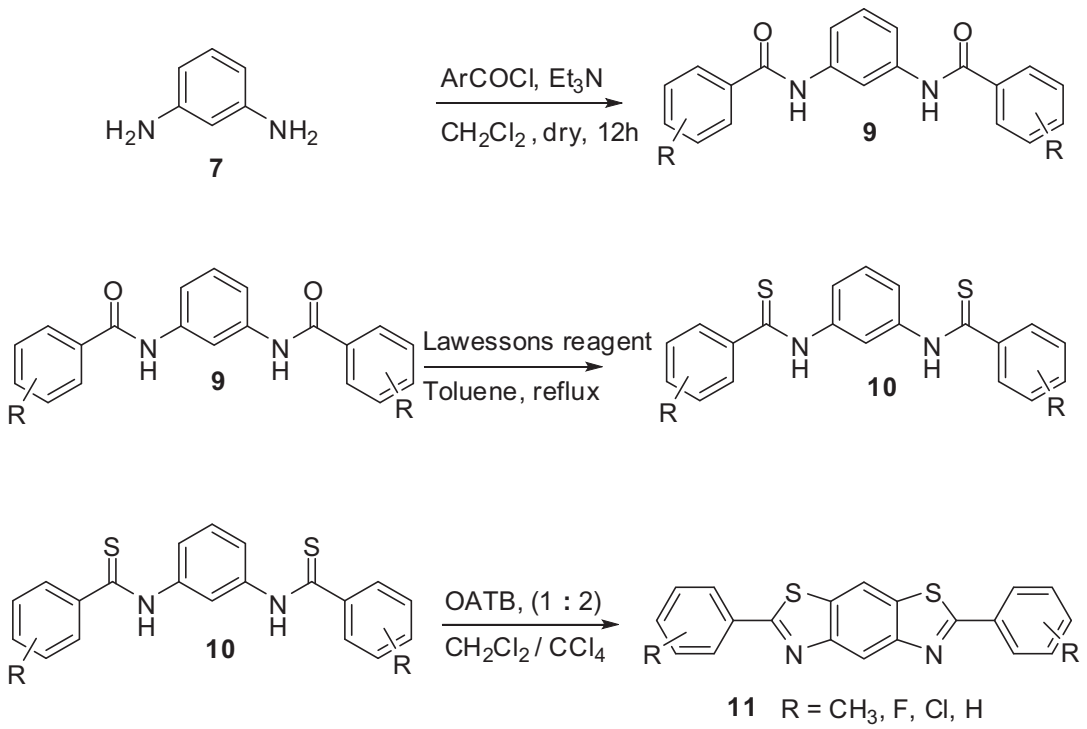
Heterocycles, in particular sulfur containing azoles, are valuable because of their important features as biologically active compounds, pharmaceuticals, and functional materials.[10] Well-known sulfur containing compounds include adrenergic receptor agonists, neuroprotective agents, antineoplastic agents, and electron-transporting materials. S. S. Kulkarni et al. have reported the essential pharmacophoric features of benzothiazole derivatives, such as metabotropic glutamate receptor-5 (mGluR5) antagonists which mediate actions of the excitatory neurotransmitter L-glutamate. Benzothiazole moieties are also found in a variety of biologically important natural products.[11] They are used as active drugs for several diseases such as tumors, diabetes, Parkinson's disease, tuberculosis, inflammatory diseases, epilepsy, viral infections, insomnia, and atherosclerosis.[12] Also, they are inhibitors of several enzymes and function as antioxidants.[13] Due to their vast importance, benzothiazole containing compounds are studied in detail during the recent couple of years.[14] Significantly, fluorinated benzodithiazoles have been reported as new dyes used in both one and two photon fluorescence microscopy, demonstrating outstanding lysosomal selectivity.[15] Benzodithiazoles with multiple functional groups can be novel ligands for their conversion with different metal salts to new metallorganic frameworks. Porous coordination polymers can be used as potential media for gas adsorption, gas separation and catalysis. The developments of efficient and economical methodologies for the functionalization of such heterocycles have received much attention in organic synthesis. Herein, the synthesis of new benzodithiazole derivatives through oxidative cyclization using *N*-benzyl DABCO tribromide has been discussed.

2.2 Results and discussion

Several conventional methods for the synthesis of different benzothiazole moieties are available in literature, like the condensation of 2-aminothiophenols with substituted nitriles, aldehydes, carboxylic acids, acid chlorides or esters.[16] Intramolecular cyclization of N-(2-halophenyl)benzothioamide is also reported for the synthesis of benzothiazoles. Hugerschoff found that aminobenzothiazoles can be synthesized from arylthioureas on reaction with liquid

bromine in chloroform.[17] Despite good yields and low reaction times, several drawbacks are associated with the use of liquid bromine, which is a highly toxic, corrosive reagent.

In recent years, investigations have shown that different benzothiazole derivatives can be synthesized efficiently through oxidative cyclization using organic ammonium tribromides (OATBs).[18] Benzyltrimethylammonium tribromide, tetrabutylammonium tribromide and *N*-benzyl-DABCO-tribromide can be used as alternative brominating reagents instead of liquid bromine. As compared to bromine, OATBs are crystalline solids, are capable of delivering a stoichiometric amount of bromine where small amounts of bromine are necessary for micro scale reactions (Figure 9). Benzyltrimethyl ammonium tribromide has been successfully used for the conversion of substituted aryl thioureas to the corresponding 2-aminobenzothiazoles.[19] Herein in this chapter, the synthesis of various arylated benzodithiazoles with different substituents has been discussed. This method can be applied broadly to obtain arylated as well as alkylated benzodithiazoles efficiently (Scheme 4).



Scheme 4. Synthesis of **10a-f**. Conditions: *i*, **7** (1.0 equiv.), Ar-COCl (2.0 equiv.), Et_3N (4.0 equiv), CH_2Cl_2, 0-20 °C, 10-12h; *ii*, **9** (1.0 equiv.), lawessons reagent (0.5 equiv), toluene, reflux at 140 °C, 1-2h; *iii*, **10** (1.0 equiv), OATB (1.0 equiv. per cyclization), CH_2Cl_2/CCl_4 (1:1, 10ml), 1-2h

Benzanilides were synthesized according to a previoisly reported method by reaction of commercially available 1,3-benzenediamine (**7**) with different benzoyl chlorides **8a-f** under basic conditions.[20] The diamides were transformed into thiobenzanilides **10a-f** by refluxing with Lawesson's reagent (**LR**) in toluene for one hour.[21] Lawesson's reagent has a four membered ring of alternating sulfur and phosphorus atoms. With heating, the central phosphorus/sulfur four-membered ring can open to form two reactive dithiophosphine ylides ($R\text{-}PS_2$). Much of the chemistry of Lawessons's reagent is in fact the chemistry of these reactive intermediates. In general, the more electron rich a carbonyl is, the faster the carbonyl group will be converted into the corresponding thiocarbonyl compounds by Lawesson's reagent. Lawesson's reagent (Figure 8) is the most promising thionating agent giving high yields and minimum reaction times (Scheme 5).

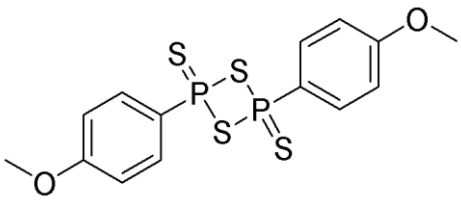
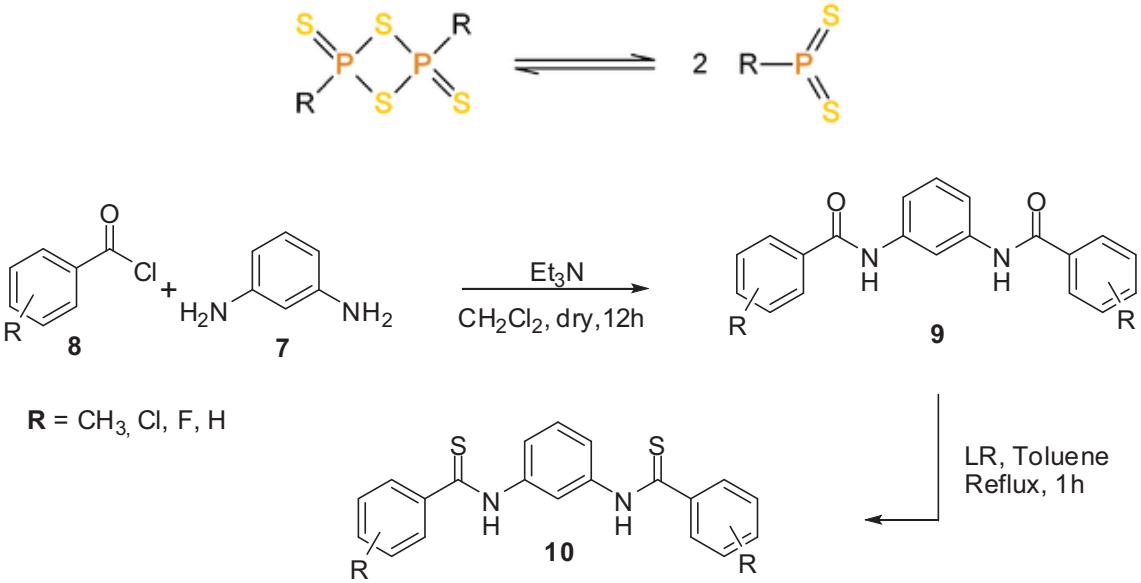


Figure 8. Lawesson's Reagent (**LR**)



Scheme 5. Thionation with Lawesson's Reagent (**LR**)

Table 3. Synthesis of thionated compounds **10a-f** using Lawesson's Reagent (**LR**)

9	Dibenzothioamide derivatives	Time	% (**10**)[a]
a	N,N'-(1,3-phenylene)bis(4-fluorobenzothioamide)	1h	82
b	N,N'-(1,3-phenylene)bis(4-chlorobenzothioamide)	1h	87
c	N,N'-(1,3-phenylene)bis(4-methylbenzothioamide)	1h	85
d	N,N'-(1,3-phenylene)dibenzothioamide	1h	90
e	N,N'-(1,3-phenylene)dipropanethioamide	1h	80
f	N,N'-(1,3-phenylene)bis(2,2-dimethylpropanethioamide)	1h	84

[a] Yields of isolated compounds

Among different reported OATBs, especially *N*-benzyl-DABCO-tribromide gives high yields and the reactions proceed in short time.[18] When thiobenzanilides **10a-f** were dissolved in a mixture of dichloromethane and carbon tetrachloride (1:1) and treated with N-benzyl-DABCO-tribromide (OATB), rapid and efficient oxidative cyclization to the corresponding benzodithiazole occured to give the corresponding products **11a-f** in good yields 70-80% (Scheme 7).

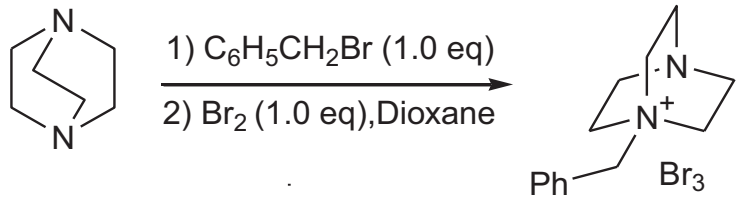
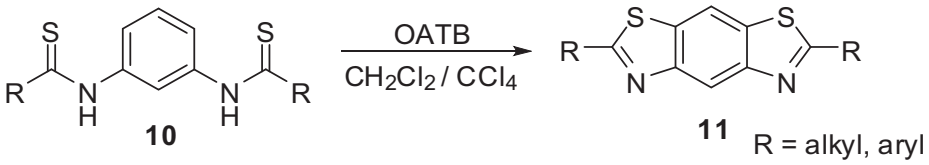


Figure 9. *N*-Benzyl-DABCO tribromide (OATB)

Scheme 6. Synthesis of *N*-benzyl-DABCO tribromide (OATB); conditions: DABCO (1.0 equiv. in dioxane, 5 ml per 0.5 M), benzyl bromide (1.0 equiv. in dioxane, 5 ml), Br_2 (1.0 equiv in dioxane, 5 ml), 20 °C, 30 min

Thiobenzanilides on reaction with OATBs (one equiv. per thiocarbonyl group) cyclize to give the corresponding benzodithiazoles. The OATBs facilitate the easy going electrophilic bromination for efficient oxidative cyclization to give the resulting products (Figure 10). Moreover, it is also important to optimize the reaction conditions, like reaction time, temperature, and the solvent system.



Scheme 7. Oxidative cyclization of benzodithiazole

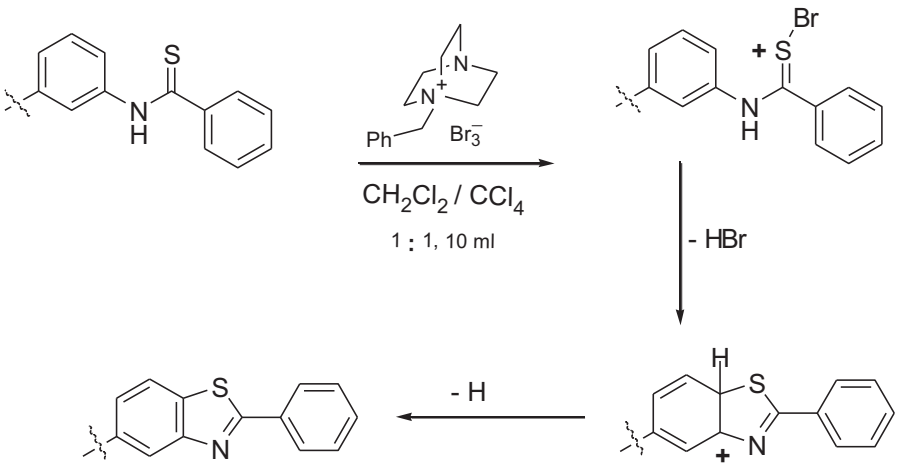
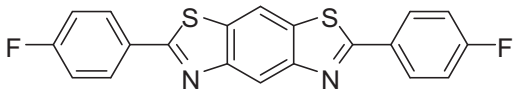
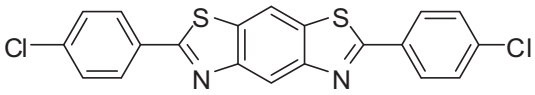
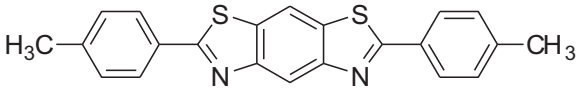
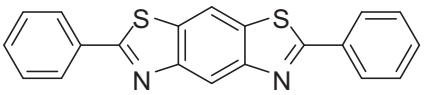


Figure 10. Proposed mechanism for ring formation

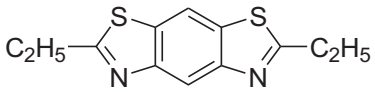
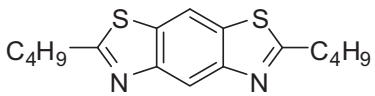
Table 4. Synthesis of different benzodithiazoles using *N*-benzyl-DABCO-tribromide

10	Benzodithiazoles	Time	(**11**)%[a]
a		90 min	72
b		60 min	67
c		40 min	75
d		40 min	70

[a] Yields of isolated compounds

I have also synthesized various alkylated benzodithiazole derivatives. The same procedures were applied successfully using different acyl chlorides R-COCl (Table 5). All the reactions were carried out in dichloromethane and carbon tetrachloride (1:1) to obtain highest yields. All compounds were characterized spectroscopic methods.

Table 5. Synthesis of different benzodithiazoles **11** using *N*-benzyl-DABCO-tribromide

10	Benzodithiazoles	Time	% (**11**)[a]
e		40 min	60
f		30 min	67

[a] Yields of isolated compounds

2.3 Conclusion

Herein, the synthesis of new benzodithiazoles from dithiobenzanilides through oxidative cyclization using *N*-benzyl DABCO tribromide has been described. *N*-Benzyl DABCO tribromide, being a crystalline solid, is safe to handle and provides high yields. It is a most efficient strategy and the reaction proceeds in short time under mild reaction conditions. Such benzodithiazol core structures can be the novel ligands to build-up new organic frameworks as porous coordination polymers which can be used as potenial media for gas adsorption, gas separation and catalysis.

3. Chemoselective Suzuki-Miyaura cross coupling reaction of 2-bromo-1-(trifluoromethanesulfonyloxy)naphthalene,1-bromo-2-(trifluoromethanesulfonyl-oxy)naphthalene and 2-acetyl-4-bromo-1-(trifluoromethanesulfonyloxy) naphthalene

3.1 General Introduction

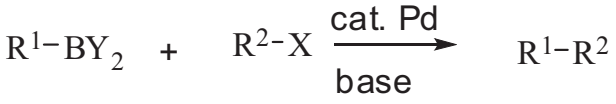
The development of new, efficient and economical reactions for the formation of carbon-carbon and carbon-heteroatom bonds have been studied as new methodologies for the formation of promising bioactive and valuable frames. These reactions very much facilitate the construction of complex molecules from simple precursors. The Grignard, Diels–Alder, and Wittig reaction have been of great use in this regard. Since the discovery of metal-catalyzed cross-coupling reactions, a variety of metals have proven to be productive in organic synthesis. For the last three decades transition metal catalyzed reactions, particularly palladium(0)-catalyzed transformations, have gained remarkable importance for carbon-carbon bond formation and many new ideas have been tested and realized.[22] Nowadays, these reactions are being used for the synthesis of a number of natural products, pharmaceuticals and advanced materials.[23-25]

3.1.2 Pd-catalyzed reactions

Since the discovery and continuing evolution of metal-catalyzed cross coupling reactions, palladium(0)-catalyzed carbon-carbon bond forming reactions provide a useful methodology, which has not only facilitated the synthesis of complex molecules but also served as an efficient route for the formation of carbon-carbon bonds used by synthetic chemists.[23] Palladium-catalyzed cross-coupling is used in research worldwide, as well as in commercial production of, for example, pharmaceuticals and molecules used in the electronic industry. The tool allows scientists to build complex chemicals such as the carbon-based ones that are the basis of life. This technique is applied in every field of chemistry, such as, total synthesis, nanotechnology, synthesis of advanced materials, medicinal and pharmacological chemistry. The most commonly applied palladium-catalyzed carbon–carbon bond forming reactions in total synthesis are, namely, the Heck[26,27], Stille[30], Suzuki[28], Sonogashira[29], Tsuji–Trost[30], and the Negishi [31] reaction. The mechanisms of these reactions are similar. The first step is usually the oxidative addition of organic halides or triflates to the Pd(0) complex to form

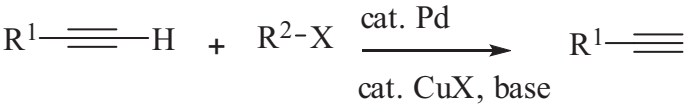
organopalladium halides. The following step is, in case of the Suzuki, Sonogashira and Stille reaction, often a transmetallation with nucleophilic compounds to give a diorganopalladium complex. This complex undergoes a reductive elimination to create carbon-carbon bond and regeneration of the catalyst.

Suzuki Reaction



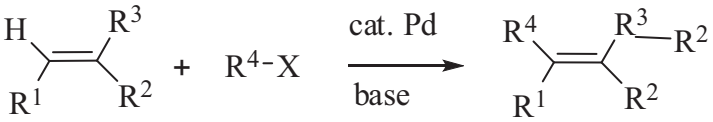
R^1 = alkyl, aryl, vinyl
R^2 = alkyl, alkynyl, vinyl, benzyl
X = Br, Cl, I, OTf, OTs

Sonogashira Reaction



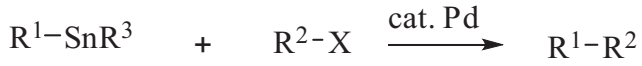
R^1 =alkyl, aryl, vinyl
R^2 = aryl, benzyl, vinyl
X = Br, Cl, I, OTf

Heck Reaction



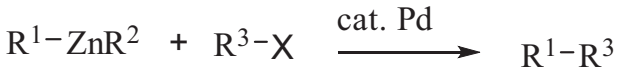
R^4 = aryl, benzyl, vinyl
X = Cl, Br, I, OTf

Stile Reaction



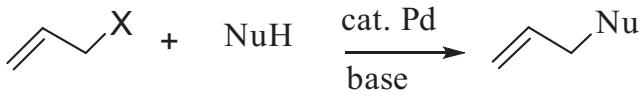
R^1 = alkyl, alkynyl, aryl, vinyl
R^2 = acyl, alkynyl, allyl, benzyl
X = Br, Cl, I, OTf, OAc

Negishi Reaction



R^1 = alkyl, akynyl, aryl, vinyl
R^3 = acyl, aryl, benzyl, vinyl
X = Br, I, OTf, OTs

Tsuji-Trost Reaction



X = Br, Cl,OCOR,
NuH = enamines, enolates

3.1.3 Suzuki-Miyaura Cross-Coupling Reaction:

The Suzuki-Miyaura coupling reaction has gained much importance for its usefulness for the cross-coupling between halides and organoboronic acids.[32,33] Advances made in this field include the development of new catalysts and modern methods have greatly increased the scope of this reaction and is now considered to be a quite general procedure for a wide range of selective carbon-carbon bond formations.[34,35] The scope of the reaction partners is not restricted to arenes, but includes also alkyl, alkenyl and alkynyl compounds. The mechanism of the Suzuki reaction involves the oxidative addition of organic halides or triflates to the Pd(0) complex to form a organopalladium halide (R1-PdII-X). This step is followed by transmetallation with a boronic acid derivative or a borane to give a diorganopalladium complex. This complex undergoes a reductive elimination with carbon-carbon bond formation and regeneration of the catalyst.[35]

The palladium-catalyzed reactions had also been carried out with aryl bis(triflates). The palladium(0) catalyzed cross-coupling reaction of aryl triflates[37] with aryl boronic acids in the presence of a base is a versatile method for preparing unsymmetrical substituted biaryls. The use of aryl triflates instead of aryl halides is particularly important in organic synthesis because it can provide a way of forming a carbon-carbon bond at a phenolic site, which is often useful when appropriate halides are unavailable.[38] Since aryl triflates are easily available from the corresponding hydroxy compounds, the scope and applications of these compounds in transition metal catalyzed reactions has therefore attracted the interest of chemists. This coupling reaction offers the advantage of high yields, clean products with less side reactions, tolerance of a variety of functional groups on either coupling partner, and no necessity for anhydrous conditions.

The reactivity order of aryl halides and aryl triflates, which act as electrophiles, is Ar-I > Ar-Br > Ar-OTf > ArCl, where electronic and steric hindrance is also playing a role in selectivities. The use of base accelerates the transmetalation. This is due to the increase of the carbanion character of the organoborane moiety by formation of an organoborate containing a tetravalent boron atom. The selection of a proper catalyst plays an important role in the success of the desired reaction. The common palladium sources employed include, for example, $Pd(OAc)_2$, $PdCl_2$, $Ph(PPh_3)Cl_2$, and Pd(dba). The use of bulky electron-rich ligands is often the key for a successful transformation. Miyaura-Suzuki reactions[37], in particular, are very attractive, due to the stability of the precursors, boronic acids, and facility of work up. In this reaction even an alkyl group (i.e. sp^3-hybridized C atom), as opposed to the more

traditionally used vinyl or aryl groups, can be transferred from the organoborane component during the palladium-catalyzed coupling process with vinyl or aryl halides or triflates. Compared to Stille reactions [39], Suzuki–Miyaura couplings have a much broader scope in that a potentially vast range of alkyl boranes (typically prepared through the regio- and chemoselective hydroboration of readily available alkene precursors) can be employed in the reaction.[40] The interest of the chemist in this field is evident from the continuous developments in the use of new reaction conditions, catalysts and ligands.[41-43]

3.2 Introduction

Biaryl linkages, due to restricted rotation, often govern the biological activity of naphthalene natural products and are responsible to introduce atropisomerism. Anti-malarial and anti-HIV active naphthylisoquinolines, such as michellamine A, have attracted the scientific community.[44-47] Resveratrol is a naturally occurring potent anticancer drug which, however, suffers from chemical and metabolic instability.[48] To solve the problem, rigid and stable arylated naphthalenes were synthesized in which the stilbene double bond was substituted by a naphthalene ring. Among these compounds, some were found to be most active against human breast cancer cell line B. Konzik *et. al.* have shown that the phenyl substituents of naphthalenes have a strong influence on their fungistatic activity.[49]

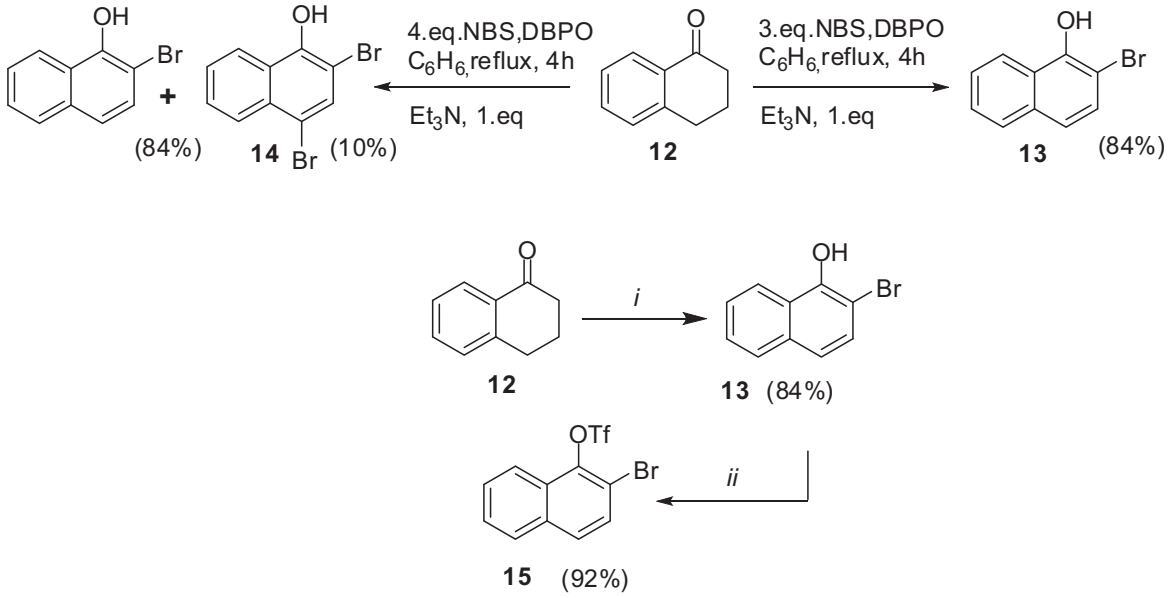
In recent years, regioselective palladium catalyzed reactions of polyhalogenated arenes or heteroarenes and of bis (triflates) have been widely studied.[50] In general, the first attack occurs at the sterically less hindered and electronically most deficient position. Another strategy for the selective functionalization of arenes or heteroarenes relies on the chemoselectivity of substrates containing different leaving groups (e. g., triflate and bromide). Recent reports show that several parameters influence the chemoselectivity of Suzuki-Miyaura reactions of arenes containing a bromide and a triflate group.[51] While various palladium catalyzed cross coupling reactions of naphthalene derivatives have been reported,[47] regio- and chemoselective transformations of naphthalenes containing two or more reactive sites, such as bromide or triflate groups, have only scarcely been studied so far.

In this chapter, the steric and electronic effect on chemoselective Suzuki-Miyaura coupling reactions has been described using 2-bromo-1-(trifluoromethane-sulfonyloxy)naphthalene **15**, 1-bromo-2-(trifluoromethane-sulfonyloxy)naphthalene **22** and 2-acetyl-4-bromo-1-(trifluoromethanesulfonyloxy)naphthalene **27**. All these reactions proceed with excellent

chemoselectivity and provide a convenient approach to various arylated naphthalene derivatives which are not readily available by other methods.

3.3 Results and discussion

In 2005, Bekaert *et. al.* described[52] the selective synthesis of 2-bromonaphth-1-ol (**13**) by reaction of 1-tetralone (**12**) with *N*-methylpyrrolidin-2-one hydrotribromide (MPHT, $[NMP]_2HBr_3$). An alternative approach to **13** was found which is based on the bromination[53] of **12** using NBS (2.2 equiv.) and $(PhCOO)_2$, 5 mol %) (Scheme 8). Inexpensive reagents and good yield (84 %) are the benefit of this method. It is notable that, although free radical conditions were applied, bromination at position 4 was not observed. The same bromination methodology provided other required halogenated naphthalenes. Later on 2-bromonaphth-1-ol **13** was transformed to its triflate **15** in very good yield (Scheme 8).



Scheme 8. Synthesis of **13** and **15**. *Conditions: i*, **12** (1.0 equiv.), NBS (2.2 equiv.), $(PhCOO)_2$ (5 mol %), benzene, reflux, 5h; *ii,* **13** (1.0 equiv), Tf_2O (1.2 equiv), pyridine (2.0 equiv), CH_2Cl_2, 20 °C, 12h

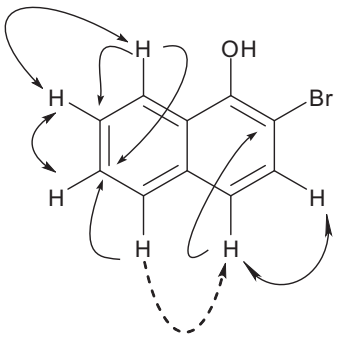
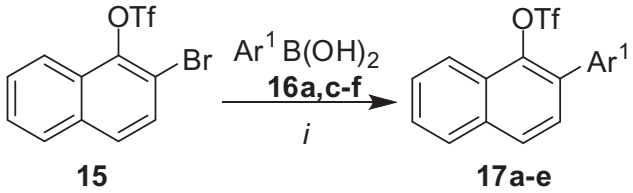


Figure 11: Important HMBC (single pointed arrow), NOESY (dashed arrow) and COSY (double pointed arrow) correlations of **13**

The bromine position was determined by 2D NMR correlation techniques (HMBC and NOESY). A clear correlation was found to assign the relative bromination position (Figure 11). In HMBC and NOESY plots of compound **13**, C-4 proton is showing a clear interaction with C-3 as well as C-5 proton to confirm the mono bromination. However, by increasing the amount of NBS up to 4.0 equiv., further bomination was observed at C-4 to obtain 2,4-dibromonaphthalen-1-ol **14** along with compound **13.** 2,4-Dibromonaphthalen-1-ol was obtained in very small amount (10 %) and further addition of NBS along with changing other parameters could not make a difference to increase their yield.

The S-M reaction of **15** with arylboronic acids **16a,c-f** (1.0 equiv.) afforded the 2-arylnaphth-1-yl trifluoromethanesulfonates **17a-e** in 60-88 % yields (Scheme 9, Table 6). The reactions proceeded with very good chemoselectivity in favour of the bromide position, while the triflate remained unattacked. Aryl bromides generally undergo Suzuki-Miyaura reactions faster than aryl triflates.[51] This reactivity order is different for other palladium catalyzed cross-coupling reactions. One of the justifications for that is based on the high borane-halide affinity. Nevertheless, other parameters control the selectivity as well. During the optimization, significance to use exactly equimolar quantities of the arylboronic acid was established and $Pd(PPh_3)_4$ (5 mol %) as the catalyst. The temperature played an imperative role as well. A good selectivity was attained only when the reaction was carried out at 90 °C (instead of 110 °C) because the reaction of the triflate was slow at this temperature. The reactions were successful for both electron-rich and electron-poor arylboronic acids, but again electron-poor boronic acids provided better yields.



Scheme 9. Synthesis of **17a-e**. *Conditions: i*, **15** (1.0 equiv.), $Ar^1B(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv.), dioxane, 90 °C, 4h.

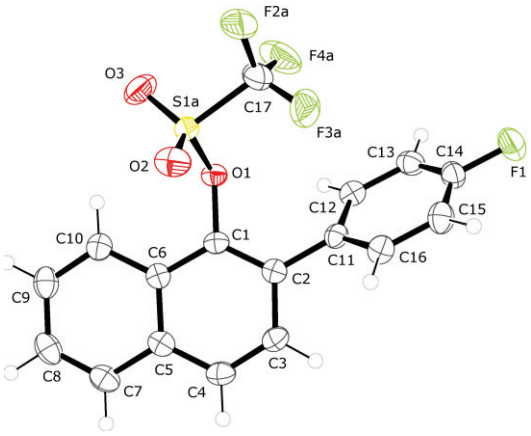


Figure 12: Ortep plot of **17e**

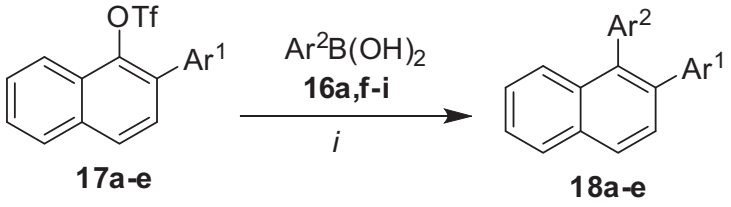
Table 6. Synthesis of **17a-e**

15	**16**	Ar	% (**17**)[a]
a	**a**	2-(MeO)C_6H_4	60
c	**b**	4-MeC_6H_4	73
f	**c**	C_6H_5	77
d	**d**	4-ClC_6H_4	88
e	**e**	4-FC_6H_4	85

[a] Yields of isolated compounds

The Suzuki-Miyaura coupling reaction of **17a-e** with arylboronic acids **16a,f-i** (1.1 equiv.) afforded the unsymmetrical 1,2-diarylnaphthalenes **18a-e** containing two different aryl groups (Scheme 10, Table 7). The reactions were carried out at 110 °C. The application of a one-pot synthesis of products **18** by sequential addition of two different arylboronic acids resulted in a

decrease of the yield (with respect to the stepwise protocol). Therefore, this strategy was not further studied.



Scheme 10. Synthesis of **18a-e**. *Conditions: i*, **17a-e** (1.0 equiv.), $Ar^2B(OH)_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv.), dioxane, 110 °C, 4 h

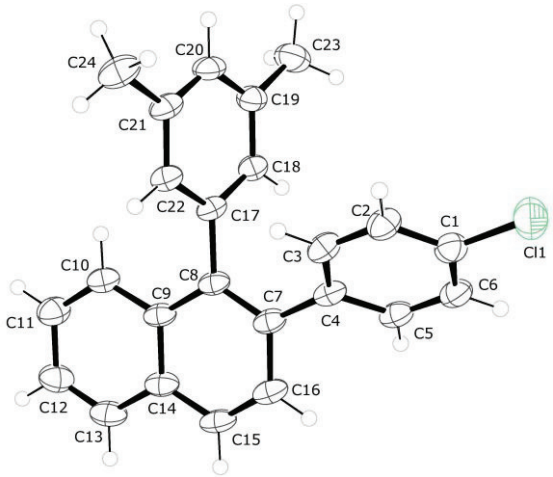


Figure 13: Ortep plot of **18d**

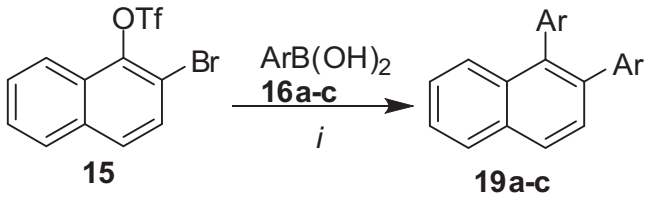
Table 7. Synthesis of **18a-e**

18	16	17	Ar^1	Ar^2	% (**18**)[a]
a	**f**	**a**	2-(MeO)C_6H_4	4-*t*BuC_6H_4	80
b	**g**	**b**	4-MeC_6H_4	2,5-$(MeO)_2C_6H_3$	65
c	**a**	**c**	C_6H_5	2-(MeO)C_6H_4	69
d	**b**	**d**	4-ClC_6H_4	3,5-$Me_2C_6H_3$	72
e	**i**	**e**	4-FC_6H_4	3-MeC_6H_4	77

[a] Yields of isolated compounds

The Suzuki-Miyaura (S-M) coupling reaction of **15** with arylboronic acids **16a-c** (2.2 equiv.) provided the symmetrical 1,2-diarylnaphthalenes **19a-c** in 62-94 % yield (Scheme 11, Table

8).[33] Both electron-poor and electron-rich arylboronic acids could be successfully employed. Better yields were observed with electron-poor arylboronic acids as compared to electron-rich arylboronic acids. The best yields were obtained using $Pd(PPh_3)_4$ (5 mol %) as the catalyst and K_3PO_4 (3.0 equiv.) as the base. 1,4-Dioxane was used as solvent and reactions were carried out at 110 °C.



Scheme 11. Synthesis of **19a-c**. *Conditions: i*, **15** (1.0 equiv.), $ArB(OH)_2$ (2.2 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (3.0 equiv.), dioxane, 110 °C, 4 h

Table 8. Synthesis of 1,2-diarylnaphthalenes **19a-c**

16,19	Ar	% (**19**)[a]
a	2-(MeO)C_6H_4	62
b	4-MeC_6H_4	79
c	4-ClC_6H_4	94

[a] Yields of isolated compounds

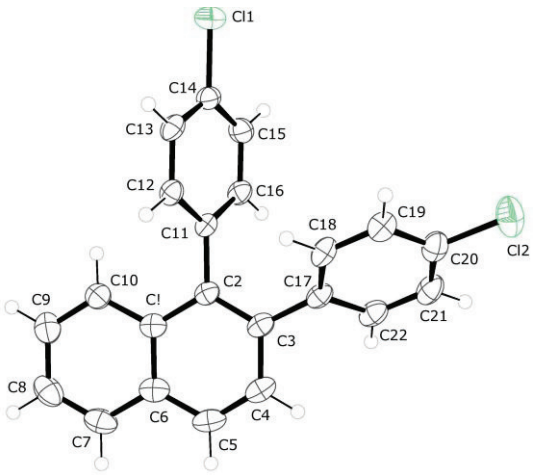


Figure 14. Ortep plot of **19c**

Structures of all compounds were established by NMR spectroscopy whereas structures of **19b** and **19c** were also confirmed independently by X-ray crystallography (Figure 15).

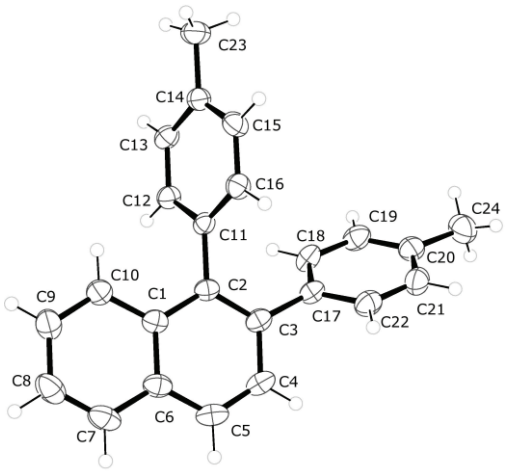
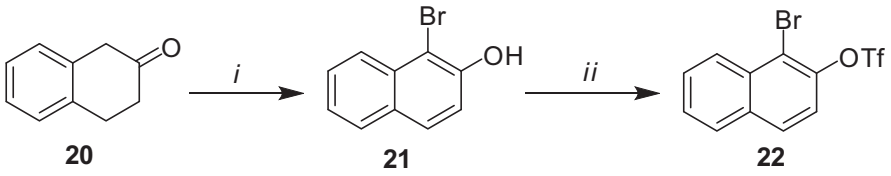


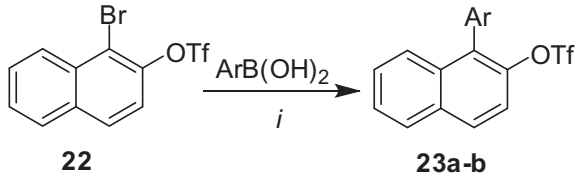
Figure 15: Ortep plot of **19b**.

To figure out whether the stronger steric hindrance of position 1 plays a role in the selectivity, 1-bromonaphthalen-2-yl trifluoromethanesulfonate (**22)** was also studied. The bromine and OTf group position were exchanged in compound **22** having bromine at C-1 along with the hydroxy group at C-2. Compound **22** was prepared from 2-tetralone (**20**) using NBS (3 equiv.). Subsequent triflation of **21** provided **22** (Scheme 12).



Scheme 12. *Reaction conditions: i,* **20** (1.0 equiv.), NBS (3 equiv.), $(PhCOO)_2$ (5 mol %), benzene, reflux, 5 h; *ii,* **21** (1.0 eq), Tf_2O (1.2 equiv.), pyridine (2.0 equiv.), CH_2Cl_2, 20 °C, 6h.

Interestingly, the S-M reaction of **22** with arylboronic acids **16a,b** (1.0 equiv.) afforded the 1-arylnaphth-2-yl trifluoromethanesulfonates **23a,b** in 60-73 % yields (Scheme 13, Table 9). This proves that the bromine-halide affinity possesses a decisive role in the selectivity of S-M reactions of compounds **15** and **22**, because in all case C-Br is attacked preferably.



Scheme 13. Synthesis of **23a-b**. *Conditions: i*, **22** (1.0 equiv.), $ArB(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv.), dioxane, 90 °C, 4h

Table 9. Synthesis of **23a-b**

23	**16**	Ar^1	% (**23**)[a]
A	**a**	4-MeC_6H_4	60
B	**b**	(2-MeO)-5-ClC_6H_3	73

[a] Yields of isolated compounds

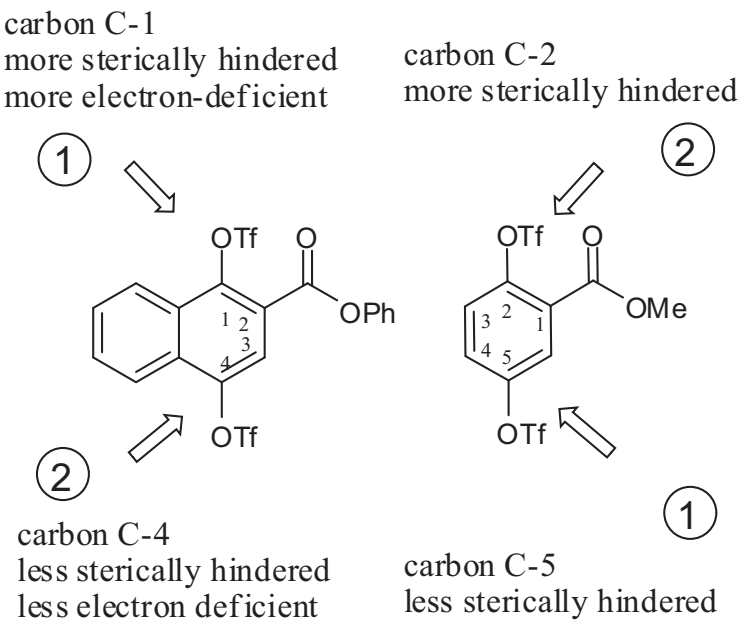
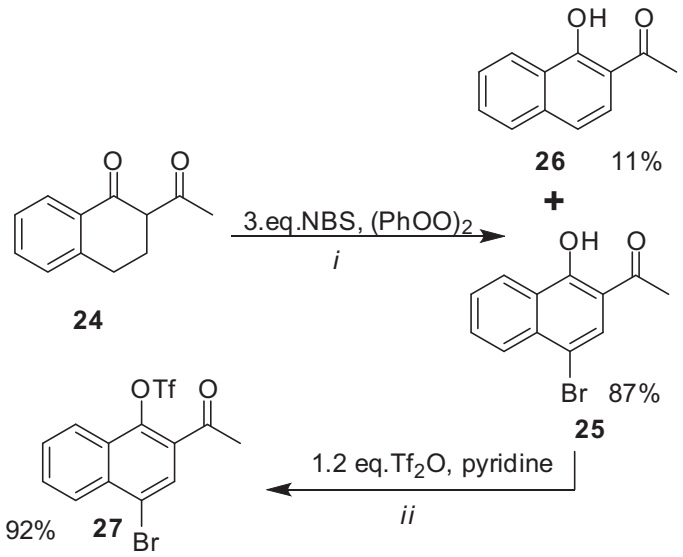


Figure 16. Previously reported site-selective S-M cross coupling reaction of phenyl 1,4-bis(trifluoromethylsulfonyloxy)-2-naphthoate

The previous results of regioselective S-M arylation of phenyl 1,4-bis(trifluoromethylsulfonyloxy)-2-naphthoate (Figure 16) show that the first attack occurs at the more electron deficient and sterically hindered position C-1.[54] In fact, the oxidative addition of the electron-rich palladium species usually occurs first at the most electron deficient carbon atom. As a consequence, the result of chemoselective S-M reactions of 2-acetyl-4-bromonaphthalen-1-yl trifluoromethanesulfonate **27** is of great interest (Figure 18).



Scheme. 14 *Reaction Conditions: i,* **24** (1.0 equiv.), NBS (3.0 equiv.), $(PhCOO)_2$ (5 mol %), benzene, reflux, 4h; *ii*, **25** (1.0 equiv.), Tf_2O (1.2 equiv.), pyridine (2.0 equiv.), CH_2Cl_2, 20 °C, 6h.

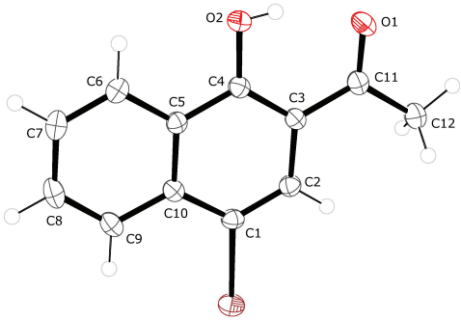
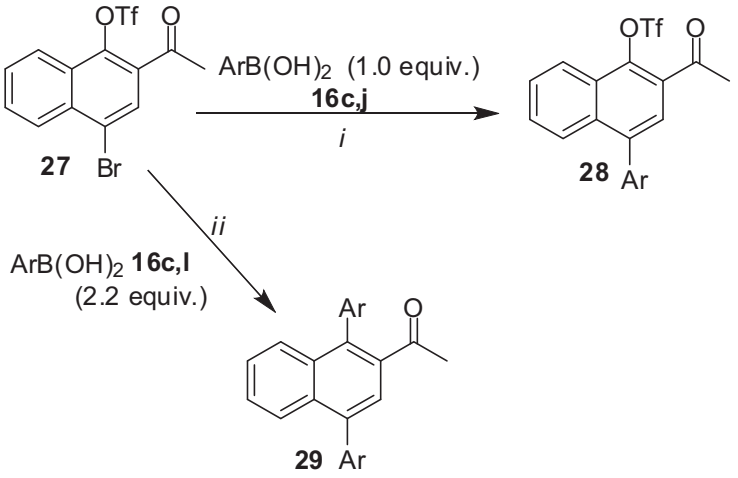


Figure 17: Ortep plot of **25**.

2-Acetyl-3,4-dihydronaphthalen-1(2H)-one **24** is a commercially available substrate and was successfully brominated using NBS (3.0 equiv.) and $(PhCOO)_2$ (5 mol %) (Scheme 14) to give a separable mixture of products **25** (82 %) and **26** (11 %). 1-(4-Bromo-1-hydroxynaphthalen-2-yl)ethanone (**25**) was transformed to its corresponding triflate **27** in high yield (Scheme 14). The bromination at C-4 was decided on the basis of X-ray analysis (Figure 17).



Scheme 15. Synthesis of **28a,b** and **29a,b.** *Conditions: i*, **27** (1.0 equiv.), $Ar^1B(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv.), dioxane, 90 °C, 4h; *ii*, **27** (1.0 equiv.), $ArB(OH)_2$ (2.2 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (3.0 equiv.), dioxane, 110 °C, 4h.

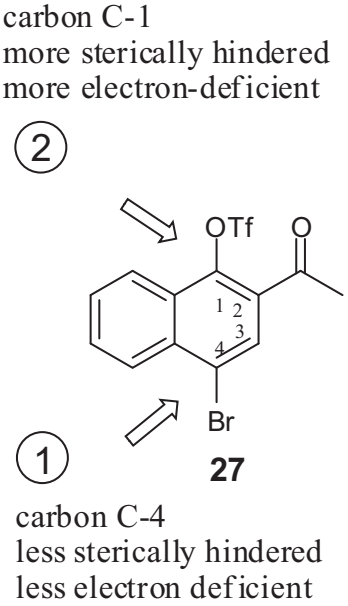


Figure 18. Chemoselective S-M coupling reaction of 2-acetyl-4-bromonaphthalen-1-yl trifluoromethanesulfonate **27**

It was expected that the electronic effect may dominate the first attack at C-1 being the electron deficient carbon as compared to C-4. Fascinatingly, the S-M reaction of **27** with arylboronic acids **16c,j** (1.0 equiv.) provided the 4-aryl-2-acetylnaphthalen-1-yl trifluoromethanesulfonates **28a-b** in 62-79 % yields (Scheme 15, Table 10). The reactions proceeded with chemoselectivity in favour of the bromide position, while the C-1 triflate remained unattacked even though being more electron deficient. This S-M cross-coupling

order is reverse to the regioselectivity as our group reported before for phenyl 1,4-bis(trifluoromethylsulfonyloxy)-2-naphthoate.[54]

Table 10. Synthesis of **27a-b**

25	**16**	Ar	% (**27**)[a]
a	**j**	4-(MeO)C_6H_4	62
b	**c**	4-ClC_6H_4	79

[a] Yields of isolated compounds

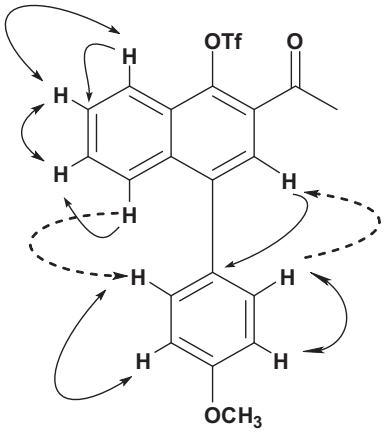


Figure 19: Important HMBC (single headed arrows), NOESY (dashed arrows) and COSY (double headed arrows) correlations of **27a.**

The structure of **27a** was elucidated by detailed 2D NMR techniques. HMBC and NOESY plots show characteristic correlations to establish the exact assignment of **27a** (Figure 19). Protons located at the naphthalene ring at position 3 and 5 show clear interations with protons of the benzene ring.

Likewise, the S-M reaction of **27** with arylboronic acids **16b-c** (2.2 equiv.) afforded the 1,2-diarylnaphthalenes **29b,c** in 62-79 % yield (Scheme 15, Table 11).

Table 11. Synthesis of **21a-b**

27	**16**	Ar	% (**29**)[a]
A	**b**	4-MeC_6H_4	62
b	**c**	4-ClC_6H_4	79

[a] Yields of isolated compounds

3.4 Conclusion

In conclusion, I have reported the chemoselective Suzuki-Miyaura reactions of 2-bromo-1-(trifluoromethanesulfonyloxy)naphthalene **15**, 1-bromo-2-(trifluoromethanesulfonyloxy) naphthalene **22** and 2-acetyl-4-bromonaphthalen-1-yl trifluoromethanesulfonate **27** to achieve symmetrical and unsymmetrical naphthalene derivatives. I have studied the effect of steric hindrance and of electronic induction on chemoselective arylation at Br *versus* OTf; whatever the case, in all these three substrates we provide unambiguous evidence that the first attack is always observed selectively at brominated carbon (*C-Br*) while *C-OTf* was attacked later on. The strategy outlined herein provides a convenient approach to 1,2-diarylnaphthalenes and 2-acetyl 1,4-diarylnaphthalenes products which are not readily available by other methods.

4. Synthesis of heteroaryl-fused benzopyranone analogues and arylated naphthaquinones via palladium-catalysed Suzuki-Miyaura coupling reactions

4.1 Introduction

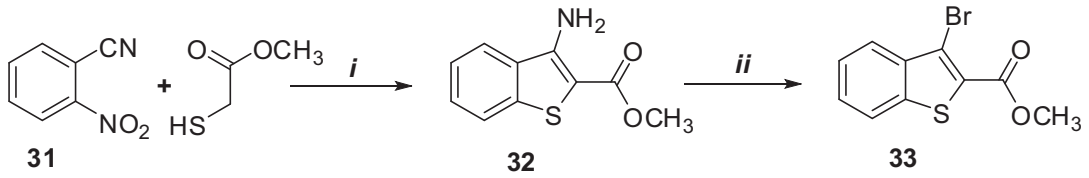
Sulphur containing heterocycles paved the way for the active research in the pharmaceutical chemistry. Benzothiophene derivatives in combination with other ring systems have been used extensively in pharmaceutical applications.[55] Raloxifene, a drug based on benzo[*b*]-thiophene, has been approved by the U.S Food and Drug Administration for the prevention and treatment of osteoporosis associated with woman post menopausal.[56,57] Benzo[*b*]thiophene containing molecules, in particular 2,3-diarylbenzo[*b*]thiophenes and their 3-carbonyl-or hetero atom-inserted analogues, are known to work as selective estrogen receptor modulators.[58] Recently, some benzothiophene derivatives, like methyl 2,3'-bibenzo[*b*]thiophene-2'-carboxylate and other analogues of its pharmaceutically acceptable salts as 3-(6-hydroxynaphthalen-2-yl)benzothiophene-2-carboxylic acid, have been reported to be the biologically most active drugs for the treatment of protein folding disorder, such as Alzheimer's disease, dementia, Parkinson's disease, Huntington's disease.[59] On the other hand, multiply arylated benzothiophenes have also been considered interesting in the field of electronics.[60] In fact polysubstituted benzothiophene compounds are playing an important role in the chemical and pharmaceutical industries as well as in the fields of optical and electronic materials. Optically most interesting dibenzodithiophenes and tetrabenzodithiophenes show characteristic photoluminescence spectral properties. Therefore, the synthesis of these arylated-benzothiophenes is of considerable importance in organic synthesis.

4.1.1 Results and discussion

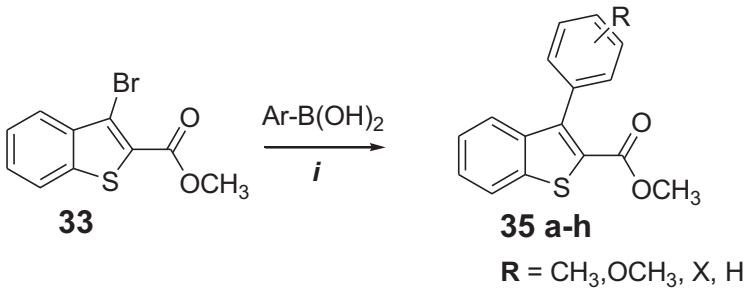
Kodumuru and coworkers have reported microwave promoted parallel syntheses of benzothiophenes, but this method has several limitations with regard to yields, and synthetic steps, and availability of the starting materials.[61] Herein, I have described the synthesis of various heteroaryl-fused benzopyranone analogues and other 3-arylated benzothiophenes.

Methyl 3-bromobenzo[b]thiophene-2-carboxylate **33** was obtained using *o*-nitrobenzonitrile according to the literature methods (Scheme 16).[62,63] The Suzuki-Miyaura (S-M) reaction of

33 with arylboronic acids **34a-h** (1.2 equiv.) provided the 3-aryl-2-methoxycarbonylbenzo[*b*]thiophenes **35a-h** in good yield (Scheme 17, Table 12). Both electron-poor and electron-rich arylboronic acids were successfully employed. The best yields were obtained using $Pd(PPh_3)_4$ (5 mol %) as the catalyst and K_3PO_4 (1.5 equiv.) as the base. 1,4-Dioxane was used as solvent and reactions were carried out at 90 °C.



Scheme 17. Synthesis of **32** and **33**. *Conditions: i*, **31** (1.0 equiv.), methyl thioglycolate (1.0 equiv.), KOH, DMF, 0 °C, 1h; *ii,* **32**, *tert*-butyl-nitrite, $CuCl_2$, CH_3CN, 0 °C, 2 h, 20 % aq HCl.

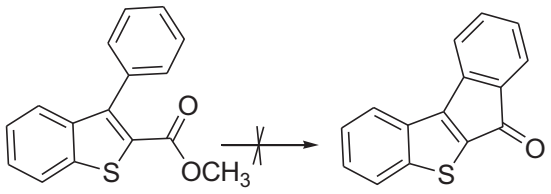


Scheme 18. Synthesis of **35a-g**. *Conditions: i*, **33** (1.0 equiv.), $ArB(OH)_2$ (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv.), dioxane, 90 °C, 4h.

Table 12. Synthesis of **35a-g**

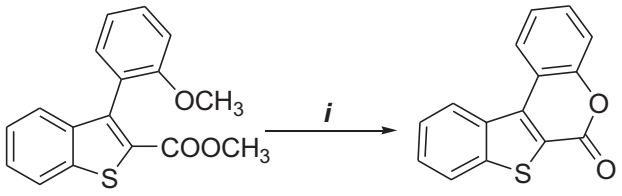
33	Ar	**35**% Yield [a]
A	C_6H_5	88
B	4-ClC_6H_4	71
C	4-MeC_6H_4	79
D	4-$(CF_3)C_6H_4$	68
E	2-$(MeO)C_6H_4$	86
F	2,6-$(MeO)_2C_6H_3$	74
G	5-Cl-2-$(MeO)C_6H_3$	70
H	1-Naphthyl	84

[a] Yields of isolated compounds



Scheme 19. *Conditions: i*, **35** (1.0 equiv.), H_2SO_4

Compounds **35a-e** were treated with H_2SO_4 to obtain the expected cyclized products, 2H-benzo[b]indeno[1,2-d]thiophen-2-ones. But this reaction failed, probably due to high ring strain in molecule. However, the Suzuki-Miyaura (S-M) reaction of **33** with *o*-methoxyphenyl boronic acids **34e,g** gave compounds **35e-g** which were transformed by BBr_3 mediated lactonization, according to literature methods,[64] to **36a,b** in 74-80 % overall yields (Scheme 19). Borontribromide was used for the demethylation process, followed by a 0.1 M solution of $(CH_3)_3COK$ as a base for the lactonization (Table 13).



35 e,g **36 a,b**

Scheme 20. Synthesis of **36a,b;** *Conditions: i*, **35** (1.0 equiv.), BBr_3 (4.0 equiv.), 0 °C, 2h, (*ii*) $(CH_3)_3COK$, (0.1 M, aq), 20 °C, 1h

Table 13. Synthesis of **36a,b**

33	Ar	**36**% Yield [a]
E	2-(MeO)C_6H_4	74
G	5-Cl-2-(MeO)C_6H_3	80

[a] Yields of isolated compounds

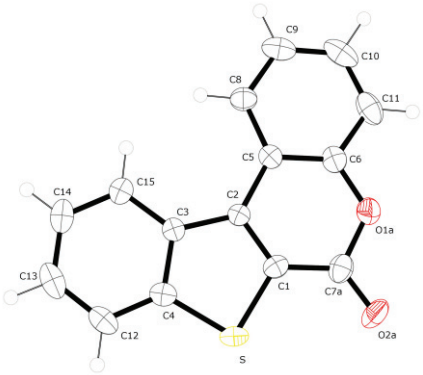


Figure 22: Ortep plot of **36a**

The structures were established by 1D and 2D NMR experiments (NOESY, HMBC), whereas the structure of **36a** was confirmed independently by X-ray crystallography (Figure 22).

In conclusion, various analogues of 6*H*-[1]benzothieno[2,3-*C*]chromen-6-ones and 3-aryl-2-methoxycarbonylbenzo[*b*]thiophenes were synthesized through Suzuki-Miyaura reactions.

4.2 Synthesis and optimization of 2,3-diaryl-1,4-naphthoquinones and 2-aryl-1,4-naphthoquinones through S-M cross coupling reactions

4.2.1 Intoduction

Highly substituted derivatives around fused aromatic cores are of particular interest due to their stability, solubility, enhanced ability to transport charge, and fluorescent properties in the solid state.[65] The biaryl linkage, due to its restricted rotation, governs the biological activity of naphthalene natural products and is responsible to introduce atropisomerism. Due to anti-malarial and anti-HIV activity, naphthylisoquinolines, such as the michellamines, have attracted the scientific community.[66,67] Resveratrol is a naturally occurring potent anticancer drug which, however, suffers from chemical and metabolic instability.[68] In connection to our earlier work on chemoselective arylation,[53] we were interested in the synthesis of 1,2,3,4-tetrarylnaphthalene derivatives. In the literature, several synthetic approaches to such phenylnaphthalenes have been described.[69]

4.2.2 Results and Discussion

In recent years, chemo- and regioselective palladium catalyzed reactions of polyhalogenated arenes or heteroarenes and of bis(triflates) have been widely studied.[71] Recent reports show that several parameters influence the chemoselectivity of Suzuki-Miyaura reactions of arenes containing a bromide and a triflate group.[53] While various palladium catalyzed cross coupling reactions of naphthalene derivatives have been reported, regio- and chemoselective transformations of naphthalenes containing two or more reactive sites, such as bromide or triflate groups, have only scarcely been studied so far (Figure 24).

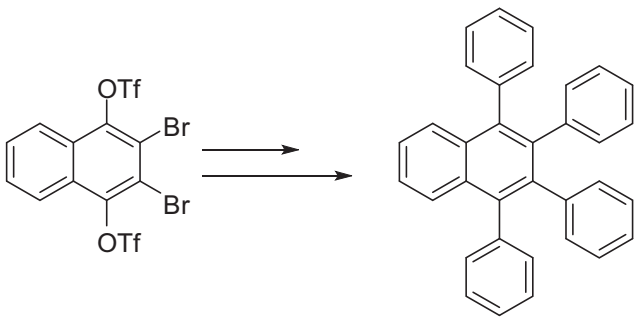
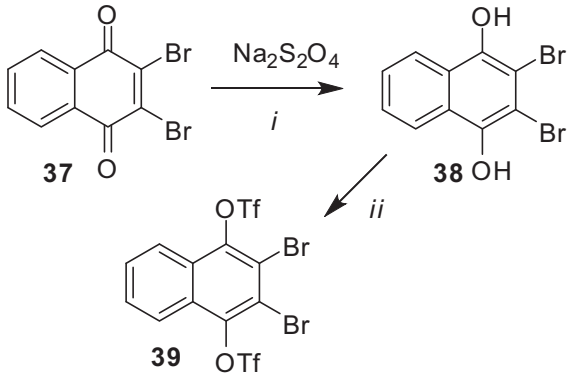


Figure 24. Our synthetic approach

2,3-Dibromonaphthalene-1,4-diol **38** was synthesized from inexpensive commercially available 2,3-dibromo-1,4-naphthaquinone **37** on treatment with aqueous sodium dithionite $Na_2S_2O_4$ in high yield (90 %).[72] Later on, **37** was transformed to give their corresponding 2,3-dibromonaphthalene-1,4-diylbis(trifluoromethanesulfonates) **39** (Scheme 21, Figure 25).



Scheme 21. Synthesis of **38** and **39**. *Conditions: i*, **38** (1.0 equiv.), $Na_2S_2O_4$ (aq), 1h; *ii,* **39** (1.0 equiv.), Tf_2O (2.2 equiv.), pyridine (2.0 equiv.), CH_2Cl_2, 20 °C, 8h

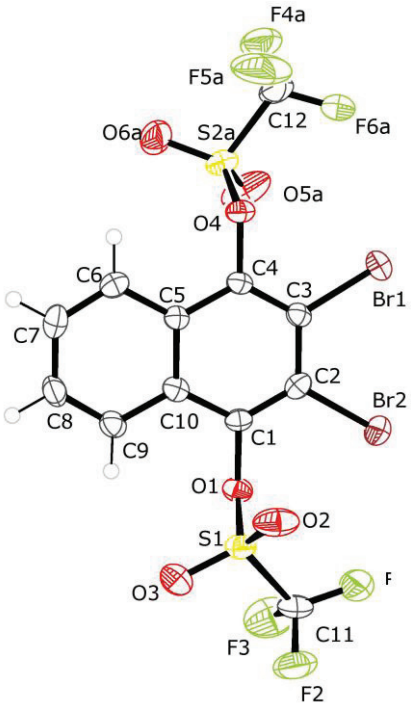
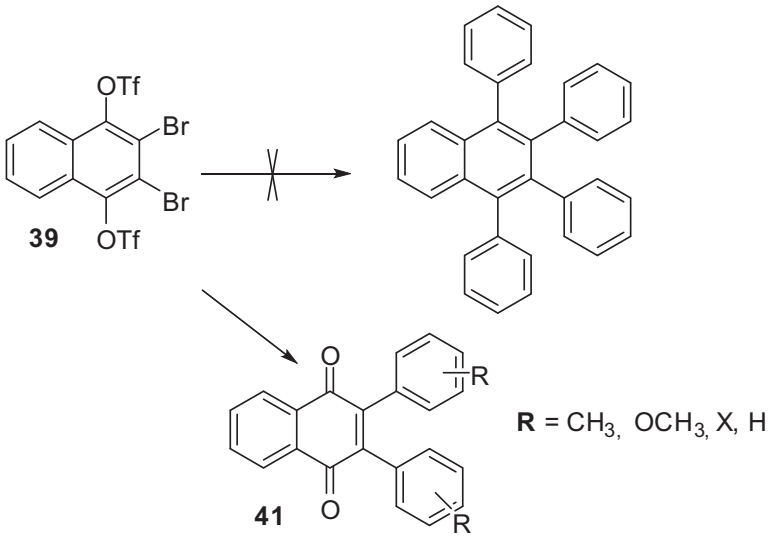


Figure 25. Ortep plot of **39**

The X-ray structure shows that both OTf groups are twisted out of plane (Figure 25). The Suzuki-Miyaura (S-M) reactions of **39** (1.0 equiv.) with arylboronic acids Ar $B(OH)_2$ **40a-e** (2.0-6.0 equiv.), using $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (2.0-8.0 equiv.), 1,4-dioxane (90-130 °C,

4-6h), were expected to give the tetra-arylated naphthalenes (Figure 24). However, the arylation occurred only at the bromine positions to give 2,3-diphenylnaphthalene-1,4-diones **41a-e** by coupling, hydrolysis of the triflate and oxidation (Scheme 22).



Scheme 22. Synthesis of **41a-g**. *Conditions: i*, **39** (1.0 equiv.), Ar $B(OH)_2$ (6.0 equiv.), $Pd(PPh_3)_4$ (10 mol %), K_3PO_4 (8.0 equiv.), dioxane, 90-140 °C, 4-8 h.

I have tried different parameters to obtain tetra-arylated products. During the optimization, several important factors were considered which may effect the carcon-carbon coupling reaction: (**i**) use of the arylboronic acids in excess; (**ii**) both electron-poor and electron-rich arylboronic acids were used; (**iii**) temperature; (**iv**) reaction time; (**v**) bases: K_3PO_4, KF, Cs_2CO_3; (**vi**) hydrolysis of the triflate was prevented by application of non-aqueous conditions; (**vii**) solvent; (**viii**) choice of palladium catalysts: $Pd(PPh_3)_4$, $Pd(OAc)_2$, $Ph(PPh_3)Cl_2$, and Pd(dba); (**vix**) mol percentage of catalyst (5-20 mol %). Unfortunately, all attemptes were unsuccessful.

Table 14. Synthesis of **41a-f**

41	Ar	% (**41**)[a]
A	2-$(MeO)C_6H_4$	70
B	4-$(MeO)C_6H_4$	74
c	4-MeC_6H_4	82
d	2-ClC_6H_4	87
e	C_6H_5	84

[a] Yields of isolated compounds

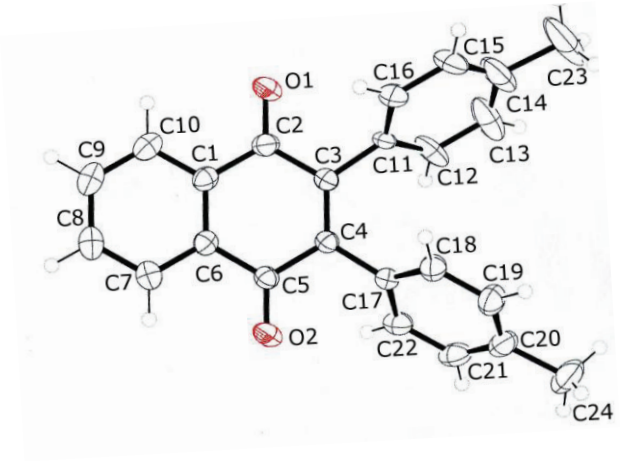
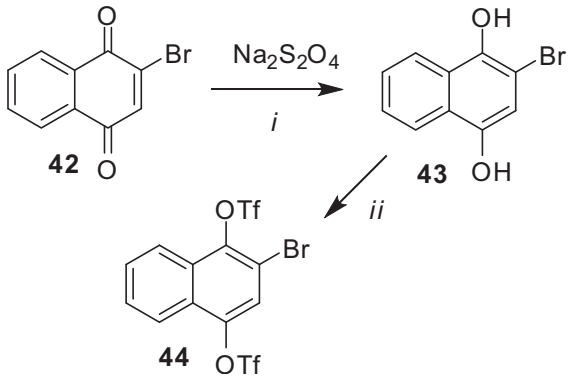


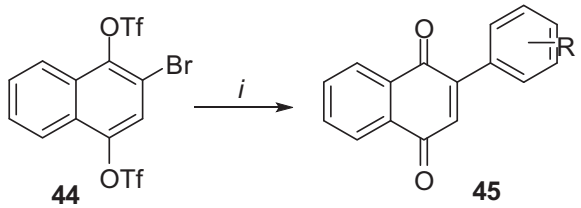
Figure 26. Ortep plot of **41c**

I have also studied 2-bromonaphthalene-1,4-diyl-bis(trifluoromethanesulfonate) **44** for Suzuki reactions (Scheme 23). The starting material **43** was prepared according to the literature.[72]



Scheme 23. Synthesis of **43**. *Conditions: i*, **41** (1.0 equiv.), $Na_2S_2O_4$ (aq), 1h; *ii,* **42** (1.0 equiv.), Tf_2O (2.2 equiv.), pyridine (2.0 equiv.), CH_2Cl_2, 20 °C, 8h

Similar results as for **41** were obtained for the Suzuki-Miyaura cross coupling reactions of **44** with arylboronic acids (4.0 equiv.). The 2-phenylnaphthalene-1,4-diones **45a,b** were formed by coupling, hydrolysis and oxidation (Scheme 24).



Scheme 24. Synthesis of **45a,b**. *Conditions: i*, **44** (1.0 equiv.), $ArB(OH)_2$ (4.0 equiv.), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (6.0 equiv.), dioxane, 90-120 °C, 4-8 h

Table 15. Synthesis of **45**

44	Ar	% (**45**)[a]
a	2-(MeO)C_6H_4	70
b	4-(Meo)C_6H_4	74

[a] Yields of isolated compounds

4.3 Conclusions

In summary, the synthesis of different benzopyranone analogues and arylnaphthaquinones via palladium-catalysed Suzuki-Miyaura coupling reactions has been discribed. Finding a simple method, benzothiophene and naphthaquinone frameworks have been synthesized which can be of considerable pharmacological relevance. In addition, the palladium-catalysed cross coupling reaction of 2,3-dibromonaphthalene-1,4-diylbis(trifluoromethanesulfonate) **39** and 2-bromonaphthalene-1,4-diyl bis(trifluoromethanesulfonate) **44** with boronic acids are not tolerable under any conditions and always resulted to give 2,3-diphenylnaphthalene-1,4-diones **41** and **45**.

Kurze Zusammenfassung der Dissertation

Diese Dissertation behandelt die Untersuchung verschiedener synthetischer Heterocyclen, insbesonders Benzodithiophene, Benzothiazole und Benzopyranone. Wir haben die Ablaeufe für diese oxidativen Reaktionen und deren cyclisierungs Muster umfassend untersucht. Darüber hinaus ist die chemoselektive Kreuzkupplung fuer Reaktionen von Brom und Triflat, unter Verwendung von Pd(0) als Katalysator, auch im Detail beschrieben. Außerdem werden die insgesammten sterischen und elektronischen Effekte chemoselektiver Kreuzkupplungsreaktionen von Benzothiophenen, Naphthalinen und Naphthochinonen vorgestellt.

Short Summary

This thesis deals with the synthetic studies of different heterocycles like benzodithiophenes, benzodithiazoles and benzopyranones. We have examined a comprehensive protocol for such oxidative reactions and their cyclization pattern. In addition, Pd(0) catalyzed chemoselective cross coupling reactions of bromine versus triflate are also described in more detail. Herein, the overall steric and electronic effects on chemoselective cross coupling reactions of benzothiophenes, naphthalenes, Naphthaquinones are presented.

Experimental Section

5 Materials and Methods

5.1 General Remarks

Reactions were carried out under inert atmosphere (Argon 4.6) in order to simultaneously exclude oxygen and water when appropriate. Pressure tubes were used to avoid condenser. Solvents for reactions were dried and distilled by standard methods or purchased from Merck, Aldrich, Acros Organics, and others whenever exclusion of water was desired. Solvents for liquid chromatography and extraction were always distilled prior to use and partly reused after fractional distillation (*n*-heptane, ethyl acetate).

5.2.1 Methods for Compound Characterization and Analysis

NMR Spectroscopy

Bruker AC 250, Bruker ARX 300, Bruker ARX 500. For NMR characterization the one-dimensional ^{1}H NMR, proton-decoupled ^{13}C NMR, and DEPT 135 spectra were collected. If necessary, other techniques (NOESY, COSY, HMQC, HMBC) were applied as well. All NMR spectra presented in this work were collected in $CDCl_3$ solution. All chemical shifts are given in ppm.

References (^{1}H NMR): TMS ($\delta = 0.00$) or residual $CHCl_3$ ($\delta = 7.26$) were taken as internal standard.

References (^{13}C NMR): TMS ($\delta = 0.0$) or residual $CHCl_3$ ($\delta = 77.0$) were taken as internal standard.

Multiplicities are given as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. More complex coupling patterns are represented by combinations of the respective symbols. For example, td indicates a triplet of doublets with the larger coupling constant associated with the first symbol (here: triplet).

Infrared Spectroscopy (IR)

Nicolet 205 FT-IR, Nicolet Protége 460 FT-IR. Peaks are given the following assignments: w = weak, m = medium, s = strong, br = broad.

Mass Spektrometry (MS)

AMD MS40, Varian MAT CH 7, MAT 731 (EI, 70 eV), Intecta AMD 402 (EI, 70 eV and CI), Finnigan MAT 95 (CI, 200 eV).

High Resolution Mass Spectrometry (HRMS)

Varian MAT 311, Intecta AMD 402.

Elemental Analysis

LECO CHNS-932, Thermoquest Flash EA 1112.

Melting Points

Micro heating table HMK 67/1825 Kuestner (Büchi Apparatus), Leitz Labolux 12 Pol with heating table Mettler FP 90. Melting points are uncorrected.

X-ray Structures

Bruker X8Apex diffractometer with CCD camera (Mo K_α radiation and graphite monochromator, $\lambda = 0.71073$ Å). The space group is determined by the XPREP program and the structures were solved via the SHELX-97 program package. Refinements were carried out according to the minimum square error method.

5.2 Chromatographic Methods

Thin Layer Chromatography (TLC)

Merck Kieselgel 60 F254 on aluminium foil from Macherey-Nagel. Detection was carried out under UV light at 254 nm and 365 nm. As colourizing reagent the following mixtures were used: 1-2/100 p-Anisaldehyde or vanillin, 10/100 glacial acetic acid, 5/100 sulphuric acid, 83-84/100 methanol.

Column Chromatography

Column chromatography was performed with Merck Silica Gel 60 or Macherey-Nagel Silica Gel 60 (0.063-0.200 mm, 70-230 mesh). The finer Merck Silica Gel 60 (0.040-0.063 mm, 230-400 mesh) was chosen when appropriate.

6 General Procedures

6.1 Synthesis of Benzo[1,2-b;5,6-b']dithiophenes and their Subsequent unsymmetrical derivatives through Suzuki-Miyaura Reaction

6.1.1 2,7-Bis(methoxycarbonyl)-3,6-dichlorobenzo[1,2-b;5,6-b']dithiophene (2):

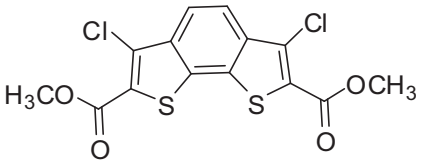
General procedure A for the synthesis of **2**. Thionyl chloride (6 ml, 80 mmol) was added portionwise to a mixture of 1,4-phenylene-diacrylic acid (2.00 g, 9.16 mmol) and of a catalytic amount of pyridine (0.2 ml). The reaction mixture was heated for 5 h at 140 °C. Upon cooling, the product solidified and the excess of thionyl chloride was removed under reduced pressure to give a greenish solid. This solid was dissolved in 50 ml of benzene and to the solution 10 ml of methanol was added. The mixture was heated at reflux for 2 h to give a crude product **2**.

6.1.2 2,7-Bis(butoxycarbonyl)-3,6-dichlorobenzo[1,2-b;5,6-b']dithiophene (3):

General procedure A for the synthesis of (**3**)**:**
Thionyl chloride (6 ml, 80 mmol) was added portionwise to a mixture of 1,4-phenylene-diacrylic acid (2.00 g, 9.16 mmol) and of a catalytic amount of pyridine (0.2 ml). The reaction mixture was heated for 5 h at 140 °C. Upon cooling, the product solidified and the excess of thionyl chloride was removed under reduced pressure to give a greenish solid. This solid was dissolved in 50 ml of benzene and to the solution 10 ml of *n*-butanol was added. The mixture was heated at reflux for 2 h to give the crude product of butyl ester **3**. The residue was purified by flash column chromatography (silica gel, heptanes / ethyl acetate = 9:1). The spectroscopic data of compound **3** were identical with those reported in the literature.

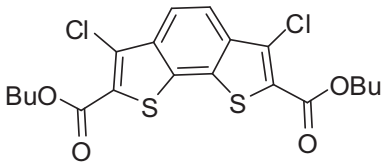
General procedure B for Suzuki–Miyaura reactions: A 1,4-dioxane solution (5 ml) of K_3PO_4 (2.0 equiv.), $Pd(PPh_3)_4$ (5 mol%) and arylboronic acids (1.2 equiv.) was stirred at 110-120 °C for 4 h. After cooling to 20 °C, H_2O was added. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (15 x 3 ml). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (flash silica gel, heptanes / dichloromethane = 1:1).

2,7-Bis(methoxycarbonyl)-3,6-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene (2); Starting with **1**



(2.00 g, 9.16 mmol), $SOCl_2$ (6 ml, 80 mmol), pyridine (0.2 ml), following the general procedure A, **2** was isolated as a yellow crystalline solid (1.94 g, 57 %), mp. 147-149 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 6H, OCH_3), 7.95 (s, 2H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.7 (OCH_3), 121.3 (CH), 126.2, 128.5, 133.1, 137.0, 160.7 (C); IR (KBr): ν = 3434, 2960, 2842, 1727 (s), 1650, 1643, 1633, 6113, 1509, 1434 (m), 1322, 1306, 1250, 1238, 1010, 1090, 1038 (s), 973, 940, 910, 817, 759, 736, 611 (m) cm^{-1}.; GC-MS (EI, 70 eV): *m/z* (%) = 374 (M^+, 2 x ^{35}Cl, 100), 343 (89), 315 (43), 256 (29); HRMS (EI, 70 eV): calcd for $C_{14}H_8Cl_2O_4S_2$ (2 x ^{35}Cl) $[M]^+$: 373.9276; found: 373.9274.

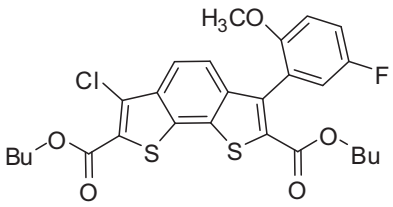
2,7-Bis(butoxycarbonyl)-3,6-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene (3): Starting with **1**



(2.00 g, 9.16 mmol), $SOCl_2$ (6 ml, 80 mmol) and pyridine (0.2 ml), following the general procedure A, **3** was obtained as a yellow crystalline solid (2.73 g, 65 %), mp. 95-97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.3 Hz, 6H, CH_3), 1.39-1.46 (m, 4H, CH_2), 1.68-1.77 (m, 4H, CH_2), 4.34 (t, J = 6.5 Hz, 4H, OCH_2), 7.91 (s, 2H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (CH_3), 19.2, 30.6 (CH_2), 65.9 (OCH_2), 121.2 (CH), 126.2, 128.2, 132.9, 137.1, 160.8 (C); IR (KBr): ν = 3418, 2956, 2931, 2872 (s), 2736 (w) 1726, 1708, 1510, 1494 (s), 1476, 1406, 1380, 1301 (m), 1235, 1211, 1095, 1082, 1060, 1045, 1017, 964 (s), 932, 850, 804, 756 (m), 756, 734, 715 (s) cm^{-1}.; GC-MS (EI, 70 eV): *m/z* (%) = 458 (M^+, 2 x ^{35}Cl, 100), 346 (78), 329 (41), 257 (33); HRMS (EI, 70 eV): calcd for $C_{20}H_{20}Cl_2O_4S_2$ (2 x ^{35}Cl) $[M]^+$: 458.0280; found: 458.0171.

6.1.3 Synthesis of unsymmetrical Benzo[1,2-*b*;5,6-*b*']dithiophenes derivatives (5a-c)

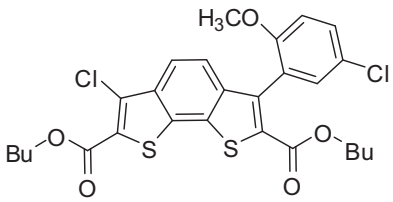
2,7-Bis(butoxycarbonyl)-3-(5-fluoro-2-methoxyphenyl)-6-chlorobenzo[1,2-*b*;5,6-*b*']



dithiophene (5a): Starting with **3** (200 mg, 0.43 mmol), 5-fluoro-2-methoxyphenylboronic acid **4a** (1.2 equiv. 88 mg, 0.53 mmol), $Pd(PPh_3)_4$ (25 mg, 5 mol %), K_3PO_4 (2.0 equiv., 185 mg, 0.85 mmol), and 1,4-dioxane (5 ml), following the general procedure B, **5a** was isolated as a white solid (195 mg, 82 %), mp. 108-110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (t, J = 7.3 Hz, 3H, CH_3), 0.92 (t, J = 7.3 Hz, 3H, CH_3), 1.11-1.38 (m, 2H), 1.40-1.48 (m, 4H), 1.66-1.74 (m, 2H), 3.61 (s, 3H, OCH_3), 4.10 (t, J = 6.3 Hz, 2H), 4.31 (t, J = 6.3 Hz, 2H), 6.86-6.95 (m, 2H), 7.04-7.10 (td, J = 8.1, 3.1 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -

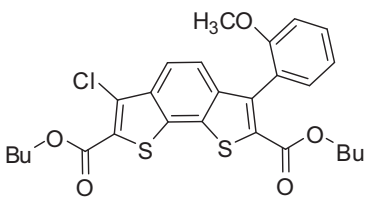
124.0. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.3, 13.7 (CH_3), 19.0, 19.2 (CH_2), 30.5, 30.6 (CH_2), 56.1 (OCH_3), 65.4, 65.7 (OCH_2), 111.9 (d, $J_{F,C}$ = 8.3 Hz, CH), 115.9 (d, $J_{F,C}$ = 22.5 Hz, CH), 117.9 (d, $J_{F,C}$ = 23.6 Hz, CH), 120.5, 122.5 (CH), 124.6 (d, $J_{F,C}$ = 8.2 Hz, CH), 128.2, 130.5, 133.0, 134.2, 136.3, 139.2, 139.8, 153.5 (C), 156.1 (d, $J_{F,C}$ = 237.7 Hz, CF), 161.0, 162.0; IR (KBr): ν = 2958, 2932, 1872, 2836, 1718, 1697 (s), 1493, 1463, 1414, 1334, 1311 (m), 1273, 1255, 1227, 1206, 1180, 1155, 1125, 1085, 1069, 1029 (s), 992, 940, 907, 877 (m), 807, 757, 729 (s) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%) = 548 (M^+, ^{35}Cl, 97), 475 (48), 461 (41), 447 (13) 405 (32), 391 (22), 381 (34), 359 (31), 325 (21); HRMS (EI, 70 eV): calcd for $C_{27}H_{26}ClFO_5S_2$ (^{35}Cl) $[M]^+$: 548.0889; found: 548.0890.

2,7-Bis(butoxycarbonyl)-3-(5-chloro-2-methoxyphenyl)-6-chlorobenzo[1,2-*b*;5,6-*b*']



dithiophene (5b): Starting with **3** (200 mg, 0.43 mmol), 5-chloro-2-methoxyphenylboronic acid **4b** (1.2 equiv., 96 mg, 0.51 mmol), $Pd(PPh_3)_4$ (25 mg, 5 mol %), K_3PO_4 (2.0 equiv. 185 mg, 0.85 mmol), and 1,4-dioxane (5 ml), following the general procedure B, **5b** was isolated as a light green solid (211 mg, 87 %), mp. 77-99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.3 Hz, 3H, CH_3), 0.93 (t, J = 7.3 Hz, 3H, CH_3), 1.14-1.21 (m, 2H), 1.38-1.42 (m, 4H), 1.44-1.48 (m, 2H), 3.60 (s, 3H, OCH_3), 4.13 (t, J = 6.5 Hz, 2H), 4.32 (t, J = 6.5 Hz, 2H), 6.88 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 2.6 Hz, 1H), 7.30-7.36 (m, 2H), 7.73 (d, J = 8.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7, 13.8 (CH_3), 19.1, 19.2 (CH_2), 30.5, 30.6 (CH_2), 55.8 (OCH_3), 65.5, 65.7 (OCH_2), 112.1, 120.5, 122.5 (CH), 124.9, 125.3, 125.4, 128.2 (C), 129.6, 130.6 (CH), 130.7, 133.0, 134.2, 136.3, 138.9, 139.8, 155.9, 161.0, 162.0 (C); IR (KBr): ν = 2974, 2961, 2930, 2911, 2825, 1721, 1686 (s), 1675, 1663, 1582, 1561 (w), 1481, 1479, 1461, 1411, 1403, 1338, 1334 (m), 1289, 1261, 1251, 1182, 1134, 1127, 1025 (s), 802, 769, 684, 667 (s) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%) = 564 (M^+, ^{35}Cl, 100), 491 (24), 477 (36), 463 (11), 421 (31), 381 (37) 325 (24); HRMS (EI, 70 eV): calcd for $C_{27}H_{26}Cl_2O_5S_2$ (^{35}Cl) $[M]^+$: 564.0593; found: 564.0594.

2,7-Bis(butoxycarbonyl)-3-(2-methoxyphenyl)-6-chlorobenzo[1,2-*b*;5,6-*b*']dithiophene



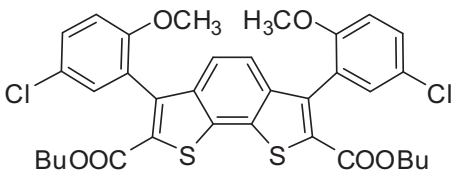
(5c): Starting with **3** (200 mg, 0.43 mmol), 2-methoxyphenylboronic acid **4c** (1.2 equiv., 78 mg, 0.52 mmol), $Pd(PPh_3)_4$ (25 mg, 5 mol%), K_3PO_4 (2.0 equiv. 185 mg, 0.85 mmol), and 1,4-dioxane (5 ml), following the general procedure B, **5c** was isolated as a light green highly viscous oil (180 mg, 80 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (t, J = 7.3 Hz, 3H, CH_3), 0.92 (t, J = 7.3 Hz, 3H, CH_3), 1.11-

1.20 (m, 2H), 1.40-1.46 (m, 4H), 1.66-1.74 (m, 2H), 3.61 (s, 3H, OCH_3), 4.10 (t, J = 6.3 Hz, 2H), 4.31 (t, J = 6.5 Hz, 2H), 6.95 (d, J = 8.3 Hz, 1H), 7.01 (td, J = 7.4, 1.2 Hz, 1H), 7.17 (dd, J = 7.4, 1.7 Hz, 1H), 7.34-7.39 (m, 2H), 7.71 (d, J = 8.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7, 13.8 (CH_3), 19.1, 19.2 (CH_2), 30.5, 30.6 (CH_2), 55.8 (OCH_3), 65.5, 65.7 (OCH_2), 110.9, 120.2, 120.5 (CH), 123.2, 125.2 (CH), 128.2 (C), 129.9 (CH), 130.1 (C), 130.9 (CH), 133.0, 134.1, 136.1, 140.2, 140.7, 157.1, 161.0, 162.2; IR (KBr): ν = 2957, 2930, 2872, 1716, 1698 (s), 1547, 1531, 1501, 1486, 1462, 1413, 1337, 1311 (m), 1274, 1228, 1175, 1123, 1114, 1071 (s) 906, 875, 727 (s) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%) = 530 (M^+, ^{35}Cl, 100), 457 (49), 443 (33), 381 (37), 325 (21); HRMS (EI, 70 eV): calcd for $C_{27}H_{27}ClO_5S_2$ (^{35}Cl) $[M]^+$: 530.0982; found: 530.0981.

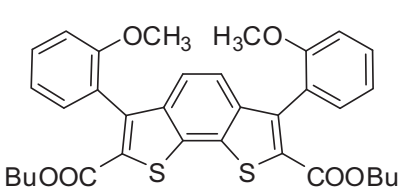
6.1.4 Synthesis of symmetrical Benzo[1,2-*b*;5,6-*b*']dithiophenes derivatives (6)

General procedure C for Suzuki–Miyaura reactions: 1,4-dioxane solution (5 ml) of $Pd(PPh_3)_4$ (5 mol%) and SPhos (10 mol%) was stirrered for 10 minutes. Adding substrate (1.0 equiv.), K_3PO_4 (4.0 equiv.), arylboronic acids (2.5 equiv.) was stirred at 110-130 °C for 4 h. After cooling to 20 °C, H_2O was added. The organic and aqueous layers were separated and the latter was extracted with CH_2Cl_2 (15 x 3 ml). The combined organic layers were dried passing through (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (flash silica gel, heptanes / dichloromethane = 1:1) to obtain compound **6b,c**.

2,7-Bis(butoxycarbonyl)-3,6-bis(5-chloro-2-methoxyphenyl)benzo[1,2-*b*;5,6-*b*'] dithiophene (6b): Starting with **3** (200 mg, 0.43 mmol), 5-chloro-2-methoxyphenylboronic acid **4b** (2.5 equiv., 220 mg,), $Pd(PPh_3)_4$ (25 mg, 5 mol %), SPhos (20 mg, 10 mol%), K_3PO_4 (4.0 equiv. 370 mg), and 1,4-dioxane (5 ml), following the general procedure C, **6b** was isolated as a light green solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, J = 7.3 Hz, 6H, CH_3), 1.15-1.22 (m, 4H, CH_2), 1.14-1.49 (m, 4H), 1.38-1.42 (m, 4H), 3.58 (s, 6H, OCH_3), 4.12 (t, J = 6.4 Hz, 4H), 6.85 (dd, J = 8.8, 2.8 Hz, 2H), 7.13 (d, J = 2.5 Hz, 2H), 7.21 (s, 2H), 7.27-7.31 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (CH_3), 19.1 (CH_2), 28.7 (CH_2), 55.8 (OCH_3), 65.4 (OCH_2), 112.1, 121.7, 129.4, 130.7 (CH), 125.4, 128.2, 130.7, 133.0, 134.4, 139.1, 155.9, 162.2 (C); HRMS (EI, 70 eV): calcd for $C_{34}H_{32}Cl_2O_6S_2$ (^{35}Cl) $[M]^+$: 670.6513; found: 670.6509.



2,7-Bis(butoxycarbonyl)-36-bis(2-methoxyphenyl)benzo[1,2-*b*;5,6-*b*']dithiophene Starting



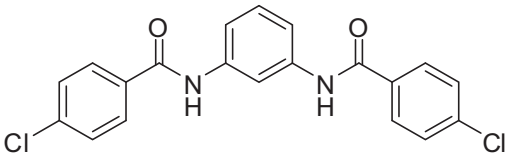
with **3** (200 mg, 0.43 mmol), 5-chloro-2-methoxyphenylboronic acid **4b** (2.5 equiv., 220 mg), $Pd(PPh_3)_4$ (25 mg, 5 mol %), SPhos (20 mg, 10 mol %), K_3PO_4 (4.0 equiv., 370 mg), and 1,4-dioxane (5 ml), following the general procedure C, **6c** was isolated as a crystalline solid. mp. 108-110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, J = 7.4 Hz, 6H, CH_3), 1.15-1.24 (m, 4H, CH_2), 1.14-1.51 (m, 4H), 1.38-1.42 (m, 4H), 3.55 (s, 6H, OCH_3), 4.13 (t, J = 6.5 Hz, 4H), 6.63-6.67 (m, 6H), 7.12 (dd, J = 8.4, 2.5 Hz, 2H), 7.29 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (CH_3), 19.1 (CH_2), 28.7 (CH_2), 55.8 (OCH_3), 65.4 (OCH_2), 112.1, 121.7, 128.6, 129.4, 130.7 (CH), 125.4, 130.7, 131.0 133.0, 134.4, 139.1, 155.1, 162.3 (C); HRMS (EI, 70 eV): calcd for $C_{34}H_{34}O_6S_2$ (^{35}Cl) $[M]^+$: 602.1764; found: 602.1764.

6.2 Synthesis of diarylatedbenzodithiazol derivatives

6.2.1 General procedure D for the synthesis of (9a-f).

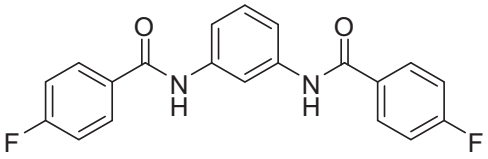
To a cold suspension of 1,3-benzenediamine **7** (1.0 equiv., 18.5 mmol) and NEt_3 (5.1 ml, 37 mmol, 2.0 equiv.) in dry dichloromethane (50ml), dichloromethane solution (10 ml) of benzoyl chloride **8a-g** (2.0 equiv.) was added drop wise. The reaction mixture was stirred at 20 °C for 12 h and subsequently poured into 100 ml of water. The organic layer was separated, washed with aqueous solution of $NaHCO_3$ and with water (30 ml), and dried through Mg_2SO_4. The solution was later concentrated under reduced pressure.

N,N'-(1,3-Phenylene)bis(4-chlorobenzamide) (9a); Starting with **7** (2.00 g, 18.5 mmol, 1.0



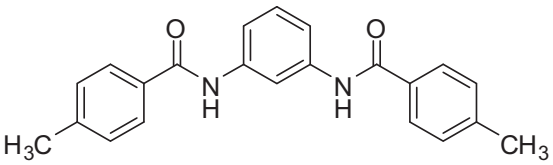
equiv.), triethylamine (5.1 ml, 37 mmol, 2.0 equiv.), 4-chlorobenzoyl chloride (4.7 ml, 37 mmol, 2.0 equiv.), dichloromethane (25 ml), following the general procedure D, **9a** was isolated as a white solid (3.91 g, 55 %); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.34 (d, J = 3.6 Hz, 1H), 7.51 (dd, J = 7.8, 2.0 Hz, 2H), 7.59-7.64 (m, 4H), 7.99-8.03 (m, 4H), 8.33 (t, 1H), 10.8 (s, 2H, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 112.9, 116.2, 128.3, 128.6, 129.6 (CH), 133.5, 136.3, 139.1, 164.4 (CO); GC-MS (EI, 70 eV): *m/z* (%) = 384 (M^+, 100), 139 (89), 111 (34), 75 (23); HRMS (EI, 70 eV): calcd for $C_{20}H_{14}Cl_2N_2O_2$ (^{35}Cl) $[M]^+$: 385.0505; found: 385.0505.

N,N'-(1,3-Phenylene)bis(4-fluorobenzamide) 9b; Starting with **7** (2.00 g, 18.5 mmol, 1.0 equiv.), triethylamine (5.1 ml, 37 mmol, 2.0 equiv.), 4-fluorobenzoyl chloride (5.1 ml, 37 mmol, 2.0 equiv.), dichloromethane (25 ml), following the general procedure D, **9b** was isolated (3.62 g, 60 %);



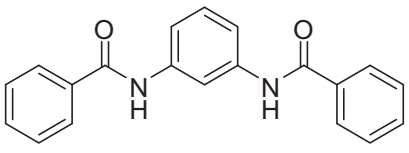
^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.29-7.34 (m, 5H), 7.51 (dd, J = 8.4, 2.6 Hz, 2H), 7.99-8.11 (m, 4H), 8.39 (t, 1H), 10.3 (s, 2H, NH) ; ^{19}F NMR (282.4 MHz, DMSO): δ = -108.8; ^{13}C NMR (75.5 MHz, DMSO): δ = 112.9 (CH), 115.1 (d, $J_{F,C}$ = 23.7 Hz, CH), 116.1, 128.5 (CH), 130.3 (d, $J_{F,C}$ = 9.8 Hz, CH) 131.3 (d, $J_{F,C}$ = 2.6 Hz, C), 139.2 (C), 164.3 (d, $J_{F,C}$ =264 Hz, CF), 166.0 (CO); GC-MS (EI, 70 eV): *m/z* (%) = 352 (M$^+$,100), 139 (89), 111 (34), 75 (23); HRMS (EI, 70 eV): calcd for $C_{20}H_{14}F_2N_2O_2$ [M]$^+$: 352.2351; found: 352.2349.

N,N'-(1,3-Phenylene)bis(4-methylbenzamide); Starting with **7** (2.00 g, 18.5 mmol, 1.0 equiv.), triethylamine (5.1 ml, 37 mmol, 2.0 equiv.), 4-methylbenzoyl chloride (4.8 mg, 37 mmol, 2.0 equiv.), dichloromethane (25 ml), following the general procedure D, **9c** was isolated (3.5 g, 55 %). mp. 257-259 °C.



^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 3.37 (s, 6H, CH$_3$), 7.29-7.37 (m, 5H), 7.51 (dd, J = 7.9, 1.8 Hz, 2H), 7.92 (d, J = 8.2 Hz, 4H), 8.34 (t, J = 3.2 Hz, 1H), 10.2 (s, 2H, NH); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 20.7 (2-CH$_3$), 112.9, 115.9, 127.7, 128.4, 128.8 (CH), 132.0, 139.3, 141.5, 165.3 (CO); GC-MS (EI, 70 eV): *m/z* (%) = 344 (M$^+$, 67), 119 (99), 91 (44), 65 (13); HRMS (EI, 70 eV): calcd for $C_{22}H_{20}N_2O_2$ [M]$^+$: 344.1519; found: 344.1522.

N,N'-(1,3-Phenylene)bis(phenylbenzamide) 9d; Starting with **7** (2.00 g, 18.5 mmol, 1.0 equiv.), triethylamine (5.1 ml, 37 mmol, 2.0 equiv.), benzoyl chloride (4.8 ml, 37 mmol, 2.0 equiv.), dichloromethane (25 ml), following the general procedure D, **9d** was isolated (3.26 g, 57 %).



^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.37 (d, J = 3.2 Hz, 1H), 7.54-7.65 (m, 8H), 8.01-8.05 (m, 4H), 8.39 (t, 1H), 10.36 (s, 2H, NH); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 112.9, 116.0, 127.6, 128.3, 128.5, 131.4 (CH), 134.9, 139.3, 165.4 (CO); GC-MS (EI, 70 eV): *m/z* (%) = 316 (M$^+$, 87), 119 (99), 91 (44), 65 (13); HRMS (EI, 70 eV): calcd for $C_{20}H_{16}N_2O_2$ [M]$^+$: 316.3501; found: 316.3502.

N,N'-(1,3-Phenylene)dipropionamide (9e) Starting with **7** (2.00 g, 18.5 mmol, 1.0 equiv.), triethylamine (5.1 ml, 37 mmol, 2.0 equiv.), propanoyl chloride (1.8 ml, 37 mmol, 2.0 equiv.), dichloromethane (25 ml), following the general procedure D, **9e** was isolated (1.80 g, 60 %). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 1.09 (t, J = 7.6 Hz, 6H, CH_3), 2.32 (q, 4H, CH_2), 7.18 (t, J = 1.6 Hz, 1H), 7.28 (d, J = 6.3 Hz, 2H), 7.93 (s, 1H), 9.84 (s, 2H, NH); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 9.6 (CH_3), 29.4 (CH_2), 109.9, 113.7, 128.6 (CH), 139.5, 171.8 (CO); GC-MS (EI, 70 eV): *m/z* (%) = 221 (M^+, 64), 164 (49), 108 (94), 80 (17); HRMS (EI, 70 eV): calcd for $C_{12}H_{16}N_2O_2$ $[M]^+$: 221.1284; found: 221.1282.

N,N'-(1,3-Phenylene)bis(2,2-dimethylpropanamide) (9f) Starting with **7** (2.00 g, 18.5 mmol), triethylamine (5.1 ml, 37 mmol, 2.0 equiv.), 2,2-dimethylpropanoyl chloride (4.5 ml, 37 mmol, 2 equiv.), dichloromethane (25 ml), following the general procedure D, **9f** was isolated (2.87 mg, 54 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (s, 18 H, CH_3), 7.13 (t, J = 1.8 Hz, 1H), 7.20-7.23 (m, 3H), 7.36 (s, 2H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 27.5 (CH_3), 39.6 (C), 111.4, 115.5, 129.3 (CH), 138.5, 176.8 (CO); GC-MS (EI, 70 eV): *m/z* (%) = 276 (M^+, 74), 192 (43), 108 (15), 57 (88); HRMS (EI, 70 eV): calcd for $C_{16}H_{24}N_2O_2$ $[M]^+$: 277.1910; found: 277.1908.

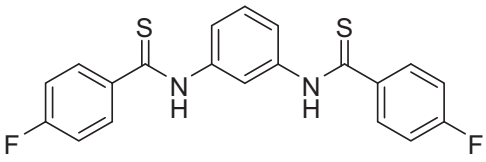
6.2.2 General procedure E for the synthesis of (10a-f).

The amide starting material (0.5 mmol), Lawesson's reagent (0.5 mmol), were refluxed in toluene (30 ml) for one hour. The reaction mixture was continuously stirred. Upon cooling, toluene solvent was evaporated using rotary evaporator. The crude mixture was purified by silica gel column chromatography using (dichloromethane / hexane, 1:1) to obtain the deep yellow colored compounds **10a-f** in high yields 76-82 %.

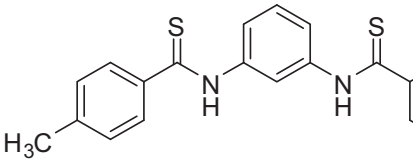
N,N'-(1,3-Phenylene)bis(4-chlorobenzothioamide) (10a) Starting with **9a** (1.00 g, 1.0 equiv.), Lawesson's reagent (0.80 g, 1.0 equiv.), toluene (25 ml), following the general procedure E, **10a** was isolated as a yellow solid (1.23 g, 95 %). mp. 227-229 °C; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.52-7.58 (m, 5H), 7.71 (d, J = 7.2 Hz, 2H), 7.88 (d, 8.4 Hz, 4H), 8.40 (s, 1H), 11.9 (s, 2H, NH), ; ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 119.6, 122.1, 128.0, 128.5, 129.2 (CH), 135.5, 139.9, 141.0, 196.13 (CS); GC-MS (EI, 70 eV): *m/z* (%) = 417 (M^+, 87), 139 (89), 111

(34), 75 (23); HRMS (EI, 70 eV): calcd for $C_{20}H_{14}Cl_2N_2S_2$ (^{35}Cl) $[M]^+$: 417.6413; found: 417.6411.

N,N'-(1,3-Phenylene)bis(4-flourobenzothioamide) (10b) Starting with **9b** (1.00g, 1.0 equiv.), Lawesson's reagent (0.80 g, 1.0 equiv.), toluene (25 ml), following the general procedure E, **10b** was isolated 1.18 g, 93 %). mp. 235-237 °C; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.34-7.40 (m, 4H), 7.53-7.77 (m, 3H), 7.99 (dd, J = 8.4, 2.7 Hz, 4H), 8.43 (s, 1H), 11.91 (s, 2H, NH); ^{19}F NMR (282.4 MHz, DMSO-d_6): δ = -109.9; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 114.8 (d, $J_{F,C}$ = 21.2 Hz, CH), 121.1 (d, $J_{F,C}$ = 4.2 Hz, C), 128.5, 129.9, 130.1 (CH), 138.8 (d, $J_{F,C}$ = 203.2 Hz, C), 140.1, 196.2 (CS); GC-MS (EI, 70 eV): *m/z* (%) = 384 (M^+, 59), 351 (23), 244 (34), 230 (66), 139 (96); HRMS (EI, 70 eV): calcd for $C_{20}H_{14}F_2N_2S_2$ $[M]^+$: 384.0561; found: 384.0558.



N,N'-(1,3-Phenylene)bis(4-methylbenzothioamide) (10c) Starting with **9c** (1.00g, 1.0 equiv.), Lawesson's reagent (0.80 g, 1.0 equiv.), toluene (25 ml), following the general procedure E, **10c** was isolated (1.34 g, (92 %); ^1H NMR (300 MHz, DMSO-d_6): δ = 2.39 (s, 6H, CH_3), 7.29 (d, J = 8.1 Hz, 4H), 7.49 (t, 3H), 7.69 (d, J = 7.6 Hz, 4H), 8.35 (s, 1H), 11.74 (s, 2H, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 20.8 (CH_3), 120.1, 122.2, 127.5, 128.3, 128.5 (CH), 139.4, 140.1, 140.9, 197.4 (CS); GC-MS (EI, 70 eV): *m/z* (%) = 376 (M^+, 76), 343 (67), 240 (43), 226 (93), 135 (70); HRMS (EI, 70 eV): calcd for $C_{22}H_{20}N_2S_2$ $[M]^+$: 377.1140; found: 377.1138.



N,N'-(1,3-Phenylene)bis(benzothioamide) (10d) Starting with **9d** (1.00g, 1.0 equiv.), Lawesson's reagent (0.80 g, 1.0 equiv.), toluene (25 ml), following the general procedure E, **10d** was isolated as a coloured solid (1.17 g, (94 %); mp. 214-216 °C. ^1H NMR (300 MHz, DMSO-d_6): δ = 7.49-7.58 (m, 7H), 7.76 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 7.2 Hz, 4H), 8.47 (s, 1H), 11.89 (s, 2H, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 119.7, 122.1, 127.4, 127.8, 128.4, 130.8 (CH), 140.1, 142.5 (C), 197.7 (CS); GC-MS (EI, 70 eV): *m/z* (%) = 348 (M^+, 97), 315 (49), 226 (40), 212 (87) , 121 (99); HRMS (EI, 70 eV): calcd for $C_{20}H_{16}N_2S_2$ $[M]^+$: 348.0749; found: 348.0744.

N,N'-(1,3-Phenylene)dipropanethioamide (10e) Starting with **9e** (1.00g, 1.0 equiv.), Lawesson's reagent (0.80 g, 1.0 equiv.), toluene (25 ml), following the general procedure E, **10e** was isolated (1.32 g, (90 %). mp. 158-160 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.28 (t, J = 7.4 Hz, 6H, CH_3), 2.78 (q, 4H, CH_2), 7.20 (t, J = 2.2 Hz, 1H), 7.34-7.8 (m, J = 7.1 Hz, 3H), 11.57 (s, 2H, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 14.1 (CH_3), 39.4 (CH_2), 120.8, 128.3, 139.5 (CH), 161.1 (C), 205.5 (CS); GC-MS (EI, 70 eV): *m/z* (%) = 252 (M^+, 84), 164 (57); HRMS (EI, 70 eV): calcd for $C_{12}H_{16}N_2S_2$ $[M]^+$: 252.3952; found: 252.3949.

N,N'-(1,3-Phenylene)bis(2,2-dimethylpropanethioamide) (10f) Starting with **9f** (1.00g, 1.0 equiv.), Lawesson's reagent (0.80 g, 1.0 equiv.), toluene (25 ml), following the general procedure E, **10f** was isolated (1.2 g, (91 %); mp. 148-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 18H, CH_3), 7.36 (t, J = 1.3 Hz, 3H), 7.80 (s, 1H), ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.3 (CH_3), 45.5 (C), 121.9, 123.8, 129.4 (CH), 139.5, 214.1 (CS); GC-MS (EI, 70 eV): *m/z* (%) = 308 (M^+, 64), 251 (23), 192 (95); HRMS (EI, 70 eV): calcd for $C_{16}H_{24}N_2S_2$ $[M]^+$: 308.5282; found: 308.5284.

6.2.3 Preparation of *N*-Benzyl-DABCO Tribromide.

To a stirred solution of DABCO (0.30 g, 1.0 equiv.) in dioxane (5 ml), a solution of benzyl bromide (0.22 g, 1.0 equiv.) in dioxane (5 ml) was added slowly for about 20 minutes. Then, a solution of bromine (0.12 g, 1.0 equiv.) in dioxane (5 ml) was cautiously added under vigorous stirring. After cooling the solution, the resulting orange crystals were filtered and dried. (1.72 g, 84 %).

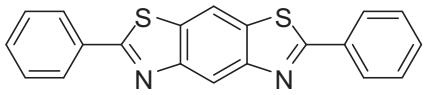
6.2.4 General Procedure F for the oxidative cyclization of thiobenzanilides.

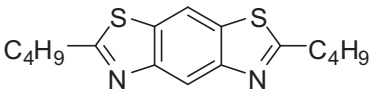
To a stirred solution of thiobenzanilide (1.0 equiv.) in CH_2Cl_2 / CCl_4 (1:1, 10 ml), *N*-Benzyl DABCO tribromide (2.0 equiv.) was added. The reaction mixture was stirred for 30 to 90 min at 20 °C. The solvent was removed under reduced pressure and the residue was subjected to column chromatography (CH_2Cl_2 / hexane, 1:1) to obtain the cyclised products **11a-f**.

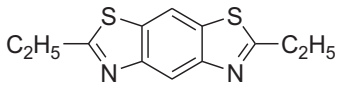
1,4-Bis[4-(Chlorophenyl]benzo[1,2-d:4,5-d]bisdithiazole (11a); Starting with **10a** (200 mg, 1.0 equiv.), *N*-Benzyl DABCO tribromide (450 mg, 2.0 equiv.), dichloromethane/carbon tetrachloride (1:1, 10 ml), following the general procedure F, **11a** was isolated as white solid (113 mg, 78 %); mp. 284-285 °C.; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.34 (d, J = 8.2 Hz, 4H), 7.87 (d, J = 8.3 Hz, 4H), 8.02 (s, 1H), 8.10 (s, 1H); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 119.4, 127.9, 128.5, 129.2 (CH), 131.3, 134.4, 141.2, 146.3, 169.3 (C); GC-MS (EI, 70 eV): *m/z* (%) = 413 (M^+, 100), 275 (18), 240 (23), 206 (12), 138 (33); HRMS (EI, 70 eV): calcd for $C_{20}H_{10}Cl_2N_2S_2$ $[M]^+$: 411.9657; found: 411.9661.

1,4-Bis[4-(Flourophenyl]benzo[1,2-d:4,5-d]bisdithiazole (11b); Starting with **10b** (200 mg, 1.0 equiv.), *N*-Benzyl DABCO tribromide (450 mg, 2.0 equiv.), dichloromethane/carbon tetrachloride (1:1, 10 ml), following the general procedure F, **11b** was isolated as yellowish solid (118 mg, 65 %). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.34 -7.40 (m, 4H), 7.53-7.77 (m, 3H), 7.99 (dd, J = 8.4, 2.7 Hz, 4H), 8.43 (s, 1H); ^{19}F NMR (282.4 MHz, DMSO-d$_6$): δ = -108.7; ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 115.2 (d, $J_{F,C}$ = 22.1 Hz, CH), 118.8 (CH), 119.3 (CH), 128. 4 (d, $J_{F,C}$ = 8.3 Hz, CH), 126.6, 130.6, 152.1 (C), 163 (d, $J_{F,C}$ = 203.7 Hz, CF); GC-MS (EI, 70 eV): *m/z* (%) = 380 (M^+,100), 259 (23), 190 (14); HRMS (EI, 70 eV): calcd for $C_{20}H_{10}F_2N_2S_2$ $[M]^+$: 381.0326; found: 381.0322.

1,4-Bis[4-(Methyl-phenyl]benzo[1,2-d:4,5-d]bisdithiazole (11c); Starting with **10c** (200 mg, 1.0 equiv.), *N*-Benzyl DABCO tribromide (450, 2.0 equiv.), dichloromethane/carbon tetrachloride (1:1, 10 ml), following the general procedure F, **11c** was isolated as a yellow solid (138 mg, 70 %); mp. 221-223 °C; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.38 (s, 6H, CH_3), 7.31 (d, J = 8.1 Hz, 4H), 7.98 (d, J = 8.4 Hz, 6H); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 26.3 (CH_3), 124.8, 125.1, 132.2, 134.8 (CH), 135.3, 141.4, 146.6, 158.6, 172.2 (C); GC-MS (EI, 70 eV): *m/z* (%) = 372 (M^+, 100), 186 (16), 138 (43); HRMS (EI, 70 eV): calcd for $C_{22}H_{16}N_2S_2$ $[M]^+$: 372.0749; found: 372.0751.

1,4-Bis[4-(Phenyl]benzo[1,2-d:4,5-d]bisdithiazole (11d); Starting with (200 mg, 1.0 equiv.),  *N*-Benzyl DABCO tribromide (450 mg, 2.0 equiv.), dichloromethane/carbon tetrachloride (1:1, 10 ml), following the general procedure F, **11d** was isolated (140 mg, 70 %). mp. 238-240 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.28-7.30 (m, 6H), 7.65-7.98 (m, 6H); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 116.1, 125.5, 127.6, 128.3, 133.5 (CH), 131.5, 134.9, 139.3, 165.5 (C); GC-MS (EI, 70 eV): *m/z* (%) = 344 (M^+, 98), 267 (56), 189 (34); HRMS (EI, 70 eV): calcd for $C_{20}H_{12}N_2S_2$ $[M]^+$: 344.2431; found: 344.2427.

1,4-Bis[tert.butyl]benzo[1,2-d:4,5-d]dithiazole (11e); Starting with **10e** (200 mg, 1.0  equiv.), *N*-Benzyl DABCO tribromide (450 mg, 2.0 equiv.), dichloromethane/carbon tetrachloride (1:1, 10 ml), following the general procedure F, **11e** was isolated (128 mg, 78 %). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 1.31 (s, 18H, CH_3), 7.83 (s, 1H), 8.96 (s, 1H); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 26.6 (CH_3), 40.2 (C), 116.7, 132.3 (CH), 135.6, 138.3, 176.7 (C); GC-MS (EI, 70 eV): *m/z* (%) = 304 (M^+, 94), 246 (53), 188 (15); HRMS (EI, 70 eV): calcd for $C_{16}H_{20}N_2S_2$ $[M]^+$: 304.2619; found: 304.2623.

1,4-Bis[Ethyl]benzo[1,2-d:4,5-d]dithiazole (11f); Starting with **10f** (200 mg, 1.0 equiv.), *N*-  Benzyl DABCO tribromide (450 mg, 2.0 equiv.), dichloromethane/carbon tetrachloride (1:1, 10 ml), following the general procedure F, **11f** was isolated (142 mg, 78 %). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 1.31 (t, *J* = 2.1 Hz, 6H, CH_3), 3.12 (q, 4H, CH_2); ^{13}C NMR (75.5 MHz, DMSO-d$_6$): δ = 14.7 (CH_3), 34.1 (CH_2), 116.8, 132.5 (CH), 135.6, 138.2, 171.0 (C); GC-MS (EI, 70 eV): *m/z* (%) = 248 (M^+, 84), 216 (63); HRMS (EI, 70 eV): calcd for $C_{12}H_{12}N_2S_2$ $[M]^+$: 248.3651; found: 248.3647.

6.3 Chemoselective S-M Cross Coupling Reaction Studies of 2-Bromo-1-(trifluoromethanesulfonyloxy) naphthalene,

6.3.1 *General procedure G* for the synthesis of 13, 21 and 25.

A benzene suspension (30 ml) of 1-tetralone **12, 20, 24** (1.0 equiv.), *N*-bromosuccinimide (NBS) (2.2 equiv.) and $(PhCOO)_2$ (5 mol %) was refluxed under Argon atmosphere for 4 h and then cooled to 20 °C. To the reaction mixture was added triethylamine (1 ml) and the solvent was removed *in vacuo*. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 x 25 ml). The combined organic layers were dried (Na_2SO_4), filtered and the

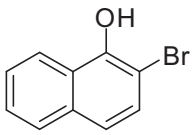
filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, heptane/ EtOAc) to give **13**, **21** and **25**.

6.3.2 General procedure H for synthesis of triflate 15, 22 and 27:

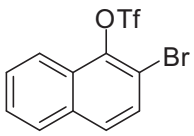
To a solution of **13, 21** or **25** (1.0 equiv.) in CH_2Cl_2 (2.5 ml/mmol) was added pyridine (2.0 equiv.) at 20 °C under an argon atmosphere. After stirring for 10 min at 0 °C, Tf_2O (1.5 equiv.) was added. The mixture was allowed to warm to 20 °C and stirred for further 6 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was directly purified by chromatography without aqueous work up (flash silica gel, heptane/EtOAc).

***General procedure* B for Suzuki–Miyaura reactions:** A 1,4-dioxane (5 ml) solution of K_3PO_4 (1.5 equiv. per cross-coupling step), $Pd(PPh_3)_4$ (5 mol %) and aryl-boronic acid **16a-h** (1.0-1.1 equiv. per cross-coupling step) was stirred at 90-110 °C for 4 h. After cooling to 20 °C, H_2O was added. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (15 x 3 ml). The combined organic layer was dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (flash silica gel, heptane-EtOAc, 9:1).

2-Bromonaphth-1-ol (13). Starting with 1-tetralone (**12**) **(**1.8 ml, 13.7 mmol), *N*-bromosuccinimide (NBS) (5.40 g, 30.2 mmol) and $(PhCOO)_2$ (0.17 g, 5 mol %), following the general procedure G, **13** was isolated as colourless solid (2.57 g, 84 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.89 (s, 1H, OH), 7.24 (d, J = 8.8 Hz, 1H), 7.38-7.46 (m, 3H), 7.66-7.75 (m, 1H), 8.12-8.19 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 104.0 (C), 121.3, 122.2, 124.1 (CH), 124.4 (C), 124.8, 127.5, 128.3 (CH), 133.7, 148.1 (C). IR (KBr): ν = 3400 (s), 3051, 1958, 1931, 1883, 1877, 1624 (w), 1586, 1574 (m), 1504 (w), 1453, 1396, 1384, 1347, 1240, 1212, 1202, 1140, 1126, 1054, 1021, 876, 856 (m), 829, 792, 768, 736 (s), 716, 641, 600, 561 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 222 (M^+ 98), 115 (92). HRMS (EI, 70 eV): calcd for $C_{10}H_7BrO$ $[M]^+$ 221.9680; found: 221.9679.



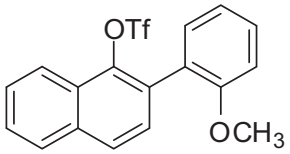
2-Bromonaphth-1-yl trifluoromethane-sulfonate (15): Starting with **13** (2.40 g, 10.8 mmol) in CH_2Cl_2 (25 ml), pyridine (1.8 ml, 21.6 mmol) and Tf_2O (2.7 ml, 16.4 mmol) following the general procedure H, **15** was isolated as a light yellow oil (3.53 g, 92 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.69 (m, 4H), 7.83 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.0. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 114.1 (C), 118.5 (q, $J_{C,F}$ = 321.0 Hz, CF_3), 121.2, 127.5 (CH),



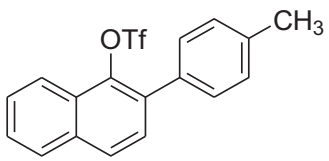
127.9 (C), 128.1, 128.5, 129.4, 129.9 (CH), 133.7, 142.6 (C). IR (KBr): v = 1589, 1501, 1457 (m), 1408 (s), 1370, 1365 (m), 1203, 1181, 1124 (s), 1032, (m) 1018, 890, 801, 761 (s), 743, 703, 665, 616, 587 (m) cm^{-1}. GC/MS (EI, 70 eV): m/z (%) = 354 (M^+, 100), 223 (52). HRMS (EI, 70 eV): calcd for $C_{11}H_6BrF_3O_3S$: 353.9173 $[M]^+$; found: 353.9171. Rf = 0.71 (heptane/EtOAC system; 4:1).

6.3.3 (2-Aryl)naphthalen-1-yl trifluoromethanesulfonates (17a-e)

(2-Methoxyphenyl)naphthalen-1-yl trifluoromethanesulfonate (**17a**): Starting with **15** (258 mg, 0.73 mmol), 2-methoxyphenylboronic acid (111 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **16a** was isolated as a yellow solid (167 mg, 60 %). mp. 73- 75 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.71 (s, 3H, OCH_3), 6.91 (d, J = 8.4 Hz, 1H), 7.01 (td, J = 8.4, 1.2 Hz, 1H), 7.35-7.41 (m, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.47-7.52 (m, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.54-7.61 (m, 1H), 7.83 (t, J = 8.1 Hz, 2H), 8.14 (d, J = 8.4, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -74.1. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 111.9 (CH), 118.0 (q, $J_{F,C}$ = 316.2 Hz, CF_3), 120.6, 121.6, (CH), 126.4, 126.7 (C), 127.4, 127.9, 128.8, 129.2, 129.6, 130.2, 131.8 (CH), 129.8, 134.4, 142.6, 156.9 (C). IR (KBr): v = 3060, 3026, 3004, 2939, 2837 (w) 1605, 1597, 1581, 1494, 1466, 1436, 1405, 1361, 1343, 1270, 1254 (m), 1200, 1132, 1079, 1048, 1026, 1007, 895, 866, 811, 748 (s), 708, 686, 634, 602, 588, 574 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 382 (M^+, 93), 249 (100), 234 (43), 218 (35), 189 (12). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_4S$ $[M]^+$: 382.0481; found: 382.0481. Anal; C, 56.54; H, 3.43; found; C, 56.41; H, 3.19.

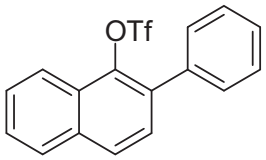


(4-Methylphenyl)naphthalen-1-yl trifluoromethanesulfonate (**17b**): Starting with **15** (258 mg, 0.73 mmol), *p*-tolylboronic acid (100 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **16b** was isolated as a brown solid (195 mg, 73 %). mp. 71-73 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3H, CH_3), 7.21 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.4 Hz, 1H), 7.51-7.54 (m, 1H), 7.57-7.62 (m, 1H), 7.83 (dd, J = 8.1, 4.8 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.1, (CH_3), 119.9, (q, $J_{F,C}$ = 314.2 Hz, CF_3), 120.0, 126.6 (CH), 126.4 (C), 126.8, 126.9, 127.4, 127.5, 128.2, 128.5 (CH), 131.8, 132.4, 132.9, 137.2, 140.9 (C). IR (KBr): v = 3051, 3028, 2918, 2862 (m), 1513, 1498, 1425, 1415, 1336, 1308, 1265, 1242, 1208, 1222, 1208, 1110, 1089, 1023, 1008, 958 (m), 807, 790, 783, 749,

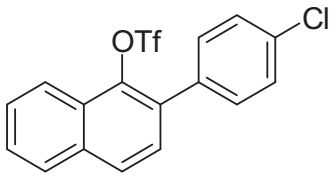


722, 683 (s), 589, 573, 552 (m), cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 366 (M^+, 78), 275 (64), 204 (27), 138 (25). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_3S$ $[M]^+$: 366.0559; found: 366.0556. Anal: C, 59.01; H, 3.58; found: C,59.02; H, 3.55.

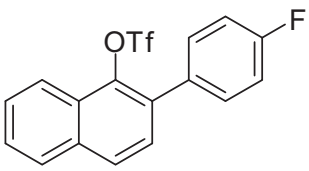
2-(Phenyl) naphthalen-1-yl trifluoromethanesulfonate (17c): Starting with **15** (258 mg, 0.73 mmol), phenylboronic acid (89 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **16c** was isolated as a light yellow solid (197 mg, 77 %). m.p. 75-77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.52 (m, 7H), 7.55-7.61 (m, 1H), 7.81 (dd, *J* = 8.2, 3.4 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.9. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 117.1 (q, $J_{C,F}$ = 316.2 Hz, CF_3), 120.6, 126.1 (CH), 126.3 (C), 126.9, 127.0, 127.3, 127.4, 127.5, 127.6, 128.7 (CH), 131.7, 133.0, 135.3, 140.9 (C). IR (KBr): *v* = 2931, 2865 (m), 1578, 1518, 1485, 1437, 1395, 1321 (s), 1253, 1237, 1202, 1198, 1073, 958 (m), 837, 756, 719, 637 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 352 (M^+, 98), 275 (60). HRMS (EI, 70 eV): calcd for $C_{17}H_{11}F_3O_3S$ $[M]^+$: 352.0412; found: 352.0411. Anal: C, 56.54 ; H, 3.45; found: C,56.52; H, 3.44.



2-(4-Chlorophenyl)naphthalen-1-yl trifluoromethanesulfonate (17d): Starting with **15** (258 mg, 0.73 mmol), phenylboronic acid (114 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **16d** was isolated as a yellow solid (248 mg, 88 %). m.p. 82-84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38-7.41 (m, 5H), 7.51-7.56 (m, 1H), 7.57-7.63 (m, 1H), 7.84 (dd, *J* = 8.1, 3.2 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.8. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 117.1 (q, $J_{C,F}$ = 263.0 Hz, CF_3), 120.6 (CH), 126.3 (C), 126.4, 126.9, 127.0, 127.1, 127.6, 127.8, 130.1 (CH), 130.6, 133.1, 133.6, 133.8, 140.8 (C). IR (KBr): *v* = 3073, 2954, 2922, 2852 (m), 1493, 1402, 1341, 1240, 1212, 1145, 1130, 1094 (s), 1028, 1018, 1006 (m), 894, 864, 837, 811, 765, 750 (s), 734, 698, 680, 634, 626, 597, 574, 549, 538 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 386 (M^+, 83), 253 (49), 218 (100), 189 (23). HRMS (EI, 70 eV): calcd for $C_{17}H_{10}ClF_3O_3S$ $[M]^+$: 385.9985; found: 385.9988. Anal; C, 52.79; H, 2.61. found: C, 52.76; H, 2.58.



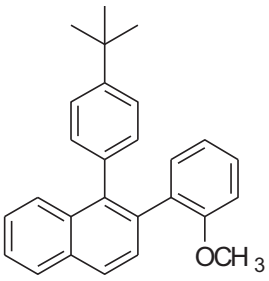
2-(4-Fluorophenyl)naphthalen-1-yl trifluoromethanesulfonate (17e): Starting with **15**



(258 mg, 0.73 mmol), *p*-fluorophenylboronic acid (102 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **16c** was isolated as a light yellow solid (229 mg, 85 %). m.p. 75-77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05-7.15 (m, 2H), 7.38-7.45 (m, 3H), 7.49-7.62 (m, 2H), 7.80-7.59 (m, 2H), 8.09 (d, J = 8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -113.2, -74.0. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 115.6 (d, $J_{C,F}$ = 21.4 Hz, CH), 117.1 (q, $J_{C,F}$ = 316.2 Hz, CF_3), 119.7 (C), 121.7, 127.3, 128.0 (CH), 128.2 (d, $J_{F,C}$ = 2.6 Hz, CH), 128.6, 131.4, 131.6 (CH), 132.3, 132.4, 134.1, 141.9 (C), 161.9 (d, $J_{F,C}$ = 248.5 Hz, CF). IR (KBr): v = 2961, 1606 (w), 1513, 1498 (m), 1405, 1341, 1201 (s), 1159 (m), 1132 (s), 1088, 1018, 1007 (m), 894 (s), 867 (m), 816, 804 (s), 764 (m), 749 (s), 703, 683, 622, 598, 556, (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 370 (M^+, 19), 237 (100), 209 (51), 183 (12). HRMS (EI, 70 eV): calcd for $C_{17}H_{10}F_4O_3S$ $[M]^+$: 370.0271; found: 370.0276. Anal; C, 55.14; H, 2.72. found: C, 54.11; H, 2.71.

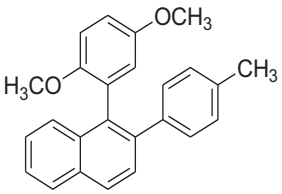
6.3.3 1,2-Diaryl usymmetricalnaphthalenes (18a-e)

1-(4-*Tert*-butylphenyl)-2-(2-Methoxyphenyl)naphthalene (18a); Starting with **17a** (100

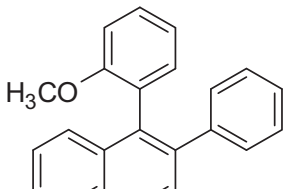


mg, 0.26 mmol), 4-*tert*-butylphenylboronic acid (40 mg, 0.31 mmol), $Pd(PPh_3)_4$ (15 mg, 5 mol %), K_3PO_4 (85 mg, 0.52 mmol) and 1,4-dioxane (5 ml), following *general procedure C*, **18a** was isolated as a viscous solid (124 mg, 66 %), 1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9H, CH_3), 3.51 (s, 3H, OCH_3), 6.96-7.13 (m, 3H), 7.23-7.29 (m, 2H), 7.33-7.37 (m, 1H), 7.39 (d, J = 8.63 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.61 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H). 13C NMR (75.5 MHz, $CDCl_3$): δ = 30.1 (3-CH_3), 33.7 (C) 55.2 (OCH_3), 116.6, 119.3, 120.3, 125.5, 125.6, 126.2, 127.3, 128.0, 128.2, 128.5, 128.7, 129.3 (CH), 131.4, 131.7, 132.4, 132.7, 134.7, 136.5, 149.4, 156.4 (C). IR (KBr): v = 3052, 3016, 2924, 2904, 2873 (m), 1625, 1577, 1551, 1493, 1454, 1413 (s), 1296, 1267, 1243 (m), 1172, 1077, 1038, 897, 826, 812, 651, 624, 574 (s) cm−1. GC-MS (EI, 70 eV): m/z (%) = 366 (M+, 98), 335 (64), 278 (58). HRMS (EI, 70 eV): calcd for $C_{27}H_{26}O$ [M]+: 366.4136; found: 366.4132.

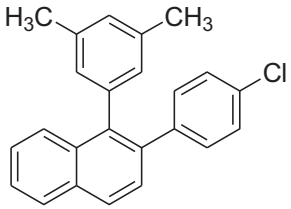
2-(4-Methylphenyl)-1-(2, 5-dimethoxyphenyl) naphthalene (18b): Starting with **17b** (100 mg, 0.27 mmol), 2,5-dimethoxyphenylboronic acid (55 mg, 0.30 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol %), K_3PO_4 (86 mg, 0.41 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **18a** was isolated as a gummy solid (62 mg, 65 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 3H, CH_3), 3.41 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 6.56 (d, J = 2.7 Hz, 1H), 6.73-6.74 (m, 2H), 6.91 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.9 Hz, 2H), 7.29-7.32 (m, 1H), 7.34-7.41 (m, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.81 (dd, J = 4.7, 4.4 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.7 (CH_3), 54.6 (OCH_3), 54.8 (OCH_3), 110.8, 112.6, 117.1, 124.3, 125.1, 125.6, 126.6, 126.8 (CH), 127.1 (2CH), 128.0 (2CH), 128.2 (CH), 128.3, 131.5, 131.7, 132.8, 134.7, 137.8, 138.2, 151.1, 152.2 (C). IR (KBr): ν = 2934, 2872 (w), 1476, 1454, 1361, 1259 (m), 1166, 1043, 975, 843, 834 (s), 742, 729, 708, 679, 647, 626 (m), 571, 542, 537 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 354 (M^+, 100), 323 (57), 263 (31), 216 (18). HRMS (EI, 70 eV): calcd for $C_{25}H_{22}O_2$ $[M]^+$: 354.1623; found: 354.1621. Anal: C, 84.72 H, 6.26; found: C, 84.69; H, 6.21.



2-(Phenyl)-1-(2,methoxyphenyl) naphthalene (18c): Starting with **17c** (100 mg, 0.28 mmol), 2-methoxyphenylboronic acid (48 mg, 0.31 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol %), K_3PO_4 (89 mg, 0.42 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **18c** was isolated as a brown gummy solid (60 mg, 69 %). mp. 103-105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.39 (s, 3H, OCH_3), 6.82-7.21 (m, 4H), 7.34-7.45 (m, 6H), 7.47-7.54 (m, 1H), 7.57-7.63 (m, 1H), 7.81-7.85 (m, 2H), 8.09 (d, J = 8.4 Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 54.6 (OCH_3), 111.2, 120.7, 121.6 (CH), 124.6 (C), 127.0, 127.8, 128.1, 128.5, 128.6, 129.2, 129.6 (CH), 129.8 (C), 130.2, 131.5, 131.8 (CH), 134.2, 142.6, 156.9 (C). GC-MS (EI, 70 eV): *m/z* (%) = 310 (M^+, 98), 279 (53), 233 (69). HRMS (EI, 70 eV): calcd for $C_{23}H_{18}O$ $[M]^+$: 310.1431; found: 310.1430. Anal: C, 89.00, H, 5.85; found: C, 89.01; H, 5.81.

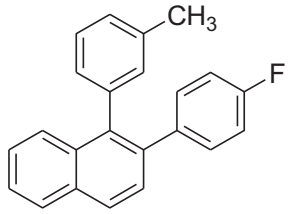


2-(4-Chlorophenyl)-1-(3, 5-dimethylphenyl) naphthalene (18d). Starting with **17d** (100 mg, 0.26 mmol), 3,5-dimethylphenylboronic acid (44 mg, 0.29 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol %), K_3PO_4 (83 mg, 0.39 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **18d** was isolated as a reddish crystaline solid (64 mg, 72 %). m.p. 106-109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 6H, $2CH_3$) 6.71 (brs, 2H), 6.84 (br s, 1H), 7.01-7.12 (m, 4H), 7.29-7.35 (m, 1H), 7.38-7.44 (m, 2H), 7.42 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4



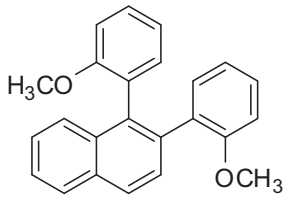
Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.3 (2 CH_3), 125.1 (C), 125.7, 126.2, 127.1, 127.4, 127.7, 127.8, 127.9, 128.4, 129.1, 131.3, 132.1, (CH), 132.1, 132.7, 132.8, 136.7, 137.2, 138.1, 138.4, 140.6 (C). IR (KBr): ν = 2978, 2853 (w), 1477, 1458, 1375, 1276, 1254 (m), 1037, 1003, 987, 821, 834, 817 (s), 739, 721, 718, 673, 665, 608 (m), 573, 543, 537 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 342 (M^+, 100), 307 (58), 238 (36). HRMS (EI, 70 eV): calcd for $C_{24}H_{19}Cl$ $[M]^+$: 342.1271; found: 342.1269. Anal: C, 84.26; H, 5.59; found: C, 84.23; H, 5.58.

2-(4-Fluorophenyl)-1-(*m*-tolyl) naphthalene (18e): Starting with **17e** (200 mg, 0.54 mmol), 3-methylphenylboronic acid (81 mg, 0.59 mmol), $Pd(PPh_3)_4$ (32 mg, 5 mol %), K_3PO_4 (173 mg, 0.81 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **18e** was isolated as a solid (130 mg, 77 %). m.p. 109-111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3H, CH_3), 6.75-6.91 (m, 4H), 7.00-7.05 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H), 7.28-7.40 (m, 2H), 7.43 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.2 Hz 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -116.6. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 114.5 (d, $J_{C,F}$ = 21.3 Hz, CH), 125.8, 126.3, 126.9, 127.6, 127.8, 127.9, 128.1, 128.5, 131.5, 131.6, 132.1 (CH), 132.7, 132.8, 137.2, 137.4, 137.9, 138.1 (d, $J_{C,F}$ = 3.3 Hz, C), 138.7 (C), 161.5 (d, $J_{C,F}$ = 245.6 Hz, CF). IR (KBr): ν = 3050, 2920 (m), 2852 (w), 1601 (m), 1499 (s), 1457 (m), 1234 (w), 1218 (s), 1155, 1092, 1023 (m), 962 (w), 863, 841 (m), 817, 803, 778, 743, 713, 693 (s), 653, 544 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 312 (M^+, 100), 222 (55), 204 (07). HRMS (EI, 70 eV): calcd for $C_{23}H_{17}F$ $[M]^+$: 312.1314; found: 312.1313.



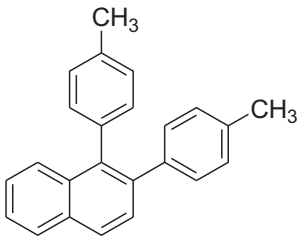
6.3.5 1, 2-Bis-arylnaphthalens (19a-c)

1, 2-Bis(2-methoxyphenyl)naphthalen (19a): Starting with **15** (258 mg, 0.73 mmol), 2-methoxyphenylboronic acid (244 mg, 1.61 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (464 mg, 2.19 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **19a** was isolated as a solid (154 mg, 62 %). m.p = 105-107 C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.46 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 6.64-6.78 (m, 4H), 6.96-7.13 (m, 4H), 7.23-7.29 (m, 1H), 7.33-7.38 (m, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.1 (OCH_3), 55.2 (OCH_3), 110.1, 110.2, 111.1, 119.6, 119.7, 120.3, 125.3, 125.7, 126.6, 127.1, 127.9, 128.1, 128.4, 128.6 (CH), 131.1, 131.4, 132.6, 132.8, 135.2, 135.9, 156.4, 157.3 (C). IR (KBr): ν = 3060, 3026, 2940, 2837 (m), 1605, 1597, 1581, 1495, 1465, 1436, 1405 (s), 1343, 1296, 1270, 1254 (m), 1201, 1132, 1079, 1048, 1026, 1007,

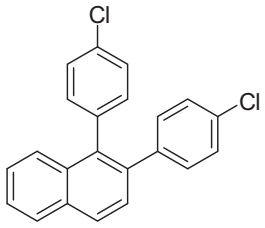


895, 866, 812, 748, 708, 686, 634, 602, 588, 574 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 341 (M^+, 98), 309 (57), 234 (47). HRMS (EI, 70 eV): calcd for $C_{24}H_{20}O_2$ $[M]^+$: 340.1534; found: 340.1531.

1, 2-Bis(4-methylphenyl)naphthalen (19b): Starting with **15** (258 mg, 0.73 mmol), *p*-tolylboronic acid (219 mg, 1.61 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (464 mg, 2.19 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **19b** was isolated as a white crystalline solid (177 mg, 79 %). m.p. 105-107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21, (s, 3H, CH_3), 2.28, (s, 3H, CH_3), 6.91 (d, *J* = 8.1 Hz, 2H), 6.96-7.03 (m, 6H), 7.26-7.31 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.1, 21.3 ($2CH_3$), 125.2, 126.1, 126.9, 127.3, 127.8, 128.4, 128.5, 128.6, 130.1, 131.2 (CH), 132.7, 132.9, 135.6, 136.1, 136.2, 137.5, 138.2, 139.2 (C). IR (KBr): *v* = 3051, 3028, 2918, 2862 (m), 1513, 1498, 1425, 1415, 1336, 1308, 1265, 1242, 1208, 1222, 1208, 1110, 1089, 1023, 1008, 958 (m), 807, 790, 783, 749, 722, 683 (s), 589, 573, 552 (m), cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 308 (M^+, 100), 293 (34), 178 (27), 252 (15), 138 (25). HRMS (EI, 70 eV): calcd for $C_{24}H_{20}$ $[M]^+$: 308.1559; found: 308.1558. Anal: C, 93.46; H, 6.54; found: C, 93.41; H, 6.52.



1, 2-Bis(4-chlorophenyl)naphthalene (19c): Starting with **15** (258 mg, 0.73 mmol), *p*-chloroboronic acid (251 mg, 1.61 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (464 mg, 2.19 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **19c** was isolated as a white crystalline solid (239 mg, 94 %). m.p. 170-180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95-6.98 (m, 2H), 7.01-7.03 (m, 2H), 7.07-7.11 (m, 2H), 7.19-7.22 (m, 2H), 7.30-7.35 (m, 1H), 7.38-7.44 (m, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 3.1 Hz, 1H), 7.89 (d, *J* = 3.0 Hz, 1H).^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 126.1, 126.4, 126.6 (CH), 127.4 (C), 127.9, 128.1, 128.2, 128.3 (CH), 129.1 (C), 131.3 (CH), 132.4, 132.5 (C), 132.6 (CH), 132.9 (C), 133.1 (CH), 136.3, 137.2, 140.1 (C). IR (KBr): *v* = 3050, 2923, 2852 (w), 1487, 1459, 1395, 1374, 1259, 1209 (m), 1086, 1013, 961, 801, 840, 824, 810 (s), 752, 739, 730, 718, 679, 657, 636, 608 (m), 573, 559, 540, 531 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 348 (M^+, 100), 278 (58), 138 (36), 69 (26). HRMS (EI, 70 eV): calcd for $C_{22}H_{14}Cl_2$ $[M]^+$: 348.0467; found: 348.0466. Anal: C, 75.66; H, 4.04; found: C, 75.64; H, 4.01.



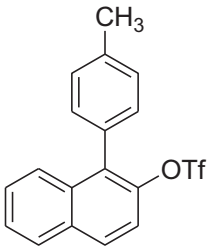
6.3.6 Synthesis of 1-bromonaphth-2-ol (**21**). Compound **21** was prepared by the literature procedure Starting with 1-tetralone (**20**, **(**0.6 ml, 4.6 mmol), *N*-bromosuccinimide (NBS) (1.80

g, 10.1 mmol) and $(PhCOO)_2$ (0.056 g, 5-mol %), following the general procedure G, **21** was isolated as colourless solid (0.81 g, 82 %). Spectral data was found in agrrement with the date reported in literature.

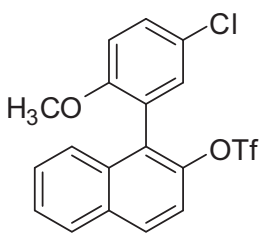
6.3.7 1-Bromonaphthalen-2-yl trifluoromethanesulfonate (22). Starting with **21** (0.80 g, 3.6 mmol) in CH_2Cl_2 (20 ml), pyridine (0.5 ml, 7 mmol) and Tf_2O (0.9 ml, 5.4 mmol) following the general procedure H, **22** was isolated as a light yellow oil (1.2 g, 92 %) Spectral data was found in agrrement with the date reported in literature.[15]

6.3.8 1-Arylenaphthalen-2-yl trifluoromethanesulfonate (23a-b)

1-*p*-Tolylnaphthalen-2-yl trifluoromethanesulfonate (23a). Starting with **22** (71 mg, 0.20 mmol), *p*-tolylboronic acid (27 mg, 0.20 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **23a** was isolated as a deep brown solid (54 mg, 73 %). m.p. 70-72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 7.21 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.39-7.46 (m, 1H), 7.49-7.56 (m, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.2. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.1, (CH_3), 119.9, (q, $J_{F,C}$ = 314.2 Hz, CF_3), 119.8, 126.8, 127.3, 127.6, 127.7, 128.1 (CH), 128.3 (C), 129.1, 130.6 (CH), 132.8, 132.6, 133.4, 138.3, 144.3 (C). IR (KBr): ν = 3019, 2927, 2869 (m), 1541, 1498, 1438, 1423, 1301, 1285, 1245, 1211, 1108, 1093, 1073, 967 (m), 817, 793, 771, 758, 712, 653 (s), 574, 542 (m), cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 366 (M^+, 98), 275 (57), 217 (44), 138 (37). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_3S$ $[M]^+$: 366.0519; found: 366.0511. Anal: C, 59.01; H, 3.58; found: C, 59.02; H, 3.55.

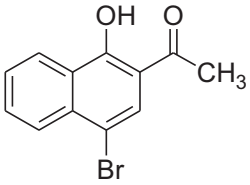


1-(5-Chloro-2-methoxyphenyl)naphthalen-2-yl trifluoromethanesulfonate (23b). Starting with **22** (71 mg, 0.20 mmol), 5-chloro-2-methoxyphenylboronic acid (37 mg, 0.20 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **23b** was isolated as a white solid (50 mg, 60 %). m.p. 75- 77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, OCH_3), 6.79 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.2 Hz, 1H), 7.10-7.11 (m, 1H), 7.16-7.21 (m, 2H), 7.33-7.47 (m, 2H), 7.80-7.89 (m, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -74.5. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 54.7 (OCH_3), 117.5 (q, $J_{F,C}$ = 316.2 Hz, CF_3), 120.1, 121.3 (CH), 126.1, 126.4 (C), 127.2, 127.6,



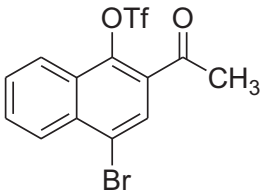
128.5, 128.8, 129.2, 130.0, 131.6 (CH), 132.7, 134.0, 137.8, 142.3, 155.1 (C). IR (KBr): ν = 3014, 2941, 2872 (w) 1655, 1572, 1581, 1466, 1436, 1405, 1361, 1343, 1270, 1254 (m), 1200, 1132, 1079, 1048, 1026, 1007, 895, 866, 811, 748 (s), 708, 686, 634, 602, 588, 574 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 416 (M^+, 81), 274 (76), 267 (43), 141 (29). HRMS (EI, 70 eV): calcd for $C_{18}H_{12}ClF_3O_4S$ $[M]^+$: 416.0135; found: 416.0131. Anal; C, 51.87; H, 2.90; found; C, 51.86; H, 2.88

Synthesis of 1-(4-Bromo-1-hydroxynaphthalen-2-yl)ethanone (25). Starting with 2-acetyl-3,4-dihydronaphthalen-1(2H)-one (**24**) (3.00 g, 13.7 mmol), *N*-bromosuccinimide (NBS) (5.40 g, 30.2 mmol) and $(PhCOO)_2$ (0.17 g, 5 mol %), following the general procedure G, **25** was isolated as green crystalline solid. m.p. 124-126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, 3H, CH_3), 7.47-7.53 (m, 1H), 7.63-7.68 (m, 1H), 7.87 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 8.3 Hz, 1H), 13.83 (s, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.8 (CH_3), 111.1, 113.9 (C), 124.8, 126.41 (CH), 126.7 (C), 127.1, 128.2, 131.2 (CH), 135.7, 161.9, 203.3 (C). IR (KBr): ν = 3130, 3071, 3033 (m), 1731, 1712, 1620, 1614, 1574, 1565, 1502, 1447, 1406, 1363, 1314, 1265, 1236, 1211, 1137 (s), 1082, 1025, 979, 871, 862, 837, 862, 837 (m), 754, 720, 686, 643, 588, 565 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 264 (M^+, 100), 251 (76), 195 (20), 114 (23). HRMS (EI, 70 eV): calcd for $C_{12}H_9BrO_2$ $[M]^+$: 263.9781; found: 263.9778. Anal: C, 54.37; H, 3.42; found: C, 54.31; H, 3.41.

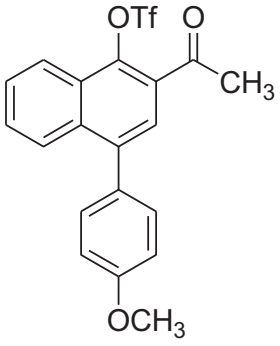


6.3.9 2-Acetyl-4-(4-aryl)naphthalen-1-yl trifluoromethanesulfonate (27)

2-Acetyl-4-Bromonaphthalen-1-yl trifluoromethanesulfonate (27). Starting with **25** (2.00 g, 7.54 mmol) in CH_2Cl_2 (25 ml), pyridine (1.5 ml, 20 mmol) and Tf_2O (1.8 ml, mmol) following the general procedure H, **27** was isolated as a light green oil (2.75 g, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, 3H, CH_3), 7.46-7.51 (m, 1H), 7.62-7.71 (m, 2H), 7.92 (s, 1H), 8.11 (d, J = 8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -72.7. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 29.6 (CH_3), 117.5 (q, $J_{C,F}$ = 321 Hz, CF_3), 121.7 (C), 122.18 (CH), 126.5, 126.6 (C), 127.0, 128.1, 129.2, 130.3 (CH), 133.3, 140.3 195.6 (C). IR (KBr): ν = 3076, 3002, 2962, 2929 (m), 1699, 1620, 1594, 1494, 1426, 1403 (s), 1370, 1351, 1318, 1266, 1243 (m), 1203, 1130, 1171, 1037, 867, 818, 760, 720, 647, 629, 603, 571, 551 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 396 (M^+, 97), 265 (95), 248 (20), 237 (73), 128 (36). HRMS (EI, 70 eV): calcd for $C_{13}H_8BrF_3O_4S$ $[M]^+$: 395.9273; found: 395.9269. Anal: C, 39.31; H, 2.02; found: C, 39.29; H, 2.01.

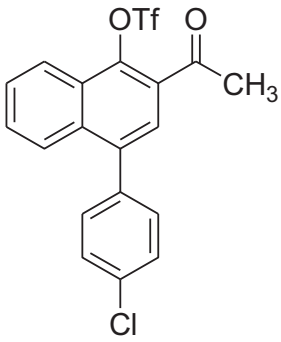


2-Acetyl-4-(4-Methoxyphenyl)naphthalen-1-yl trifluoromethanesulfonate (28a). Starting



with **27** (79 mg, 0.20 mmol), 4-methoxyphenylboronic acid (30 mg, 0.20 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **28a** was isolated as a light brown oil (53 mg, 62 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.64 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.96-7.01 (m, 2H), 7.18 (s, 1H), 7.31-7.34 (m, 1H), 7.50-7.55 (m, 2H), 7.59-7.64 (m, 1H), 7.87 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -72.8. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 29.7 (CH_3), 55.4 (OCH_3), 114.1 (CH), 117.5 (q, $J_{C,F}$ = 321 Hz, CF_3), 122.5, 125.0, 126.6 (CH), 126.9 (C), 128.1, 128.7 (CH), 129.5, 130.7 (C), 131.0 (CH), 134.5, 140.9, 141.1, 159.6 (C), 198.3 (CO). IR (KBr): v = 3073, 3003, 2957, 2929, 2838 (m), 1697, 1607, 1572, 1515, 1499, 1456, 1423, 1404, 1366 (s), 1290, 1256 (w), 1244, 1204, 1177, 1149, 1134, 1028 (s), 978, 943, 937, 886 (m), 831, 793, 764, 721, 707, 636, 604, 588, 574 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 424 (M^+, 81), 291 (98), 277 (17), 263 (36), 235 (12), 149 (29). HRMS (EI, 70 eV): calcd for $C_{20}H_{15}F_3O_5S$ $[M]^+$: 424.0678; found: 424.0668 Anal: C, 56.61; H, 3.56; found: C, 56.59; H, 3.54.

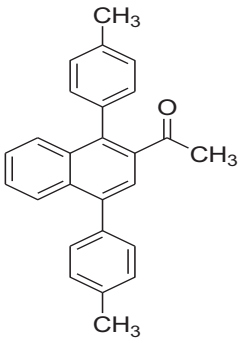
2-Acetyl-4-(4-Chlorophenyl)naphthalen-1-yl trifluoromethanesulfonate (28b). Starting



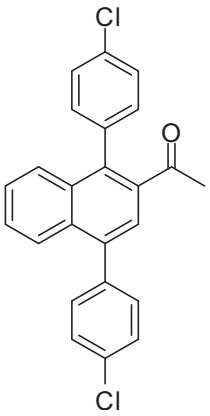
with **27** (79 mg, 0.20 mmol), 4-chlorophenylboronic acid (31 mg, 0.20 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **28b** was isolated as a semisolid (74 mg, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61 (s, 3H, CH_3), 6.91-6.97 (m, 2H), 7.13 (s, 1H), 7.28-7.332 (m, 1H), 7.47-7.52 (m, 2H), 7.56-7.61 (m, 1H), 7.81 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -72.3. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 29.4 (CH_3), 113.8 (CH), 116.9 (q, $J_{C,F}$ = 321 Hz, CF_3), 121.7, 121.8, 121.4 (CH), 125.6 (C), 127.7, 127.9 (CH), 128.2, 129.8 (C), 131.0 (CH), 133.7, 140.0, 141.1, 158.9 (C), 198.0 (CO). IR (KBr): v = 3067, 3023, 2975, 2883 (m), 1687, 1636, 1552, 1423, 1404, 1386 (s), 1266 (w), 1231, 1209, 1176, 1141 (s), 972, 934, 874 (m), 831, 773, 761, 709, 570 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 428 (M^+, 98), 317 (76), 279 (37), 168 (09). HRMS (EI, 70 eV): calcd for $C_{19}H_{12}ClF_3O_4S$ $[M]^+$: 428.0156; found: 428.0154. Anal: C, 53.22; H, 2.82; found: C, 53.19; H, 2.79.

6.3.10 1-(1,4-Diarylnaphthalen-2-yl)ethanone (29)

1-(1,4-Di-*p*-tolylnaphthalen-2-yl)ethanone (29a); Starting with **27** (79 mg, 0.20 mmol), *p*-tolylboronic acid (60 mg, 0.44 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (127 mg, 0.60 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **29a** was isolated as a light yellow gummy solid (60 mg, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.1 (s, 3H, CH_3), 2.3 (s, 3H, CH_3), 2.4 (s, 3H, CH_3), 7.21-7.27 (m, 6H), 7.33-7.41 (m, 4H), 7.50 (s, 1H), 7.63-7.72 (m, 1H), 7.88-7.91 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.2, 21.3, 30.8 (CH_3), 125.1, 126.2, 126.4, 127.1, 127.6, 129.1, 129.2, 129.9, 130.6 (CH), 132.5, 132.8, 135.3, 137.1, 137.3, 137.6, 137.7, 137.9, 140.1 (C), 204.9 (CO). IR (KBr): 3022, 2921, 2865 (w), 1711 (s), 1591, 1511 (w), 1485, 1378, 1367 (m), 1241, 1220, 1192 (s), 1099, 1020, 926 (m), 814, 746 (s), 687, 595 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 350 (M^+, 99), 259 (66), 91 (07); Anal: C, 89.11; H, 6.33; found: C, 89.09; H, 6.31; HRMS (EI, 70 eV): calcd for $C_{26}H_{22}O$ $[M]^+$: 350.1745; found: 350.1741.



1-(1,4-Bis(2-chlorophenyl)naphthalen-2-yl) ethanone (29b). Starting with **27** (79 mg, 0.20 mmol), 2-chlorophenylboronic acid (69 mg, 0.44 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (127 mg, 0.60 mmol) and 1,4-dioxane (5 ml), following the general procedure B, **29b** was isolated as a light yellow gummy solid (229 mg, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.1 (s, 3H, CH_3), 7.17-7.21 (m, 1H), 7.31-7.33 (m, 5H), 7.38-7.39 (m, 2H), 7.41-7.43 (m, 2H), 7.50 (s, 1H), 7.59 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.80 (dd, *J* = 7.2, 1.5 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 29.7 (CH_3), 120.6, 124.1, 124.8, 125.9, 126.4, 126.7, 127.1, 127.3, 127.8, 128.6, 128.8, 128.9, 129.4 (CH), 131.2, 131.4, 133.3, 133.5, 135.6, 136.2, 138.2, 139.0, 140.5 (C), 202.3 (CO). IR (KBr): ν = 3063 (w), 2929, 2857 (w), 1714 (m), 1588 (w), 1498, 1362, 1353, 1244 (m), 1218, 1192, 1087 (s), 1013, 907 (m), 823, 764, 740, 690 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 390 (M^+, 99), 347 (23), 279 (61). Anal: C, 73.67; H, 4.12; found: C, 73.64; H, 4.09; HRMS (EI, 70 eV): calcd for $C_{26}H_{16}Cl_2O$ $[M]^+$: 390.0651; found: 390.0646.

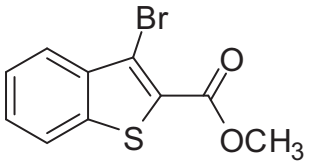


6.4 Synthesis of Heteroaryl-Fused Benzopyranone Analagues and Arylated Naphthaquinones.:

6.4.1 3-Bromo-2-methoxycarbonylbenzo[*b*]thiophene (33):

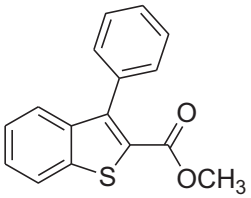
General procedure I for the synthesis of 33; To a cold solution (ice bath) of o-nitrobenzonitrile (0.60 g, 4 mmol in DMF, 10 ml) and KOH (3.00 g, aqueous), was added methyl thioglycolate (0.50 g, 4.0 mmol) dropwise. The mixture was stirred at ice bath temprature for 1 h and poured into ice water and extracted with DCM to obtain the crude product. This crude product was added to the stirring solution of anhydrous $CuBr_2$ (4.0 mmol), *tert*-butyl nitrite (5.0 mmol) in acetonitrile (10 ml). During this addition the reaction solution turned completely black. The reaction solution was then poured into 200 ml of 20 % HCl (aqueous) and extracted with 200 ml of ether, and the organic layer was washed once with 200 ml water. The resulting ether solution was dried over Mg_2SO_4 and the ether was removed under reduced pressure, purified through chromatography eluating with heptan/EtOAc to obtain the product **33.**

3-Bromo-2-methoxycarbonylbenzo[*b*]thiophene (33): Starting with **32** (0.50 g, 2.4 mmol), *tert*-butyl nitrite (0.30 g, 6.5 mmol), $CuBr_2$ (0.60 g, 2.9 mmol) following the general procedure I, compound **33** was obtained as yellowish solid (0.52 g, 80 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, OCH_3, 3H), 7.89-7.93 (m, 1H), 7.73-7.79 (m, 1H), 7.38-7.48 (m, 2H); ^{13}C NMR: (75.5 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 115.1, 127.5 (C), 122.6, 125.3, 125.6, 128.1 (CH), 139.3, 138.6 (C), 161.8 (CO); IR (KBr): ν = 3420 (s), 3056, 2922, (m), 1718 (s), 1532, 1486, 1426 (m), 1269, 1232, 1173, 1056 (s), 1028, 826 (m), 756, 752, 736, 692, 609 (s) cm^{-1}; GC-MS: (EI, 70 eV): *m/z* (%): (M^+, 272 (87), 241 (100), 213 (21), 132 (50); Anal. Calcd for $C_{10}H_7BrO_2S$: C, 44.11; H, 2.57; Found: C, 44.07; H, 2.60; HRMS: (EI, 70 eV): calcd for $C_{10}H_7BrO_2S$ $[M+H]^+$: 271.9402; found: 271.9404.



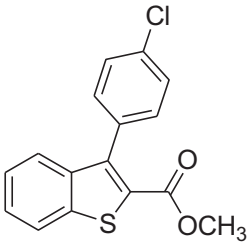
6.4.2 3-Phenyl-2-methoxycarbonylbenzo[*b*]thiophene (35a-h)

3-Phenyl-2-methoxycarbonylbenzo[*b*]thiophene (35a); Starting with **33** (100 mg, 0.36 mmol), phenylboronic acid (52 mg, 1.2 equiv.), $Pd(PPh_3)_4$ (21 mg, 5 mol %), K_3PO_4 (114 mg, 1.5 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **35a** was obtained as white solid product (72.58 mg, 74 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3H, OCH_3), 7.79-7.82 (m, 1H), 7.43-7.83 (m, 1H), 7.38-7.42 (m, 4H), 7.25-7.34 (m, 3H); ^{13}C NMR: (75.5

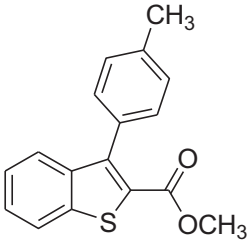


MHz, $CDCl_3$): δ = 52.1 (OCH_3), 122.5, 124.8, 125.4, 127.31, 128.1, 129.6 (CH), 128.9, 134.5, 140.1, 140.4, 144.2 (C), 161.8 (CO); IR (KBr): ν = 3400 (s), 3056, 2922, (m), 1718 (s), 1532, 1486, 1426 (m), 1269, 1232, 1173, 1056 (s), 1028, 826 (m), 756, 752, 736, 692, 609 (s) cm^{-1}; GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 268 (100), 237 (90), 208 (26), 165 (34); Anal. Calcd for $C_{10}H_8BrO_2S$: C, 71.64; H, 4.47; S, 11.94; Found: C, 70.2; H, 4.39; S, 11.81; HRMS: (EI, 70 eV): calcd for $C_{16}H_{12}O_2S$ [M^+]: 268.0552; found: 268.0553.

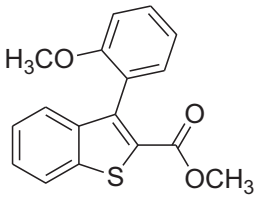
3-(4-Chlorophenyl)-2-methoxycarbonylbenzo[*b*]thiophene (35b); Starting with **33** (100 mg, 0.36 mmol), 4-chlorophenylboronic acid (68 mg, 1.2 equiv.), $Pd(PPh_3)_4$ (21 mg, 5 mol %), K_3PO_4 (114 mg, 1.5 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **35b** was obtained as yellow powder product (86.2 mg, 78 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, OCH_3, 3H), 7.79-7.82 (m, 1H), 7.73-7.45 (m, 4H), 7.24-7.31 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.2 (OCH_3), 122.5, 124.9, 125.1, 127.3, 128.3, 131.1 (CH), 132.8, 134.1, 139.7, 140.4, 142.7 (C), 162.7 (CO); IR (KBr): ν = 3411, 2960, 2949 (s), 1713, 1531, 1482, 1434 (s), 1348, 1318, 1299 (m), 1271, 1237, 1173, 1081, 1059, 1013, 985 (s), 949, 910, 860 (m), 844, 809, 798, 757, 738, 708 (s) cm^{-1}; GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 302 (100), 271 (53), 236 (41), 208 (28); Anal. Calcd for $C_{16}H_{11}ClO_2S$: C, 63.15; H, 3.61, Found: C, 63.28; H, 3.27; HRMS: (EI, 70 eV): calcd for $C_{16}H_{11}ClO_2S$ [M^+]: 302.0162; found: 302.0166.



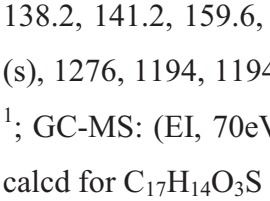
3-(4-Tolyl)-2-methoxycarbonylbenzo[*b*]thiophene (35c); Starting with **33** (100 mg, 0.36 mmol), 4-methylphenylboronic acid (59 mg, 1.2 equiv), $Pd(PPh_3)_4$ (21 mg, 5 mol %), K_3PO_4 (114 mg, 1.5 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **35c** was obtained as colorless solid (79.1 mg, 76 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.4 (s, 3H, CH_3), 3.87 (s, OCH_3, 3H), 7.73-7.42 (m, 1H), 7.72-7.47 (m, 4H), 7.24-7.31 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.6 (CH_3), 51.5 (OCH_3), 121.6, 123.7, 125.1, 126.3, 127.4, 132.1 (CH), 132.2, 133.8, 139.7, 140.7, 141.8 (C), 162.2 (CO); IR (KBr): ν = 3433, 3062, 2995, 2949 (s), 1720, 1561, 1516, 1488 (s), 1433, 1385 (m), 1322, 1305, 1271, 1242, 1230, 1154, 1114, 1093, 1086, 1072, 1056 (s), 982, 922, 906 (m), 800, 784, 750, 735, 723, 696, 677, 649 (s) cm^{-1}; GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 282 (100), 251 (56), 236 (47), 221 (21), 208 (31); Anal. Calcd for $C_{17}H_{14}O_2S$: C, 72.34; H, 4.91; Found: C, 72.21; H, 4.87; HRMS: (EI, 70 eV): calcd for $C_{17}H_{14}O_2S$: [M^+]: 282.0756; found: 282.0759.



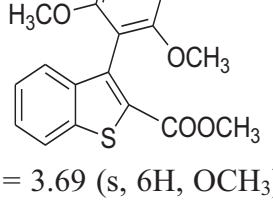
3-(2-Methoxyphenyl)-2-methoxycarbonylbenzo[*b*]thiophene (35d); Starting with **33** (100 mg, 0.36 mmol), 2-methoxyphenylboronic acid (65 mg, 1.2 equiv), $Pd(PPh_3)_4$ (21 mg, 5 mol %), K_3PO_4 (114 mg, 1.5 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **35e** was obtained as solid (83.6 mg, 76 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3H, OCH_3, 3H), 3.86 (s, OCH_3, 3H), 7.86 (dd, *J* = 7.6, 3.4 Hz, 1H), 7.69 (dd, *J* = 7.3, 3.3 Hz, 1H), 7.34-7.41 (m, 2H), 6.26-6.37 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.2 (OCH_3), 54.1 (OCH_3), 114.1, 114.3, 121.6, 125.6, 125.9, 127.89, 128.2, 129.8 (CH), 128.8, 132.1, 137.3, 138.2, 141.2, 159.6, (C), 162.3 (CO); IR (KBr): v = 2951, 2923, 2852 (s), 1723, 1615, 1409 (s), 1276, 1194, 1194, 1152, 1131 (s), 990, 957, 832, 817 (m), 754, 731, 722, 652, 546 (s) cm^{-1}; GC-MS: (EI, 70eV): m/z (%) = (M^+, 298 (100), 267 (47), 203 (14); HRMS: (EI, 70 eV): calcd for $C_{17}H_{14}O_3S$ $[M]^+$: 298.0727; found: 298.0731.



3-(2,5-Dimethoxyphenyl) -2-methoxycarbonylbenzo[*b*]thiophene (35e); Starting with **33** (100 mg, 0.36 mmol), 2,5-dimethoxyphenylboronic acid (75 mg, 0. 1.2 equiv), $Pd(PPh_3)_4$ (21 mg, 5 mol %), K_3PO_4 (114 mg, 1.5 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **35f** was obtained as brown solid (92 mg, 76 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 6H, OCH_3), 3.87 (s, OCH_3, 3H,), 7.88 (dd, *J* = 7.3, 3.3 Hz, 1H), 7.17 (dd, *J* = 6.7, 3.2 Hz, 1H), 7.37-7.45 (m, 2H), 6.37-6.43 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.4 (OCH_3), 54.2 (OCH_3), 114.1, 114.3, 121.6, 125.6, 125.9, 128.2, 129.8 (CH), 128.8, 132.3, 137.6, 138.3, 141.7, 159.8, 160.7 (C), 162.1 (CO); IR (KBr): *v* = 1733, 1615, 1426 (s), 1226, 1196, 1184, 1156, 1121 (s), 990, 907, 837, 807 (m), 750, 736, 742, 622, 556 (s) cm^{-1}; GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 328 (100), 305 (91), 285 (16), 257 (12), 208 (21); Anal. Calcd for C, 65.84; H, 4.91; S, 9.76, Found: C, 65.13; H, 4.79; S, 9.19; HRMS: (EI, 70 eV): calcd for $C_{18}H_{16}O_4S[M]^+$: 328.0831; found: 328.0828.

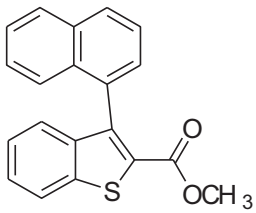


3-(5-Chloro-2-methoxyphenyl)-2-methoxycarbonylbenzo[*b*]thiophene (35f); Starting with **33** (100 mg, 0.36 mmol), 2-methoxy-5-chlorophenylboronic acid (80 mg, 0. 1.2 equiv), $Pd(PPh_3)_4$ (21 mg, 5 mol %), K_3PO_4 (114 mg, 1.5 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **35g** was obtained (76 mg, 62 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, OCH_3, 3H), 3.86 (s, OCH_3, 3H), 7.81 (dd, *J* = 8.1, 3.4 Hz, 1H), 7.72 (dd, *J* = 8.3, 3.3 Hz, 1H), 7.35-7.43 (m, 2H), 7.11 (d, *J* = 2.6 Hz, 1H), 6.83 (dd, 6.6, 2.6 Hz, 1H), 6.65 (d, *J* = 8.6 Hz,



1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 113.2, 114.0, 121.2, 124.6, 126.3, 128.7, 133.4 (CH), 128.2, 131.2, 135.9, 137.2, 137.6, 143.7, 155.3 (C), 161.7 (CO); IR (KBr): ν = 2956, 2847 (s), 1747, 1675, 1590 (s), 1366, 1276, 1147, 1126 (w), 987, 947, 876, 827 (m), 755, 726, 621, 566 (s) cm^{-1}; GC-MS (EI, 70eV): *m/z* (%) = (M^+, 332 (100), 272 (16), 251 (12); Anal. Calcd for C, 61.35; H, 3.94; Found: C, 61.23; H, 3.76; HRMS: (EI, 70 eV): calcd for $C_{17}H_{13}O_3S[M]^+$: 332.0342; found: 332.0346.

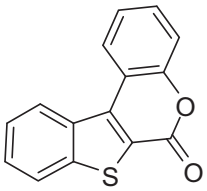
3-(Naphthalen-2-yl)-2-methoxycarbonylbenzo[*b*]thiophene (35h); Starting with **33** (100 mg, 0.36 mmol), 2-naphthylboronic acid (74 mg, 1.2 equiv,), $Pd(PPh_3)_4$ (21 mg, 5 mol %), K_3PO_4 (114 mg, 1.5 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **35h** was obtained as colorless solid (75.1 mg, 64 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, OCH_3, 3H), 7.87 (dd, *J* = 8.3, 2.8 Hz, 2H), 7.79-7.82 (m, 3H), 7.38-7.52 (m, 5H), 7.23-7.31 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.2 (OCH_3), 121.5, 123.8, 124.3, 125.1, 125.3, 126.2, 126.5, 126.8, 126.8, 127.1, 127.5 (CH). 131.1, 131.9, 132.1, 139.2, 139.3, 143.2 (C), 161.9 (CO); IR (KBr): ν = 3419, 2985, 2922, 2852 (s), 1718, 1598, 1523, 1434, 1274, 1267, 1228 (s), 1199, 1153, 1121, 1080, 1056, 1015 (m), 985, 963, 949, 907, 892, 865 (w), 817, 794, 778, 754, 748, 736, 718, 660, 621, 604, 556 (s) cm^{-1}; GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 318 (100), 287 (61), 258 (33), 215 (14); Anal. Calcd for C, 75.45; H, 4.43; Found: C, 75.13; H, 4.12; HRMS: (EI, 70 eV): calcd for $C_{20}H_{14}O_2S[M]^+$: 318.0709; found: 318.0713.



6.4.3 6*H*-[1]Benzothieno[2,3-*C*]chromen-6-one (36);

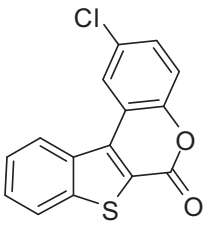
General procedure J; To a CH_2Cl_2 solution of **35** BBr_3 was added at 0 °C. The solution was stirred and allowed to warm to room temp during 2 h. To the solution was added an aqueous solution of KO-*tert*-BuOH (0.1 M) and the solution was stirred for 15 min. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2. The combined organic portion was dried over (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The product was purified by chromatography (silica gel, heptane/EtOAc).

6*H*-[1]Benzothieno[2,3-*C*]chromen-6-one (36a); Starting with **35e** (75 mg, 0.25 mmol),



BBr_3 (1.5 ml, 4 equiv.), Pot. *tert*-butoxide (0.1 M, aqueous sol), following the general procedure J, **36a** was obtained as white crystalline solid (37.8 mg, 60 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57-8.61 (m, 1H), 8.43-8.46 (m, 1H), 7.95-7.98 (m, 1H), 7.50-7.58 (m, 2H), 7.46-7.48 (m, 2H), 7.36-7.41 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 118.1, 118.3, 123.4, 123.9, 124.7, 125.6, 125.9, 128.2 (CH), 126.2, 129.8, 135.1, 138.6, 143.6, 152.7, 157.9 (CO); IR (KBr): v = 1734 (s), 1572, 1466, 1432 (m), 1289, 1221, 1193, 1034 (s), 1022, 831 (m), 776, 732, 721, 682, 619 (s) cm^{-1}; GC-MS: (EI, 70 eV): *m/z* (%) = (M^+, 252.9 (100), 224 (25), 195 (18), 152 (17); Anal. Calcd for $C_{15}H_8O_2S$; C, 71.41; H, 3.20; S, 12.71; Found: C, 71.45; H, 3.19; S, 11.97; HRMS: (EI, 70 eV): calcd for $C_{15}H_8O_2S[M^+]$: 252.0245; found: 252.0241.

2-Chloro-6*H*-[1]Benzothieno[2,3-*C*]chromen-6-one (36b); Starting with **35g** (50 mg, 0.180



mmol), BBr_3 (1.5 ml, 4 equiv.), Pot. *tert*-butoxide (0.1 M, aqueous sol), following the general procedure J, **36a** was obtained as white powder (21.5 mg, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 3.1 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.30-7.46 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 113.8, 114.6, 121.7, 125.2, 126.8, 129.3, 133.8 (CH), 129.1, 131.7, 136.3, 137.5, 138.3, 144.5, 156.2, 162.3 (CO); IR (KBr): v = 1720, 1687, 1576 (s), 1349, 1256, 1172, 1186 (s), 982. 347 (m), 751, 734, 614, 586 (s) cm^{-1}; GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 286 (100), 25 (31); Anal. Calcd for C, 62.83; H, 2.46; Cl, 12.36; Found: C, 61.88; H, 2.34; HRMS: (EI, 70 eV): calcd for $C_{15}H_7ClO_2S[M^+]$: 285.9945; found: 285.9941.

6.4.4 Synthesis of 2,3-dibromonaphthalene-1,4-diol (38);

General procedure K for the synthesis of 38; A suspension of **37** (2.0 g) in 30 ml of diethyl ether was shaken in a separatory funnel with a freshly prepared solution of $Na_2S_2O_4$ (5.00 g) in 10 ml of water. After the mixture was shaken for 1h, the organic layer was separated, washed with brine (2 x 25 ml), dried over Na_2S0_4, and then concentrated on rot.vap to give of **38** as a brown solid (2.2 g, 90 %).

Synthesis of 2,3-Dibromonaphthalene-1,4-diol (38); Starting with **37** (2.0 g, 1.0 equiv.), $Na_2S_2O_4$ (5.00 g), following the general procedure K, compound **38** was obtained as brown solid (1.9 g, 94 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.63 (s, 2H), 7.47-7.50 (m, 2H), 8.09-8.12 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 104.1 (C), 122.5 (2-CH), 127.1 (2-CH), 134.5 (C), 143.3 (C); HRMS: (EI, 70 eV): calcd for $C_{10}H_6Br_2O_2[M^+]$: 315.2741; found: 315.2745.

6.4.5 2,3-Dibromonaphthalene-1,4-diyl bis(trifluoromethanesulfonate) (39);

To a solution of **39** (1.0 equiv.) in CH_2Cl_2 (2.5 ml/mmol) was added pyridine (2.0 equiv.) at 20 °C under an argon atmosphere. After stirring for 10 min at 0 °C, Tf_2O (1.5 equiv.) was added. The mixture was allowed to warm to 20 °C and stirred for further 6 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was directly purified by chromatography without aqueous work up (flash silica gel, heptane/EtOAc).

2,3-Dibromonaphthalene-1,4-diyl bis(trifluoromethanesulfonate) (39); Starting with **38** (1.0 g, 1.0 equiv.) in CH_2Cl_2 (25 ml), pyridine (1.0 ml, 1.5 mmol) and Tf_2O (2.7 ml, 2.5 equiv.), following the general procedure H, compound **39** was obtained as white crystalline solid (1.77 g, 96 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69-7.72 (m, 2H), 8.10-8.13 (m, 2H); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -71; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 116.1 (2C), 118.8 (q, $J_{F,C}$ = 319.0 Hz, $2CF_3$), 122.2 (2-CH), 127.3 (2C), 129.9 (2-CH), 142.6; GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 582 (100), 449 (51), 385 (66), 357 (43), 237 (72), 207 (60), 181 (40); HRMS: (EI, 70 eV): calcd for $C_{12}H_4Br_2F_6O_6S_2[M^+]$: 581.7694 found: 581.7691.

6.4.6 2,3-Bis(2-methoxyphenyl)naphthalene-1,4-dione (41a);

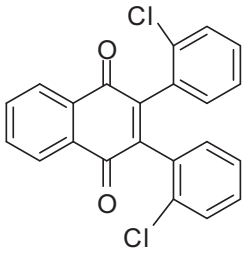
General procedure B for Suzuki–Miyaura reactions: A 1,4-dioxane (5 ml) solution of K_3PO_4 (1.5 equiv. per cross-coupling step), $Pd(PPh_3)_4$ (5 mol %) and aryl-boronic acid (1.0-1.1 equiv. per cross-coupling step) was stirred at 90-110 °C for 4 h. With out aqua workup the DCM filtrate was concentrated in vacuo. The residue was purified by column chromatography (flash silica gel, heptane-EtOAc 9:1).

2,3-Bis(2-methoxyphenyl)naphthalene-1,4-dione (41a); Starting with **39** (100 mg, 0.17 mmol), 2-methoxyphenylboronic acid (60 mg, 2.0 equiv.), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (216 mg, 3.0 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **41a** was obtained (45.2 mg, 60 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 6H, CH_3), 6.66 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 2.6 Hz, 2H), 7.11 (dd, J = 8.8, 2.4 Hz, 2H), 7.69-7.72 (m, 2H), 8.08-8.11 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.8 (2-OCH_3), 111.7 (2-CH), 124.6 (2C), 124.9 (2C), 126.7 (2-CH), 129.1, (2-CH), 129.7 (2-CH), 132.6 (2C), 133.7 (2-CH), 144.6 (2C),155.2 (2C), 183.3 (2CO); GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 438 (98), 407 (67), 372 (56); HRMS: (EI, 70 eV): calcd for $C_{24}H_{16}Cl_2O_4[M^+]$: 438.0427; found: 438.0426.

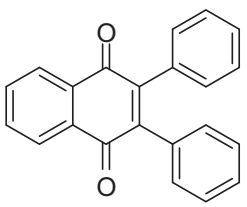
2,3-Bis(4-methoxyphenyl)naphthalene-1,4-dione (41b); Starting with **39** (100 mg, 0.17 mmol), 4-methoxyphenylboronic acid (60 mg, 2.0 equiv.), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (216 mg, 3.0 equiv.)and 1,4-dioxane (5 ml), following the general procedure B, **41b** was obtained (44.6 mg, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.71 (s, 6H, OCH_3), 6.68-6.73 (m, 4H), 6.93-6.98 (m, 4H), 7.68-7.71 (m, 2H), 8.09-8.12 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 53.2 (2-OCH_3), 108.1 (4-CH), 120.4 (2C), 121.3 (4-CH), 128.4 (2-CH), 131.3 (2C), 132.6 (2C), 139.5 (2-CH), 154.1 (2C), 179.9, (2CO); GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 370 (98), 311 (67); HRMS: (EI, 70 eV): calcd for $C_{24}H_{18}O_4[M^+]$: 370.7315; found: 370.7311.

2,3-Di-p-tolylnaphthalene-1,4-dione (41c); Starting with **39** (100 mg, 0.17 mmol), 4-methylphenylboronic acid (45 mg, 2.0 equiv.), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (216 mg, 3.0 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **41c** was obtained (43 mg, 74 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (s, 6H, CH_3), 7.89 (dd, J = 8.2, 3.3 Hz, 4H), 7.81 (dd, J = 8.1, 3.4 Hz, 4H), 7.66-7.71 (m, 2H), 8.07-8.11 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.3 (2-CH_3), 126.6 (2C), 127.3 (2-CH), 128.4 (4-CH), 130.5 (4-CH), 132.2 (2C), 133.7 (2CH), 138.1 (2C), 145.5 (2C), 184.9 (2CO); GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 338 (92), 156 (63); HRMS: (EI, 70 eV): calcd for $C_{24}H_{18}O_2[M^+]$: 338.2362; found: 338.2357.

2,3-Bis(2-chlorophenyl)naphthalene-1,4-dione (41d); Starting with **39** (100 mg, 0.17 mmol), 2-chlorophenylboronic acid (50 mg, 2.0 equiv.), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (216 mg, 3.0 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **41d** was obtained (41.6 mg, 64 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.12 (dd, J = 8.6, 2.7 Hz, 4H), 7.09-7.15 (m, 2H), 7.28 (d, J = 8.6 Hz, 2H), 8.73-7.76 (m, 2H), 8.13-8.16 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 125.7 (2-CH), 125.9 (2-CH), 127.9 (2-CH), 128.2 (2-CH), 128.9 (2-CH), 131.1 (2C), 132.0 (2C), 132.8 (2C), 145.0 (2C), 182.3 (2CO); GCMS: (EI, 70eV): *m/z* (%) = (M^+, 378 (97); HRMS: (EI, 70 eV): calcd for $C_{22}H_{12}Cl_2O_2[M^+]$: 378.1754; found: 378.1751.

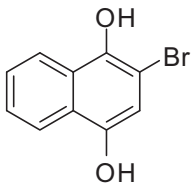


2,3-Diphenylnaphthalene-1,4-dione (41e); Starting with **39** (100 mg, 0.17 mmol), phenylboronic acid (42 mg, 2.0 equiv.), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (216 mg, 3.0 equiv.) and 1,4-dioxane (5 ml), following the general procedure B, **41e** was obtained (37 mg, 70 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.05-7.11 (m, 4H), 7.19-7.27 (m, 6H), 7.76-7.82 (m, 2H), 8.17-8.23 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 123.7 (4-CH), 125.6 (4-CH), 127.9 (2-CH), 128.2 (2CH), 128.9 (2C), 131.1 (2C), 132.8 (2C), 181.3 (2CO); GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 310 (92); HRMS: (EI, 70 eV): calcd for $C_{22}H_{14}O_2[M^+]$: 310.2561; found: 310.2557.



6.4.7 2-Bromonaphthalene-1,4-diol (43);

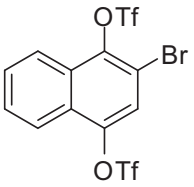
2-Bromonaphthalene-1,4-diol (43); Starting with **42** (1.0 g, 1.0 equiv.), $Na_2S_2O_4$ (5.00 g), following the general procedure K, compound **43** was obtained as brownish solid (0.9 g, 88 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.68 (s, 2H), 6.73 (s, 1H), 7.62-7.63 (m, 2H), 8.14-8.17 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 104.1 (C), 105.3 (C), 122.5 (2-CH), 127.1 (2-CH), 131.5 (CH), 134.5 (C), 143.3 (2C); HRMS: (EI, 70 eV): calcd for $C_{10}H_7BrO_2[M^+]$: 237.1643; found: 237.1643.



6.4.8 2-Bromonaphthalene-1,4-diyl bis(trifluoromethanesulfonate) (44);

To a solution of **39** (1.0 equiv.) in CH_2Cl_2 (2.5 ml/mmol) was added pyridine (2.0 equiv.) at 20 °C under an argon atmosphere. After stirring for 10 min at 0 °C, Tf_2O (1.5 equiv.) was added. The mixture was allowed to warm to 20 °C and stirred for further 6 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was directly purified by chromatography without aqueous work up (flash silica gel, heptane/EtOAc).

2-Bromonaphthalene-1,4-diyl bis(trifluoromethanesulfonate) (44); Starting with **38** (0.5 g, 1.0 equiv.) in CH_2Cl_2 (15 ml), pyridine (0.5 ml, 0.8 mmol) and Tf_2O (1.5 ml, 2.5 equiv.), following the general procedure H, **44** was obtained (0.7 g, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69-7.72 (m, 3H), 8.10-8.13 (m, 2H); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 109.6 (CH), 115.7 (2-CH), 118.8 (q, $J_{F,C}$ = 317.0 Hz, $2CF_3$), 122.2 (2-CH), 127.3 (2C), 128.9 (C), 141.3 (C), 142.6 (C); GC-MS: (EI, 70eV): *m/z* (%) = (M^+, 502 (97), 124 (61); HRMS: (EI, 70 eV): calcd for $C_{12}H_5BrF_6O_6S_2[M^+]$: 501.8773; found: 501.8769.



General procedure **B for Suzuki–Miyaura reactions:** A 1,4-dioxane (5 ml) solution of K_3PO_4 (1.5 equiv. per cross-coupling step), $Pd(PPh_3)_4$ (5 mol%) and aryl-boronic acid **16a-h** (1.0-1.1 equiv. per cross-coupling step) was stirred at 90-110 °C for 4 h. After cooling to 20 °C, with out work up the DCM filtrate was concentrated in vacuo. The residue was purified by column chromatography (flash silica gel, heptane-EtOAc 9:1).

Appendix

7 Crystallographic Data

7.1 Crystal data and structure refinement for **2,8-Bis(methoxycarbonyl)-3,6-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene (2)**

Identification code	zh-145	
Empirical formula	$C_{14}H_8Cl_2O_4S_2$	
Formula weight	375.22	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group (H.-M.)	F d d 2	
Space group (Hall)	F 2 -2d	
Unit cell dimensions	a = 51.286 (4) Å	α = 90.00°.
	b = 3.8608 (3) Å	β = 90.00°.
	c = 14.4525 (9)Å	γ = 90.00°.
Volume	2861.6(3) $Å^3$	
Z	8	
Density (calculated)	1.742 Mg/m^3	
Absorption coefficient	0.759 mm^{-1}	
F(000)	1520	
Θ range for data collection	4.910 to 40.817°.	
Reflections collected	1870	
Independent reflections	1732 [R(int) = 0.026]	
Absorption correction	multi-scan	
Max. and min. transmission	0.9975 and 0.9127	

7.2 Crystal data and structure refinement for **2,7-Bis(butoxycarbonyl)-3,6-dichlorobenzo[1,2-*b*;5,6-*b*']dithiophene (3)**

Identification code	zh-260	
Empirical formula	$C_{20}H_{20}Cl_2O_4S_2$	
Formula weight	459.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	C 2/c	
Space group (Hall)	C 2yc	
Unit cell dimensions	a = 17.2094 (12) Å	α = 90.00°
	b = 12.1821 (8) Å	β = 91.956 (3)°
	c = 10.0334 (6) Å	γ = 90.00°.
Volume	2102.2(2) $Å^3$	
Z	4	
Density (calculated)	1.451 Mg/m^3	
Absorption coefficient	0.531 mm^{-1}	
F(000)	952	
Crystal size	0.45 × 0.08 × 0.06 mm^3	
Θ range for data collection	5.7–58.8°.	
Reflections collected	2499	
Independent reflections	2986 [R(int) = 0.032]	
Absorption correction	multi-scan	
Max. and min. transmission	0.9924 and 0.9700	
Refinement method	Full-matrix	
Goodness-of-fit on F^2	0.0690	
Final R indices [I>2σ(I)]	R1 = 0.0477, wR2 = 0.1157	
R indices (all data)	R1 = 0.0879, wR2 = 0.1271	

7.3 Crystal data and structure refinement for **2-(4-Fluorophenyl)naphthalen-1-yl trifluoromethanesulfonate (17e)**

Identification code	zh-67	
Empirical formula	$C_{17}H_{10}F_4O_3S$	
Formula weight	370.31	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/c	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 15.3267(9) Å	α = 90.00°.
	b = 13.8391(8) Å	β = 103.902(2)°.
	c = 7.7406(4) Å	γ = 90.00°.
Volume	1593.75(16) $Å^3$	
Z	4	
Density (calculated)	1.543 Mg/m^3	
Absorption coefficient	0.260 mm^{-1}	
F(000)	752	
Crystal size	0.34 × 0.24 × 0.18 mm^3	
Θ range for data collection	5.9–54.1°.	
Reflections collected	16730	
Independent reflections	4253 [R (int) = 0.042]	
Absorption correction	multi-scan	
Max. and min. transmission	2.74 and 29.1	
Refinement method	Full-matrix	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2σ(I)]	R1 = 0.0432, wR2 = 0.1071	
R indices (all data)	R1 = 0.0663, wR2 = 0.1153	

7.4 Crystal data and structure refinement for **2-(4-Chlorophenyl)-1-(3, 5-dimethylphenyl) naphthalene (18d)**

Identification code	zh-103a	
Empirical formula	$C_{24}H_{19}Cl$	
Formula weight	342.84	
Temperature	173(2) K	
Wavelength	0.71073Å	
Crystal system	Triclinic	
Space group (H.-M.)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	a = 6.4048 (4) Å	α = 98.989 (3)°
	b = 10.9621 (5) Å	β = 92.056 (3)°
	c = 13.4750 (7) Å	γ = 104.637(2)°
Volume	901.32 (8) $Å^3$	
Z	2	
Density (calculated)	1.263 Mg/m^3	
Absorption coefficient	0.214 mm^{-1}	
F(000)	360	
Crystal size	0.99 × 0.12 × 0.04 mm^3	
Θ range for data collection	5.4–58.8°.	
Reflections collected	4748	
Independent reflections	2590 [R(int) = 0.066]	
Absorption correction	multi-scan	
Max. and min. transmission	0.992 and 0.816	
Refinement method	Full-matrix	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2σ(I)]	R1 = 0.049, wR2 = 0.1480	
R indices (all data)	R1 = 0.0778, wR2 = 0.1342	

7.5 Crystal data and structure refinement for **1, 2-Bis(4-methylphenyl)naphthalen (19b)**

Identification code	zh-74	
Empirical formula	$C_{24}H_{20}$	
Formula weight	308.40	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/c	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 6.562(2) Å	α = 90.00°.
	b = 10.835(3) Å	β = 93.020 (15)°.
	c = 25.028(8) Å	γ = 90.00°.
Volume	1777.0 (10) $Å^3$	
Z	4	
Density (calculated)	1.153 Mg/m^3	
Absorption coefficient	0.065 mm^{-1}	
F(000)	656	
Crystal size	0.80 × 0.24 × 0.12 mm^3	
Θ range for data collection	5.0–56.7°.	
Reflections collected	14259	
Independent reflections	4007 [R (int) = 0.0374]	
Absorption correction	multi-scan	
Max. and min. transmission	0.9499 and 0.9922	
Refinement method	Full-matrix	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2σ(I)]	R1 = 0.0767, wR2 = 0.1411	
R indices (all data)	R1 = 0.0492, wR2 = 0.1287	

7.6 Crystal data and structure refinement for **1, 2-Bis(4-chlorophenyl)naphthalene (19c)**

Identification code	zh-66	
Empirical formula	$C_{22}H_{14}Cl_2$	
Formula weight	349.23	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/c	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 6.4479(2) Å	α = 90.00°.
	b = 11.1817(4) Å	β = 90.344 (2)°.
	c = 23.3422(8) Å	γ = 90.00°.
Volume	1682.91(10) $Å^3$	
Z	4	
Density (calculated)	1.378 Mg/m^3	
Absorption coefficient	0.385 mm^{-1}	
F(000)	720	
Crystal size	0.40 x 0.13 x 0.10 mm^3	
Θ range for data collection	5.045 to 59.364°.	
Reflections collected	5277	
Independent reflections	3188 [R (int) = 0.0278]	
Absorption correction	multi-scan	
Max. and min. transmission	0.8614 and 0.9626	
Refinement method	Full-matrix	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2σ(I)]	R1 = 0.0429, wR2 = 0.0923	
R indices (all data)	R1 = 0.0821, wR2 = 0.1013	

7.7 Crystal data and structure refinement for **Synthesis of 1-(4-Bromo-1-hydroxynaphthalen-2-yl)ethanone (25)**

Identification code	zh-104	
Empirical formula	$C_{12}H_9BrO_2$	
Formula weight	265.10	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/c	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 10.4784(2) Å	α = 90.00°.
	b = 14.4026(3) Å	β = 108.9280 (10)°.
	c = 7.0563(2) Å	γ = 90.00°.
Volume	1007.33(4) $Å^3$	
Z	4	
Density (calculated)	1.153 Mg/m^3	
Absorption coefficient	4.054 mm^{-1}	
F(000)	528	
Crystal size	0.67 × 0.18 × 0.06 mm^3	
Θ range for data collection	5.0–72.0°.	
Reflections collected	14554	
Independent reflections	2922 [R (int) = 0.0268]	
Absorption correction	multi-scan	
Max. and min. transmission	2.83 and 30.00	
Refinement method	Full-matrix	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2σ(I)]	R1 = 0.0258, wR2 = 0.0702	
R indices (all data)	R1 = 0.0348, wR2 = 0.0734	

7.8 Crystal data and structure refinement for **6*H*-[1]benzothieno[2,3-*C*]chromen-6-ones (36a)**

Identification code	zh-22	
Empirical formula	$C_{15}H_8O_2S$	
Formula weight	252.27	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group (H.-M.)	P 21 21 21	
Space group (Hall)	P 2ac 2ab	
Unit cell dimensions	a = 3.8891 (3) Å	α = 90°.
	b = 15.1701 (12) Å	β = 90°.
	c = 18.5215 (16) Å	γ = 90°.
Volume	1092.73 (15) $Å^3$	
Z	4	
Density (calculated)	1.533 Mg/m^3	
Absorption coefficient	0.284 mm^{-1}	
F(000)	520	
Crystal size	0.95 × 0.13 × 0.09 mm^3	
Θ range for data collection	5.2–58.3°	
Reflections collected	3859	
Independent reflections	864 [R(int) = 0.109]	
Absorption correction	multi-scan	
Max. and min. transmission	0.7745 and 0.9749	
Refinement method	Full-matrix	
Goodness-of-fit on F^2	1.03	
Final R indices [I>2σ(I)]	R1 = 0.0400, wR2 = 0.0858	
R indices (all data)	R1 = 0.0617, wR2 = 0.0792	

5.8 Crystal data and structure refinement for **2,3-Dibromonaphthalene-1,4-diyl bis(trifluoromethanesulfonate) (39)**

Identification code	zh-93	
Empirical formula	C12H4Br2F6O6S2	
Formula weight	582.09	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	C 2/c	
Space group (Hall)	-C 2yc	
Unit cell dimensions	a = 26.7321(13) Å	α = 90°.
	b = 5.9885(2) Å	β = 115.335 (2).
	c = 24.5279(12) Å	γ = 90°.
Volume	3548.9(3) Å3	
Z	8	
Density (calculated)	2.179 Mg/m3	
Absorption coefficient	4.894 mm-1	
F(000)	2240	
Crystal size	0.51 × 0.06 × 0.02 mm3	
Θ range for data collection	2.98– 26.50°	
Reflections collected	2414	
Independent reflections	3692 [R(int) = 0.0606]	
Absorption correction	multi-scan	
Max. and min. transmission	0.9085 and 0.1892	
Refinement method	Full-matrix	
Goodness-of-fit on F2	0.974	
Final R indices [I>2σ(I)]	R1 = 0.0818, wR2 = 0.0733	
R indices (all data)	R1 = 0.0871, wR2 = 0.0414	

Abbreviations

Ac	Acetyl
Anal.	Elemental Analysis
bp.	Boiling point
calcd	Calculated
CI	Chemical Ionization
COSY	Correlated Spectroscopy
DEPT	Distortionless Enhancement by Polarization Transfer
dr	Diastereomeric ratio
ee	Enantiomeric excess
EI	Electron Impact
Et_2O	Diethyl ether
EtOH	Ethanol
GC	Gas Chromatography
GP	General Procedure
HMBC	Heteronuclear Multiple Bond Correlation
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
IR	Infrared Spectroscopy
MS	Mass Spectrometry
mp	Melting point
NaOEt	Sodium ethanolate
*n*BuLi	*n*-Butyllithium
NEt_3	Triethylamine
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser and Exchange Spectroscopy
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTf	Triflate
Ph	Phenyl
ppm	Parts per million

R_f	Retention factor
Tf_2O	Trifluoromethanesulfonic anhydride (triflic anhydride)
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
Tol	Tolyl (*p*-MeC_6H_4)
Tos	Tosyl (*p*-$MeC_6H_4SO_2$

Declaration/Erklärung

Here by I declare that this work has so far neither submitted to the Faculty of Mathematics and Natural Sciences at the University of Rostock nor to any other scientific Institution for the purpose of doctorate. Further more, I declare that I have compiled this work by myself and I have not used any other sources.

Hiermit erkläre ich, daß diese Arbeit bisher von mir weder an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht wurde.

Ferner erkläre ich, dass ich diese Arbeit selbständig verfasst und keine anderen als die darin angegebenen Hilfsmittel benutzt habe.

I hereby apply irrevocably to take oral examination and a presentation.

_____

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Research Projects

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International Centre for Chemical and Biological Sciences,
HEJ Research Institute of Chemistry, ICCBS, University of Karachi.

″ Isolation & Characterization of bioactive natural products from *Carthamus Oxycantha* ″

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1. **Zahid Hassan,** Sebastian Reimann, Kai Wittler, Ralf Ludwig, Alexander Villinger, Peter Langer, *Adv. Synth. Cat,* **2012, *4*,** 731-739

   Cyclization of 1,4-Phenylenediacrylic Acid with Thionyl Chloride and Subsequent Suzuki–Miyaura Reactions Revisited. The Products are Benzo[1,2-b;5,6-b']dithiophenes and not Benzo[1,2-b;4,5-b']dithiophenes.

2. **Zahid Hassan**, Alexander Villinger, Peter Langer, *Tetrahedron*, **2012**, (*in press*)

   Synthesis of arylated naphthalenes through Chemoselective cross coupling reactions (Br versus OTf, Cl) and role of electronic and steric effects.

3. **Zahid Hassan**, Munawar Hussain, Peter Langer, *Synlett,* **2011**, *13*, 1827-1830

   ***Synthesis of 1,2-Diaryl naphthalenes by Chemoselective Suzuki-Miyaura Reactions of 2-Bromo-1-(trifluoromethanesulfonyloxy) naphthalene*.**

4. **Zahid Hassan**, Peter Langer, *Synthesis,* **2011**, manuscript submitted.

   Synthesis of arylated quinones, A unique behaviour of triflates in Pd(0) catalyzed S-M cross coupling reactions.

5. **Zahid Hassan**, Peter Langer, **2012**, manuscript in prep.

   ***Synthesis of benzodithiazoles using N-benzyl DABCO tribromide (OATB) through oxidative cyclization of thiobenzanilides*.**

6. **Zahid Hassan**, Viqar Uddin Ahmad, Javid Hussain, Aqib Zahoor, Imran Nafees Siddiqui, Nasir Rasool and Muhammad Zubair, *Natural Product Communications,* **2010**, 5 (3), 351-506

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Awards / Scholarships

Mecklenburg-State Fellowship, Wissenschaftlicher Mitarbeiter, University of Rostock, Germany,

International Research Support Initiative Fellowship, IRSIP HEC Higher Education Commission Pak, 2007-2008.

Junior Research Fellow, HEJ Research Institute of Chemistry, ICCBS, University of Karachi, Pak, 2005-2007.

Minister Merit Scholarship, KPK- Pak.

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