TECHNISCHE UNIVERSITÄT WIEN
Vienna | Austria

Diploma Thesis

Novel Annulated Heterocycles Based on the Indolo[3,2,1-*jk*]carbazole Scaffold

conducted at the

Institute of Applied Synthetic Chemistry

at the **TU Wien**

under the supervision of

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Abstract

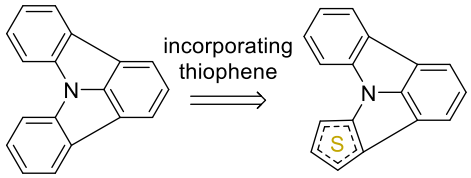
The field of organic electronics has seen an evolution from basic research to the emergence of sophisticated commercially available devices in just a few decades. This rapid development, especially in the field of organic light emitting diodes, was possible owing to tremendous efforts in research and the development of new organic materials with better functionality.

In the 1980s the first organic light emitting devices sparked enough interest to kickstart a whole research field even though they lacked the efficiencies to compete with their inorganic counterparts.

With the development of phosphorescent emitters, which allow for a theoretical quantum efficiency of 100%, a high demand for new and better host materials emerged. In a quest for a balanced and fast transport of electrons as well as holes in those host materials, bipolar molecules are a promising group of components.

Based on established triarylamine donor subunits, our research group recently introduced the fully planar indolo[3,2,1-*jk*]carbazole (ICz) as a novel building block, using a new CH activation protocol. Characterization of this particular molecular scaffold revealed weak acceptor characteristics of the ICz moiety. In previous works this tendency was increased by the introduction of pyridine-like nitrogen atoms into the aromatic system.

The goal of this thesis was to reverse this trend and develop donor building blocks based on the ICz scaffold *via* the incorporation of electron rich thiophene. Also, a fine tuning of the energy levels depending on the positioning of the sulfur atom was matter of interest.



Electron rich building block base on the ICz scaffold

Furthermore, the possibility to incorporate the ICz moiety into larger annulated systems was explored, owing to a high triplet energy (E_T) and thermal stability of the ICz building block.

Kurzfassung

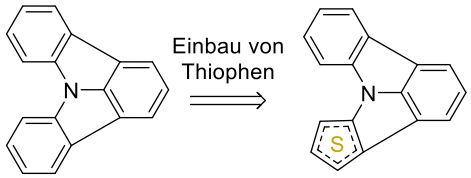
Der Bereich der organischen Elektronik hat die Entwicklung vom Stadium der Grundlagenforschung zur Marktreife in nur wenigen Jahrzehnten durch intensive Forschungsarbeit in der Entwicklung neuer und besserer funktioneller organischer Materialien durchgemacht.

Die ersten organischen Leuchtdioden in den 1980er Jahren konnten, obwohl sie hinsichtlich der Effizienz nicht an ihre anorganischen Pendants heranreichten, genug Aufmerksamkeit erregen, um ein eigenes Forschungsgebiet ins Leben zu rufen.

Mit der Entwicklung von phosphoreszenten Emittern, durch die eine theoretische interne Quanten-ausbeute von 100 % ermöglicht wird, stieg die Nachfrage nach neuen und besseren Host Materialien sprunghaft an. Um einen, für hohe Effizienz notwendigen, ausgewogenen Transport von Elektronen sowie Löchern zu erreichen, stellen bipolare Moleküle eine attraktive Klasse an Materialien dar.

In Anlehnung an etablierte Triarylamin Donoren und unter Verwendung einer neuen Methode der CH Aktivierung, wurde kürzlich Indolo[3,2,1-*jk*]carbazol (ICz) von unserer Forschungsgruppe als neuer molekularer Baustein vorgestellt. Die beobachteten geringen Akzeptor-eigenschaften des Moleküls wurden in vorangehenden Arbeiten durch den Einbau von Stickstoff in die aromatische Struktur weiter erhöht.

Das Ziel dieser Arbeit war die Herstellung elektronenreicher Bausteine für die organische Elektronik durch den Einbau elektronenreicher Thiophene in das ICz System. Außerdem sollte die Möglichkeit der genauen Anpassung der Energie-niveaus durch die Positionierung des Schwefels realisiert werden.



Elektronenreicher Baustein

Darüber hinaus wurde, aufgrund der hohen Tripletenergie (E_T) und thermischen Stabilität des ICz Bausteins, dessen Einbau in größere, annelierte Systeme untersucht.

General remarks

Labeling of substances

Identification of substances is achieved by strict sequential numbering. Substances previously reported in literature receive Arabic numbers, whereas substances unknown to literature are labeled with Roman numbers.

References to literature citations

References to literature are given within the text by superscript Arabic numbers in square brackets.

Nomenclature

The nomenclature of chemical compounds not described in literature is based on the rules of Chemical Abstracts. Other compounds, reagents and solvents may be described by simplified terms, trivial or trade names.

Abbreviations

Besides common abbreviations in the English language and chemical element symbols the below listed short forms are used.

ACN	acetonitrile
aq.	aqueous
Cz	9*H*-carbazole
CBP	4,4'-bis(9-carbazolyl)biphenyl
dba	dibenzylideneacetone
DCM	dichloromethane
DMAc	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethylsulfoxide
AcOH	acetic acid
$Pd(OAc)_2$	palladium(II)acetate
Dppf	1,1'-bis(diphenylphosphino) ferrocene
EA	ethylacetate
E_T	triplet energy
eq.	equivalents
GC	gas chromatography
MS	mass spectrometry
HOMO	highest occupied molecular orbital
HR-MS	high resolution mass spectrometry
ICz	indolo[3,2,1-*jk*]carbazole
LUMO	lowest unoccupied molecular orbital
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NHC-lig.	1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium chloride
NMR	nuclear magnetic resonance
OLED	organic light emitting diode
PCz	9-phenyl-9*H*-carbazole
PhOLED	phosphorescent OLED
rf	reflux
rt	room temperature
S_NAr	nucleophilic aromatic substitution
THF	tetrahydrofuran
TLC	thin layer chromatography
DMDO	dimethyldioxirane
m-CPBA	*meta*-chloroperoxybenzoic acid

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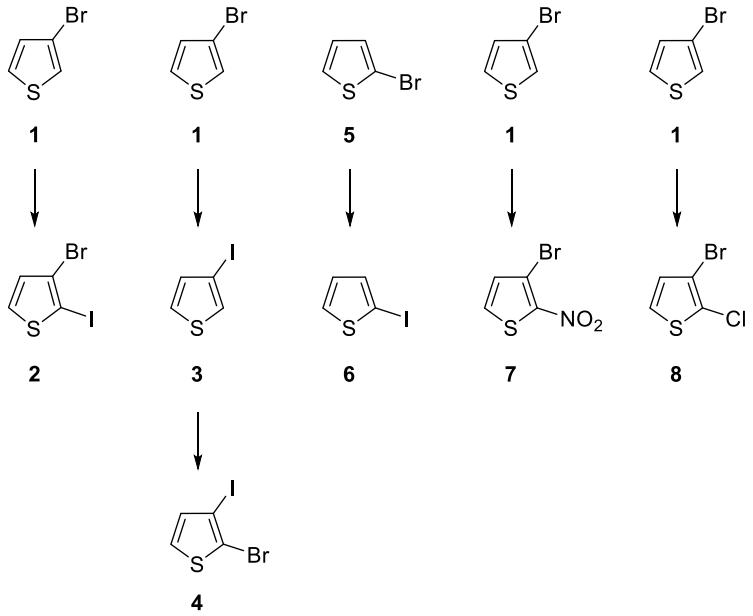
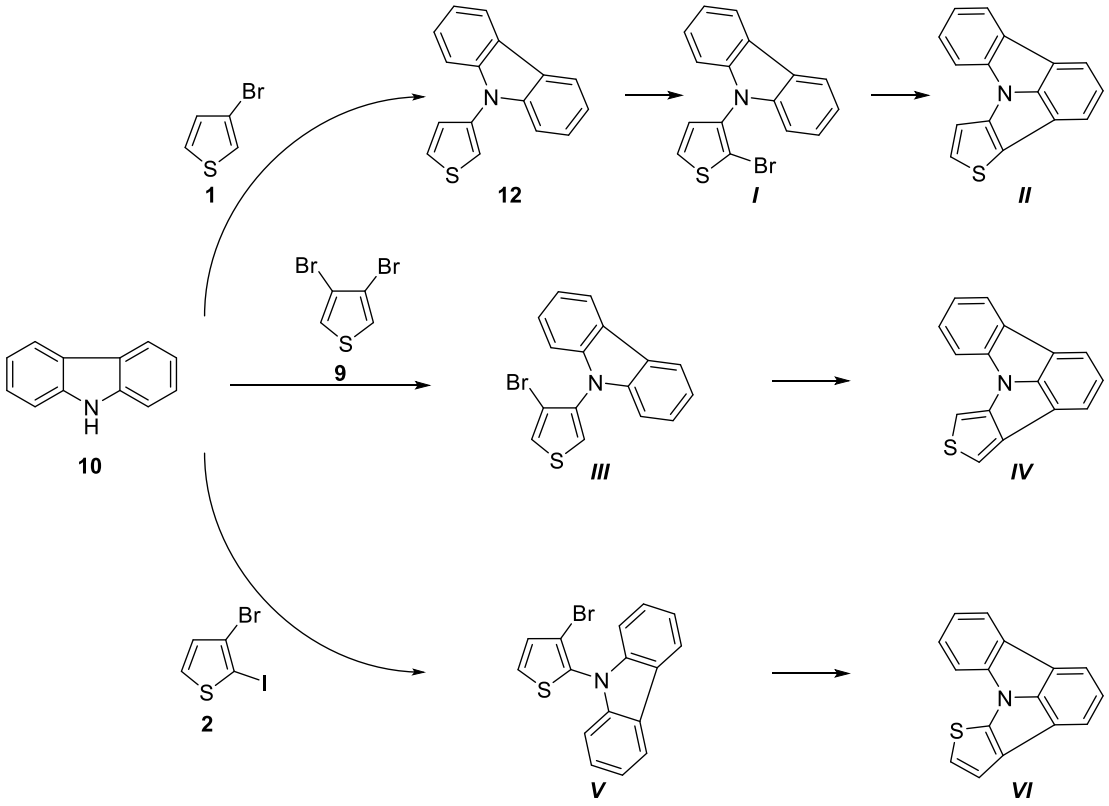
A Formula scheme

A.1 Synthesis towards SICz systems

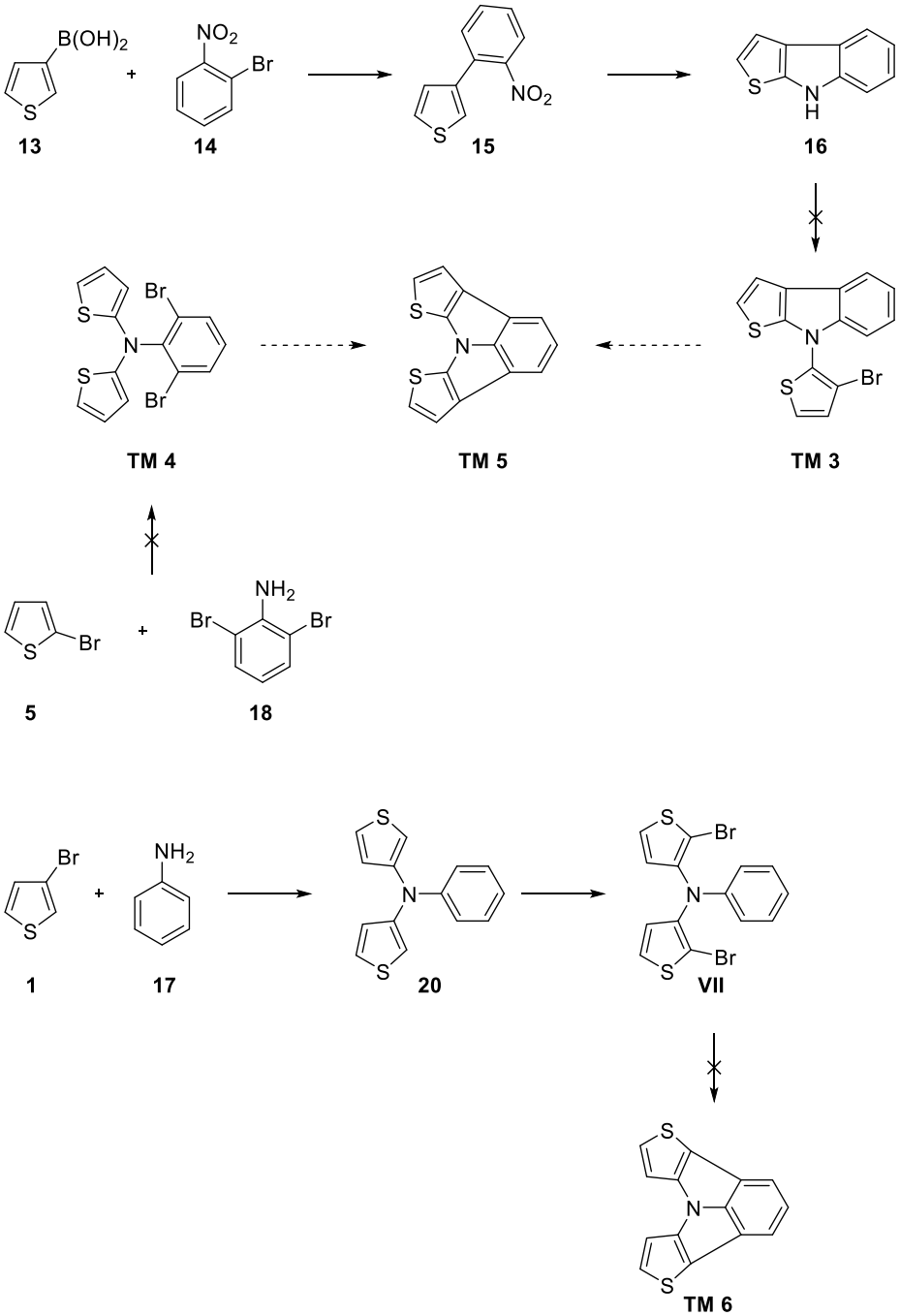
A.1.1 Precursors



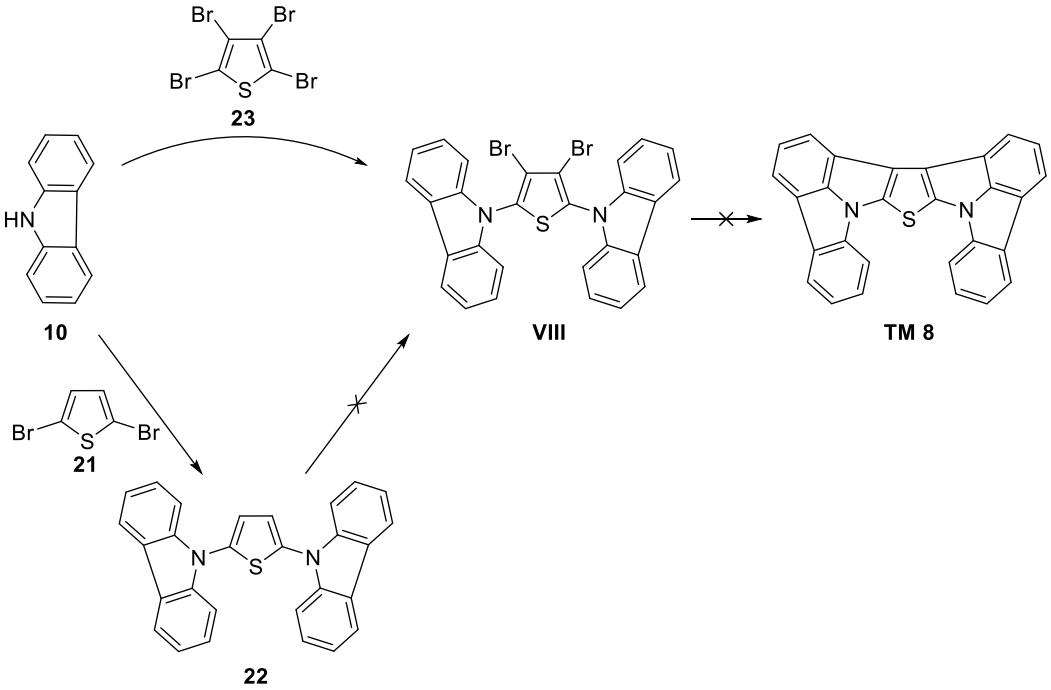
A.1.2 Target molecules

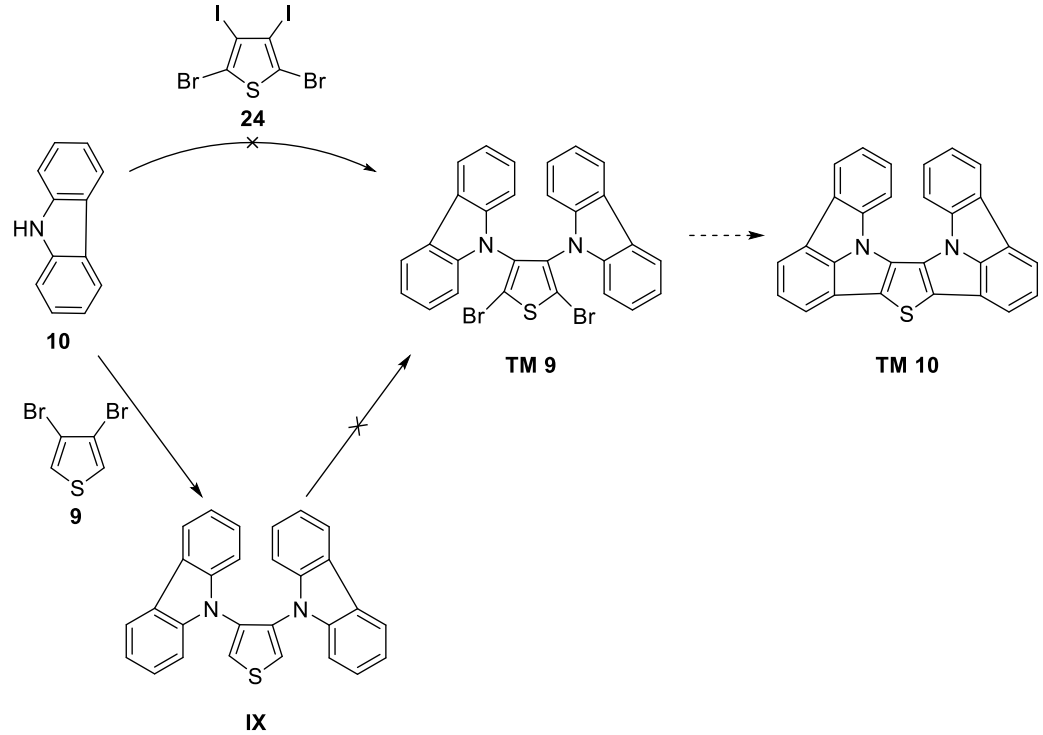


A.2 Synthesis towards S_2ICz systems

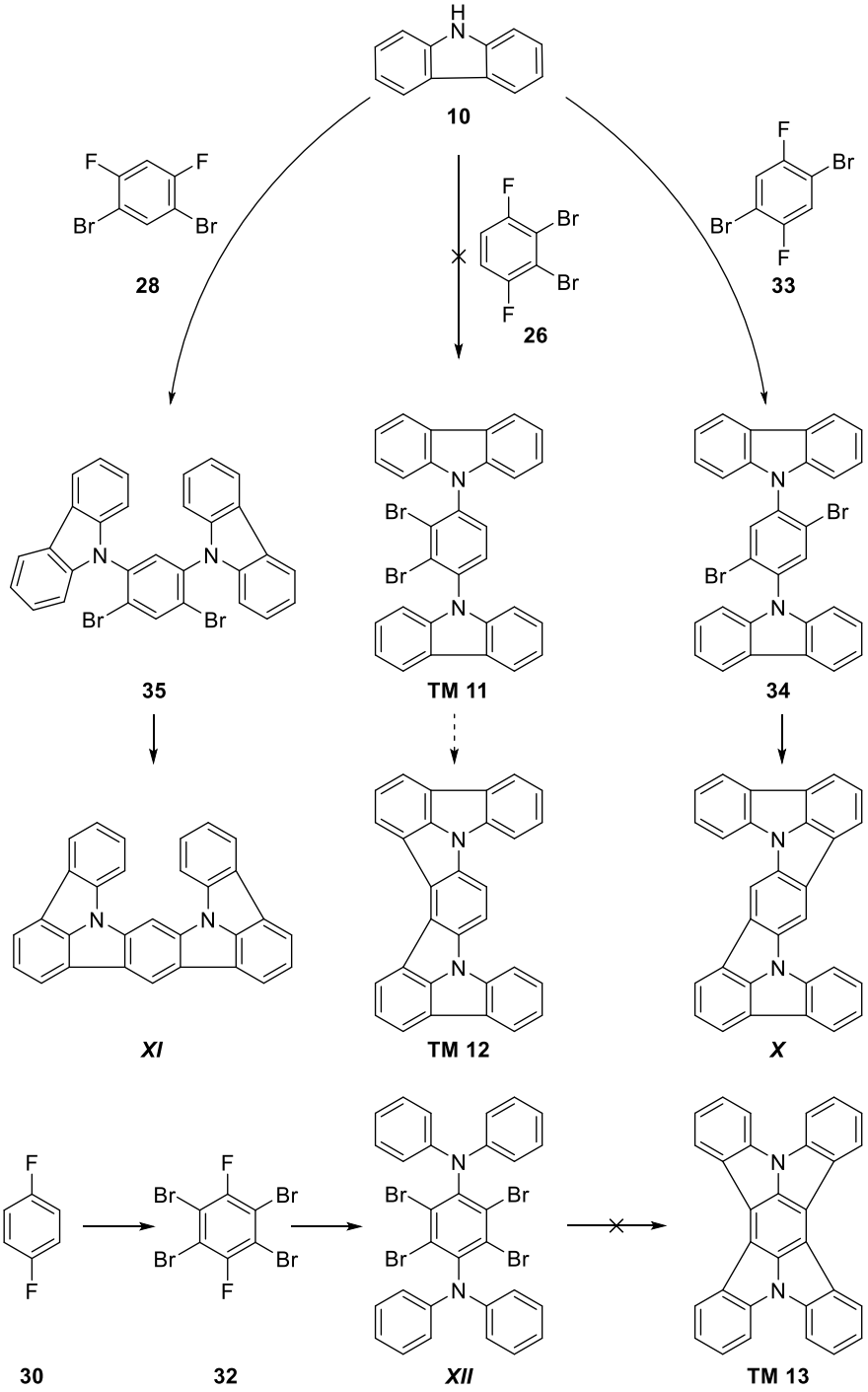


A.3 Synthesis towards large annulated thiophene linked systems





A.4 Synthesis towards large annulated benzene linked systems



B General part

B.1 Organic electronics

The field of organic electronics deals with the development of novel semiconducting organic small molecules or polymers and the investigation of their structure-property relationships. Recent years have seen advances in this field leading to the implementation of functional organic materials in devices on a commercial level. The most prominent aspect of this development to date is the use of OLED displays in handheld mobile devices and flat screen TVs. In the future ongoing research potentially will allow organic electronics to surpass their inorganic, silicon-based counterparts in certain applications while featuring the same functionality at lower cost with some advantages unique to organic materials. However, the field is not limited to light emitting devices. Other aspects of modern electronics such as photovoltaics, transistors or sensing applications can greatly benefit from the use of organic materials, which enable new and unique features such as thin film and flexible devices.[1–3]

B.1.1 Organic light emitting diodes (OLEDs)

Though electroluminescence was already known, the widespread interest in this research field was first sparked by the report of a thin-film light emitting diode by Tang and van Slyke in the 1980s.[2] Since then the simple two-layered architecture has been modified and modern devices are comprised of multiple layers to allow for better efficiency. Still the working principle remains the same. The organic semiconductor is sandwiched between two electrodes. For lighting or display applications one of the electrodes, usually the cathode, is reflective while the anode is transparent to allow for emission of the light. Charge carriers (electrons and holes) are injected into the transporting layers from the cathode and the anode, respectively, and migrate, driven by an applied electric field, towards each other. Upon recombination an electron-hole-pair, an exciton, is formed. Subsequently, the exciton decays and a photon is emitted.[3,4]

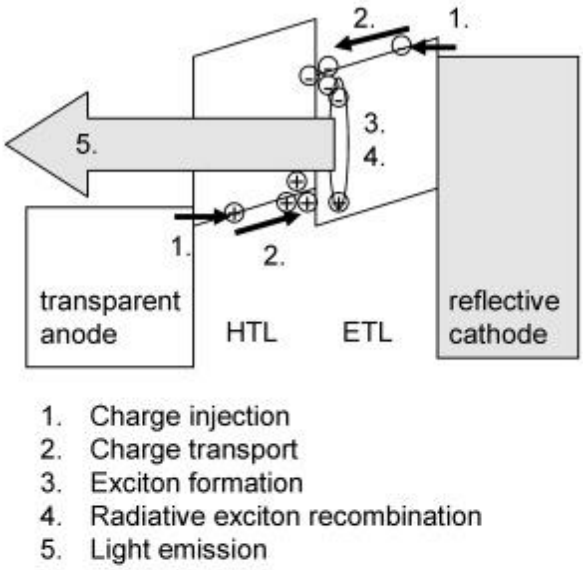


Figure 1: Working principle of an OLED device[3]

Several types of OLEDs can be differentiated based on the exact mechanism of electroluminescence. The first devices harnessed light from fluorescent emission originating from an excited singlet state. Upon electronic excitation singlet and triplet excitons are formed in a ratio of 1:3, limiting the internal quantum yield of those devices to 25%. More recently, other OLED emitters were investigated to overcome this drastic efficiency limitation. Some examples are phosphorescent and thermally activated delayed fluorescence (TADF) emitters.

B.1.2 Phosphorescent OLEDs (PhOLEDs)

In contrast to the aforementioned fluorescent dyes, a phosphorescent emitter can harvest both singlet and triplet excitons for light emission and thus has a theoretical internal quantum yield of 100%. A lot of research and development towards PhOLEDs have been following first reports by Forrest et al. in 1998.[5] To date a variety of different transition-metal complexes (Ir(III), Pt(II), Au(III), Os(II), Ru(II)), which exhibit strong phosphorescent electroluminescence are used for the fabrication of high-efficiency PhOLED devices. However, when triplet exited states are employed, increased concentration quenching effects due to elevated lifetimes have to be taken into account. To mitigate this efficiency roll-off, the dispersion of small amounts of the emitters into a host matrix is of crucial importance. [6]

B.1.3 Host materials

As mentioned above, the employment of a host material is indispensable for high-efficiency PhOLEDs. In the emission layer of such a device the guest (phosphorescent emitter) is

dispersed in a host. Some prerequisites exist for the host materials to guarantee the efficient use of the generated excitons and to prevent quenching processes. A good charge carrier mobility of the host material is necessary since electrons and holes need to migrate from the electrodes to form excitons, which then need to be transferred to the emitters. Another important aspect is the triplet energy E_T of the host material. It must not be lower than that of the emitter to prevent reverse energy transfer. Furthermore, a high thermal and morphological stability is required to keep the homogeneous dispersion system stable and enable a satisfactory device lifetime.[6]

B.1.3.1 Bipolar host materials

The use of unipolar molecules for electron and hole transport leads to an unbalanced mobility, which in turn causes a shift of the recombination zone towards either electrode, which decreases its overall volume. This smaller recombination zone causes increased triplet-triplet annihilation and thus reduces the device efficiency. One attractive solution to this problem is the employment of bipolar host materials. This donor-acceptor approach combines electron and hole transport in one single molecule. HOMO and LUMO levels of all host materials should match those of neighboring layers to facilitate charge injection.[6,7]

B.1.4 Organic field effect transistors (OFETs)

The use of organic semiconductors for the fabrication of field effect transistors is very attractive as it opens the door for cheap, mass producible, flexible thin film devices such as electronic papers or chemical sensors. The core principle of an OFET is the modulation of an electric current between a source and a drain by application of a gate voltage. Such a device consists of a gate electrode, a gate dielectric, an organic semiconductor and source and drain electrodes. Upon application of a gate voltage, charge carriers accumulate on the interface between the dielectric and the organic semiconductor. These charge carriers act as a conductive channel between the source and drain electrode. One crucial parameter for OFET materials is the mobility of said carriers. One relatively well studied model system is pentacene which exhibits high mobilities of well over 1 $cm^2\ V^{-1}\ s^{-1}$. However, the exact value is largely dependent on contaminations due to facile oxidation under ambient conditions. In order to increase device performance extensive research efforts are made to develop new high performing organic semiconductor materials.[8–10]

Chemical and biological sensing employing OFETs is a very intriguing new aspect of the ever-growing field of organic electronics. Such sensors could potentially enable the fabrication of low cost (even disposable) devices for medical tests and analysis. Patients would greatly benefit from cheap, easy-to-use and portable tools for disease diagnosis and management. The sensing capabilities of OFETs is realized by the implementation of

recognition sites such as antibodies, enzymes or capturing proteins. Employing OFET technology for sensing not only brings advantages in regard to processability but, compared to other sensing methods, allows for label free detection and direct output of an electronic signal which facilitates miniaturization.[11]

B.2 Recent developments

A major challenge for PhOLEDs to date is the relatively high efficiency roll-off at high luminance. As mentioned, this undesired effect can be limited with high and balanced charge carrier mobilities achieved by bipolar host materials. Thus, the development of novel building blocks with electron donating as well as withdrawing properties is an important field of research to further push PhOLEDs towards commercial viability.

Triarylamines, such as triphenylamine (TPA) and carbazole derivatives such as phenylcarbazole (PCz), represent essential building blocks as electron donors for bipolar molecules due to their high E_T and good hole mobilities (Figure 2). Recently, our group introduced the fully planar indolo[3,2,1-*jk*]carbazole (ICz) as a novel building block (Figure 2). This scaffold was made accessible *via* a newly developed CH activation protocol allowing for a simple two step synthesis with high functional group tolerance (see chapter C.2.3). Systematic investigations were conducted to evaluate the properties of this new motif and its derivatives. Through incorporation of TPA, phenylcarbazole (PCz) and ICz into a bipolar molecule, containing oxadiazole as acceptor, it was revealed that with increased planarity the donor strength of the building block decreased to a point where ICz even shows acceptor characteristics to some extent.[12,13]

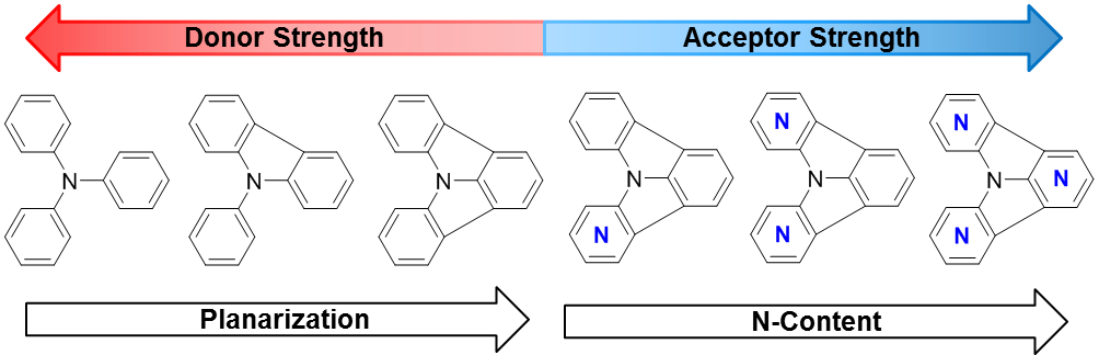


Figure 2: Evolution of the donor strength of tirarylamines dependent on planarization and N content.

Consequently, the ICz scaffold was modified to further increase the acceptor strength by the incorporation of pyridine-like nitrogen into the aromatic system to decrease the electron density. It was observed, that the acceptor strength was dependent on the N content, but the

HOMO and LUMO levels could also be fine-tuned by the position of the nitrogen in the aromatic ring. In Figure 3 the HOMO and LUMO levels of selected building blocks are compared to highlight the effect on the substitution position.[14]

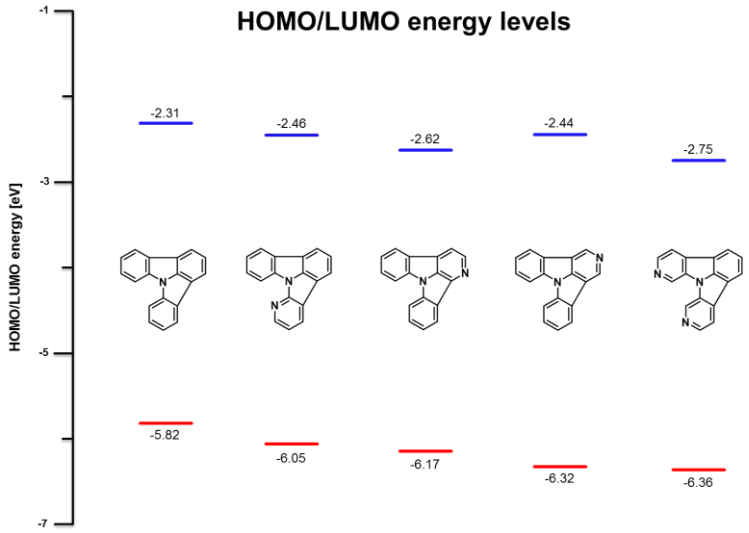
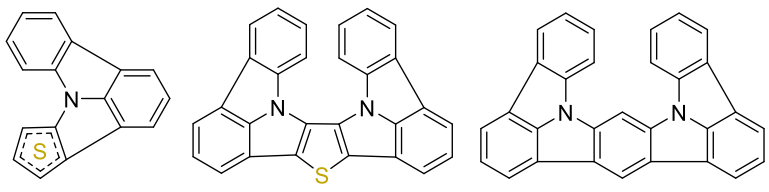


Figure 3: HOMO/LUMO energy levels of ICz moieties containing nitrogen atoms, which were previously synthesized in our group. HOMO and LUMO energies were calculated from the onset of the oxidation respectively reduction peak from CV-measurements in acetonitrile.[14]

B.3 Aim of thesis

The aim of this thesis was to synthesize novel donor building blocks for organic electronic applications based on the indolo[3,2,1-*jk*]carbazole scaffold. Thus, one benzene unit of the parent ICz scaffold should be replaced by electron rich thiophene (Scheme 1). Furthermore, the effect of the position of the sulfur atom, as well as the incorporation of a second thiophene unit on the electrochemical and photophysical properties were matter of interest.

Additionally, the scope of the CH activation protocol, regarding the synthesis of large annulated systems containing a thiophene unit should be explored. Furthermore, the preparation of large, benzene linked, highly annulated systems with various annulation patterns should be investigated (Scheme 1).



Scheme 1: Examples of the target molecules presented in this thesis

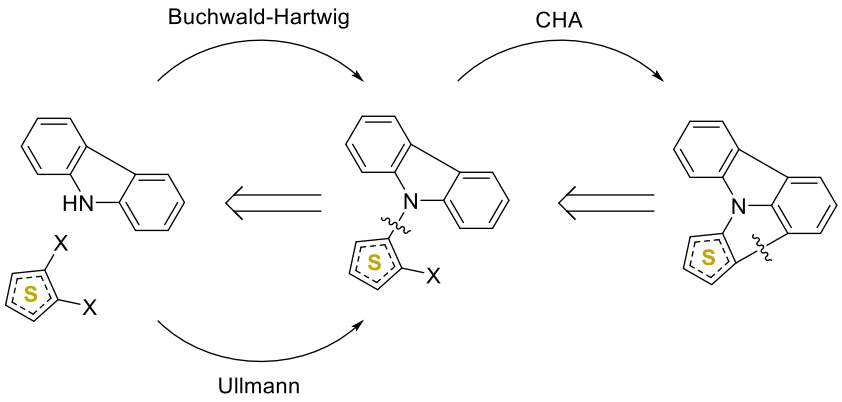
C Specific part

C.1 Introduction

The goal of this thesis was the development of novel building blocks for applications in the field of organic electronics, as described in chapter B.3. The main focus from a synthetic standpoint was to utilize and expand the scope of a CH activation protocol, that has been previously refined in our research group. The application of this protocol allows for an easy preparation of ICz and its derivatives. In the past, the incorporation of nitrogen into the ICz scaffold was explored yielding electron poor building blocks with good acceptor properties.[14] Reversing this trend, it was aimed to create a reliable pathway towards the thiophene substituted ICz (SICz) building blocks as well as the bigger annulated systems with CH activation as a final, ring closing step.

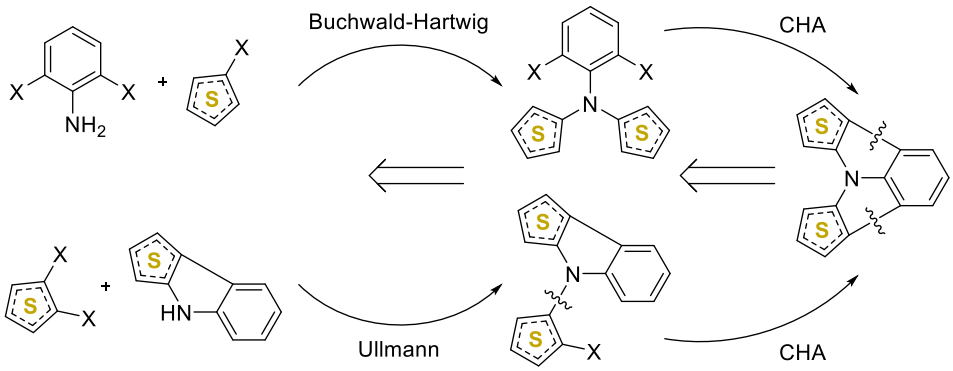
C.2 Synthesis towards SICz and S_2ICz

A retrosynthetic analysis of SICz reveals that the target molecules are available from carbazole (**10**) and simple halogenated thiophenes. For the first step, two possible approaches were considered: Buchwald-Hartwig amination and Ullmann condensation, followed by CH activation (Scheme 2).



Scheme 2: Retrosynthetic analysis of SICz. X = halogen

S_2ICz may be obtained *via* a similar pathway, using a thienoindole instead of carbazole in an Ullmann condensation or alternatively (halogenated) anilines and thiophenes employing Buchwald-Hartwig amination (Scheme 3).



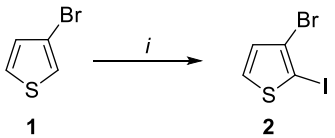
Scheme 3: Retrosynthetic analysis of S_2ICz. X = halogen.

C.2.1 Precursors

As shown in the retrosynthetic analysis of SICz and S_2ICz (Scheme 2 and Scheme 3), a set of halogenated thiophenes with different substitution patterns were required as a starting point towards those building blocks. Furthermore, different thiophene derivatives were needed for the synthesis of 8*H*-thieno[3,2-*b*]indole (**16**) (from this point on just called thienoindole for simplicity). The thiophenes were either acquired commercially or synthesized from simple brominated thiophenes.

C.2.1.1 3-Bromo-2-iodothiophene

3-Bromo-2-iodo-thiophene (**2**) was derived from 3-bromothiophene (**1**) *via* an iodation according to Kautny.[15] Starting compound **1** was reacted with iodine and HIO_3 in a mixture of CCl_4, acetic acid and sulfuric acid at 60 °C. The product could be isolated with a satisfying yield of 78%. The pure compound is a colorless liquid (upon condensation while distillation) but immediately turns deep red on contact with air.

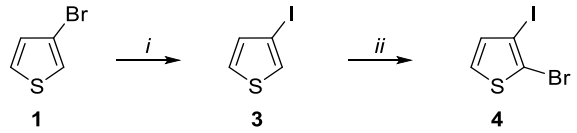


Scheme 4: Synthesis of **2**: ***i***) I_2/HIO_3, $CCl_4/HOAc/H_2SO_4$, 60 °C.

C.2.1.2 2-Bromo-3-iodothiophene

The synthesis of **4** was performed in two steps. First 3-bromothiophene (**1**) was reacted with potassium iodide in ethanol with Cu_2O/L-prolin as a catalyst according to a procedure by Feng et al.[16] The reported high yields for six-membered heteroarylbromides could not be achieved with 3-bromothiophene (**1**), which only yielded 27% of the product. In a second

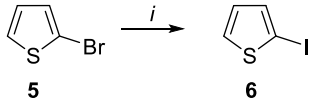
step, the 3-iodothiophene (**3**) was reacted with NBS in DMF at -20 °C to give **4** with a good yield of 75%.



Scheme 5: Synthesis of **4**: ***i***) KI, Cu_2O/L-prolin, EtOH, reflux; ***ii***) NBS, DMF, -20 °C.

C.2.1.3 2-Iodothiophene

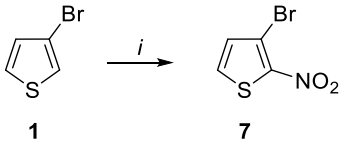
Compound **6** was synthesized following the same procedure as for **3**.[16] The yield was again rather low at 26%.



Scheme 6: Synthesis of **6**: ***i***) KI, Cu_2O/L-prolin, EtOH, reflux.

C.2.1.4 3-Bromo-2-nitrothiophene

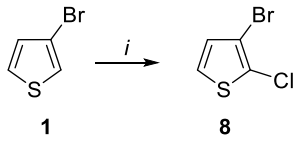
Nitro compound **7** was prepared from **1** by nitration with fuming nitric acid in a mixture of acetic acid and acetic anhydride. The product could be isolated with a moderate yield of 31%.



Scheme 7: Synthesis of **7**: ***i***) AcOH/Ac_2O, fuming HNO_3, 5 °C.

C.2.1.5 3-Bromo-2-chlorothiophene

Dihalogenated compound **8** was synthesized *via* chlorination of **1**. The starting compound was dissolved in AcOH and reacted with NCS at reflux to yield the product, a colorless liquid, after workup and distillation in a yield of 77%.

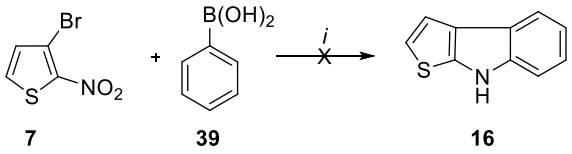


Scheme 8: Synthesis of **31: *i)*** NCS, AcOH, reflux.

C.2.1.6 8*H*-Thieno[2,3-*b*]indole

For the Buchwald-Hartwig approach towards S_2ICz, the carbazole analogon thienoindole had to be prepared.

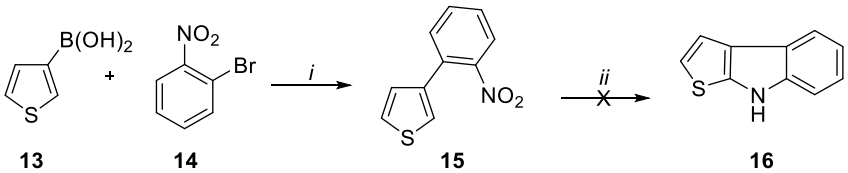
First a one-pot synthesis following a protocol by Woo[17] for carbazoles was investigated using 3-bromo-2-nitrothiophene (**7**) and phenylboronic acid.



Scheme 9: One-pot synthesis towards thienoindole **16: *i)* 7** (1 eq.), **39** (1.3 eq.), PPh_3 (2.5 eq.), K_2CO_3 (2 eq.), $Pd(OAc)_2$ (0.02 eq.), *o*-DCB, 180 °C.

Thiophene **7**, phenylboronic acid (**39**), palladiumacetate, PPh_3 and K_2CO_3 were dissolved in *o*-DCB and reacted under an argon atmosphere at 180 °C overnight. Unfortunately, no product could be isolated.

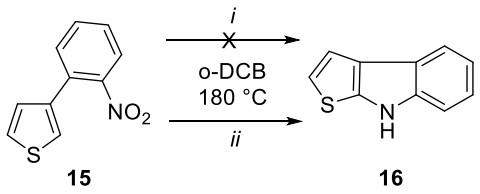
In another attempt, the synthesis was performed according to Appukkuttan[18] in two steps. First, a microwave assisted Suzuki coupling of a thienylboronic acid **13** and bromonitrobenzene **14** was performed, followed by a microwave assisted Cadogan cyclization.



Scheme 10: Two step synthesis towards thienoindole **16: *i)* 13** (1.3 eq.), **14** (1 eq.), $NaHCO_3$ (3 eq.), $Pd(PPh_3)_4$ (0.05 eq.), H_2O/DMF, 150 °C in a microwave reactor; ***ii)* 15**, $P(OEt)_3$, 210 °C in a microwave reactor.

A microwave vial was charged with boronic acid **13**, bromonitrobenzene **14**, $NaHCO_3$ and flushed with argon. The catalyst $Pd(PPh_3)_4$ and the solvent (DMF/H_2O, 1:1) were added and the vial was sealed. The reaction was performed in a microwave oven at 150 °C for 15 min. After workup, the product **15** could be isolated with a yield of 93%. For the following Cadogan cyclization, **15** was dissolved in $P(OEt)_3$ and the solution was degassed in a microwave vial. The vial was sealed and put in the microwave oven to be heated to 210 °C. However, the absorption of $P(OEt)_3$ proved to be too low and the reaction mixture only reached a temperature of 187 °C after 30 min. Even after an additional 15 min of irradiation the temperature did not rise. Therefore, the reaction was stopped and the mixture diluted with EA and 6N HCl and heated to reflux for 3 h. After workup, only traces of product could be detected, showcasing that this method was not viable with this reaction setup.

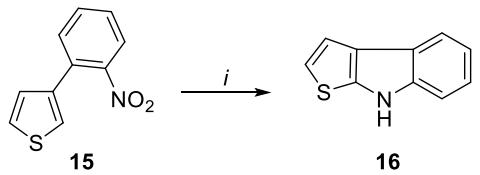
The cyclization of **15** was performed by conventional heating, refluxing **15** in *o*-DCB. $P(OEt)_3$ and alternatively PPh_3 were employed as reducing agents (Scheme 11).



Scheme 11: Cadogan cyclization using ***i)*** $P(OEt)_3$; ***ii)*** PPh_3

The first approach with $P(OEt)_3$ did not yield any product. The second reaction with PPh_3 as a reducing agent did work in principle, however the yield was very low, and the product could not be separated from the significant amounts of $POPh_3$.

Finally, the thienoindole **16** could be synthesized in satisfying yield using a procedure by Baert et al.,[19] which employs $MoO_2Cl_2(dmf)_2$ as a catalyst.



Scheme 12: Synthesis of thienoindole **16**: ***i)*** **15** (1 eq.), PPh_3 (2.4 eq.), $MoO_2Cl_2(dmf)_2$ (0.05 eq.), toluene, 110 °C.

First the catalyst was synthesized from $Na_2MoO_4 \cdot 2H_2O$ according to Sanz et al.[20] 3-(2-Nitrophenyl)thiophene (**15**), PPh_3 and the catalyst were dissolved in anhydrous toluene and

heated to reflux under an argon atmosphere. After 24 h another 0.01 eq. of the catalyst in 0.5 ml DMSO were added and the reaction was refluxed for further 30 min. After workup and purification, the product **16** could be isolated with a yield of 60%.

C.2.2 Substrates for CHA

As described in the retrosynthetic analysis, two possible pathways (Buchwald-Hartwig amination and Ullmann condensation) were considered for the synthesis of the CH activation substrates leading to SICz and S_2ICz. Both these pathways were explored, as will be discussed in the following chapters.

C.2.2.1 Buchwald-Hartwig amination

In the late 90s efficient Pd-catalyzed amination reactions of aryl halides were reported by Buchwald and Hartwig.[21–23] Although these findings made many arylamines readily available, no such procedures existed for aminothiophenes until a report of Watanabe et al. in 2000. Watanabe and coworkers used a Pd catalyst in combination with P(*t*Bu)$_3$ ligands for the synthesis of mono- and disubstituted (diarylamino)thiophenes starting from halothiophenes.[24] The scope of this procedure was later studied and expanded by Ogawa et al. and Luker et al.[25,26] In 2015 a similar procedure was presented by Kamimoto et al. reporting a one-pot synthesis of different thienoindoles. Employing Pd(dba)$_2$ and P(*t*Bu)$_3$, they were able to perform a CH activation in a first step, followed by a ring closing Buchwald-Hartwig amination.[27]

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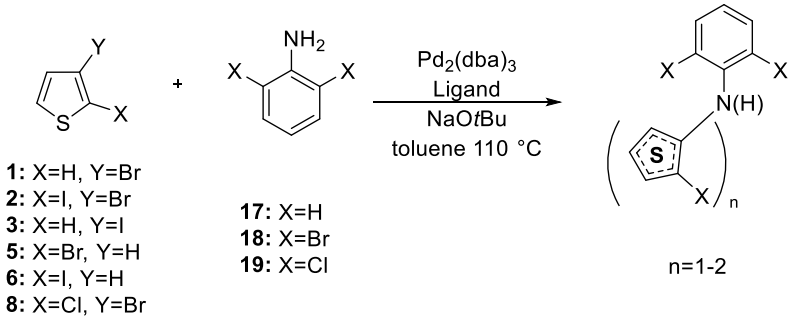


Scheme 13: Investigated Buchwald-Hartwig aminations of various halothiophenes and different amines (overview Table 1)

It was attempted to utilize these procedures for the synthesis of the precursors for the SICz and S_2ICz systems (Scheme 13). Unfortunately, the success using Buchwald-Hartwig amination was very limited and only two reactions did yield the desired product.

All experimental results of the attempted Buchwald-Hartwig aminations are summarized in Table 1.

Table 1: Overview of Buchwald-Hartwig aminations. **General conditions**: thiophene (2.5 eq.), amine (1 eq.), $Pd_2(dba)_3$ (0.02 eq.), ligand (0.1 eq.), NaO*t*Bu (2.5 eq.), anhydrous toluene, 110 °C, argon atmosphere, overnight.

Entry	Thiophene	Amine	Catalyst	Ligand	Product yield
1	**2**	Carbazole (**10**)	$Pd_2(dba)_3$	dppf	-
2	**2**	Carbazole (**10**)	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-
3	**2**	**17**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-
4[a]	**2**	**17**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-
5	**6**	**18**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-
6	**1**	**18**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-
7	**1**	**17**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	62% (**20**)
8[b]	**3**	**17**	$Pd_2(dba)_3$	JhonPhos	-
9	**8**	**17**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-
10	**1**	**19**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-
11[c]	**1**	**19**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	32% (*ii*)(**XIII**)
12	**1**	**19**	$Pd_2(dba)_3$	dppf	
13	**5**	**19**	$Pd_2(dba)_3$	P(*t*Bu)$_3$·HBF$_4$	-

[a] 1 eq. silver acetate was added; [b] Cs_2CO_3 was used as base; [c] 1 eq. thiophene

Table 1 clearly shows that Buchwald-Hartwig amination was no suitable pathway for the majority of combinations of thiophenes and amines. There were no traces of product detected (GCMS) for all but two reactions: entry 7 and 11. Since these two thiophenes reacted on the less electron rich 3 position, it is possible that, for a successful coupling with a primary arylamine, a more electron deficient system would be preferable. In accordance with these findings, Luker et al. were only able to successfully use thiophenes with electron withdrawing substituents[26] and Kamimoto and Watanabe only employed secondary amines.[24,27] Furthermore, an excess of thiophene seems to hinder the reaction as is demonstrated by entries 10 and 11. The reaction with 2.5 eq. thiophene (entry 10) shows no conversion, while entry 11 with identical conditions but only 1 eq. thiophene yields the product.

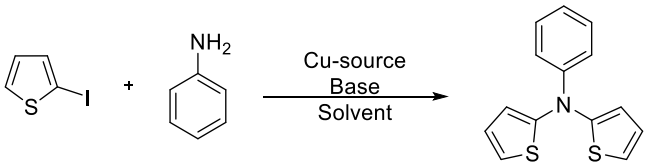
For a better understanding, a thorough investigation of this reaction would be necessary, but such a task would be beyond the scope of this thesis. Instead, an alternative route *via* Ullmann condensation was explored.

C.2.2.2 Ullmann condensation

As the approach *via* Buchwald-Hartwig amination was rather unsuccessful, another possibility, namely Ullmann condensation, was employed.

This copper catalyzed reaction between an aryl halide and a nucleophile was discovered by Fritz Ullmann in the early 1900s. Since that time, this type of reaction has gained a lot of attention due to its versatility paired with the low cost of copper compared to other catalysts (e.g. palladium). Nevertheless, there is still some ambiguity regarding the exact mechanism which leads to a certain degree of unpredictability.[28] However, it could be shown by Paine, that the catalytically active species is Cu(I), regardless of the oxidation state of the added copper.[29]

There is a great deal of different conditions known to literature. Thus, a screening was performed to find suitable conditions for the thiophenes used in this work.



6 **17** **TM 1**

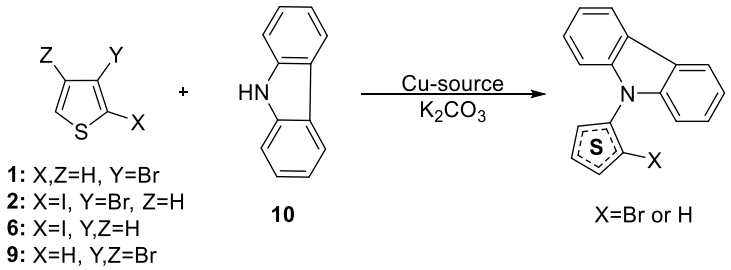
Scheme 14: Screening of possible Ullmann conditions.

Since the reactivity of haloarenes in Ullmann reactions follows the order I>Br>Cl,[28] first experiments were conducted with 2-iodothiophene (**6**) and aniline (**17**) (Scheme 14).

Table 2: Overview of the screening for suitable Ullmann conditions. **General procedure:** An 8 ml reaction vial was charged with the solids and evacuated and flushed with argon three times. The thiophene and degassed solvent were added, the vial was sealed and stirred on a heating block. **1,2)** thiophene **6** (2.2 eq.), aniline **17** (1 eq.), CuI (0.3 eq.), K_3PO_4 (3.5 eq.), 1,2-DACH (0.5 eq.); **3)** thiophene **6** (2.2 eq.), aniline **17** (1 eq.), CuCl (0.4 eq.), KOH (7.8 eq.), phenantroline (0.4 eq.); **4)** thiophene **6** (2.2 eq.), aniline **17** (1 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (1.5 eq.), **5)** thiophene **6** (2.2 eq.), aniline **17** (1 eq.), Cu-powder (6 eq.), K_2CO_3 (6 eq.).

Entry	Cu-source	Base	Additive	Solvent	Temperature	Product yield
1	CuI	K_3PO_4	1,2-DACH	toluene	110 °C	-
2	CuI	K_3PO_4	1,2-DACH	dioxane	110 °C	-
3	CuCl	KOH	phenantroline	toluene	110 °C	-
4	$CuSO_4 \cdot 5H_2O$	K_2CO_3	-	-	230 °C	-
5	Cu-powder	K_2CO_3	-	DMF	150 °C	-

As shown in Table 2, none of the investigated conditions worked with the chosen starting materials. Suspecting that, similar to the Buchwald-Hartwig reactions, a primary amine may not be ideal for this reaction, more experiments with carbazole (**10**) were conducted.



Scheme 15: Screenig of Ullmann conditions with carbazole (**10**).

An overview of the used thiophenes is given in Scheme 15. The reaction conditions as well as the yields are summarized in Table 3.

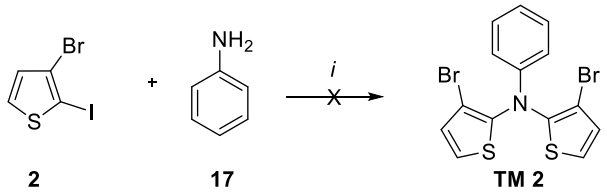
Table 3: Screening of Ullmann condtitions with carbazole (**10**). **General procedure:** An 8 ml reaction vial was charged with the solids, evacuated and flushed with argon three times and the thiophene added *via* syringe. The vial was sealed and placed on a preheated heating block. **1,2)** thiophene (1 eq.), **10** (2 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (1.5 eq.); **3)** thiophene (1.1 eq.), **10** (1 eq.), Cu-powder (3 eq.), K_2CO_3 (3 eq.); **4,5,6)** thiophene (1.5 eq.), **10** (1 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (1.5 eq.); **7)** thiophene (1.2 eq.), **10** (1 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (1.2 eq.), **8)** thiophene (1 eq.), **10** (1 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (1 eq.).

Entry	Thiophene	Cu-source	Solvent	Temperature	Time	Product yield
1	**6**	$CuSO_4 \cdot 5H_2O$	-	230 °C	4 d	56%
2	**2**	$CuSO_4 \cdot 5H_2O$	-	230 °C	30 h	traces
3	**2**	Cu-powder	DMF	120 °C	3 d	5%
4	**2**	$CuSO_4 \cdot 5H_2O$	-	150 °C	7 d	8%
5	**2**	$CuSO_4 \cdot 5H_2O$	-	210 °C	4.5 h	18%
6	**2**	$CuSO_4 \cdot 5H_2O$	-	250 °C	1.5 h	26%
7	**1**	$CuSO_4 \cdot 5H_2O$	-	250 °C	2.5 h	78%
8	**9**	$CuSO_4 \cdot 5H_2O$	-	250 °C	2 h	42%

Using carbazole (**10**), a first success was achieved applying a protocol by Xu et al. (entry 1).[30] Employing these conditions and using 2-bromo-3-iodothiophene (**2**), traces of product could be found together with dehalogenated product. Furthermore, a byproduct containing iodine in the 2-positon due to halogen exchange was identified. An iodine substituent renders the substance unfit for CH activation because of possible catalyst poisoning. To counter those unwanted side reactions the synthesis was performed at lower temperatures, resulting in some improvement regarding yield, but significant amounts of the same side products were still present. Ultimately, the best results were obtained by heating to 250 °C and stopping the reaction after 1.5 h. In this way, an acceptable yield of 26% was achieved. Still a ratio of roughly 3:1 of product to side product was obtained, but complete separation *via* column chromatography was achieved easily.

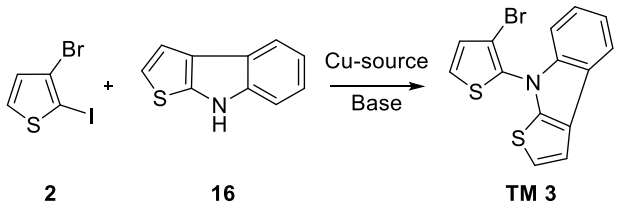
Unsurprisingly, reactions starting from 3-bromothiophene (**1**) using the same conditions gave much higher yield due to the lack of possible side reactions. 3,4-Dibromothiophene (**9**) could also be reacted rather successfully and the only side product was twofold substituted product, which again was separated easily using column chromatography.

To investigate the influence of the amine, one additional experiment was conducted using the same conditions but employing aniline (**17**) instead of carbazole (**10**). This synthesis, like all previous experiments with primary amines did not yield any product.



Scheme 16: Investigation of the optimized Ullmann conditions using aniline. ***i)*** **2** (2 eq.), aniline (**17**) (1 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (3 eq.), 250 °C.

Since hardly any success in the synthesis towards S_2ICz was made using Buchwald-Hartwig amination, thienoindole (**16**) was used for a screening of different conditions for an Ullmann condensation.



Scheme 17: Screening of conditions for Ullmann condensation with thienoindole.

The overall reaction is depicted in Scheme 17 and the reaction conditions and yields are summarized in Table 4.

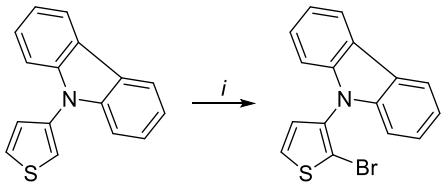
Table 4: Screening of conditions for Ullmann condensation with thienoindole. **General procedure**: An 8 ml reaction vial was charged with thienoindole **16** (1 eq.), K_2CO_3 (1.5 eq.), **2** (1 eq.) and the Cu-source, evacuated, flushed with argon three times and sealed.

Entry	Cu-source	Base	Solvent	Temperature	Reaction time	Product yield
1	$CuSO_4 \cdot 5H_2O$	K_2CO_3	-	250 °C	1 h	-
2	$CuSO_4 \cdot 5H_2O$	K_2CO_3	-	250 °C	0.5 h	-
3	$CuSO_4 \cdot 5H_2O$	K_2CO_3	-	150 °C	1 h	-
4	Cu-powder	K_2CO_3	nitrobenzene	220 °C	24 h	-
5	Cu-powder	K_2CO_3	*o*-DCB 18-crown-6	150 °C	48 h	-
6	Cu-powder	Cs_2CO_3	DMF	150 °C	48 h	-

Unfortunately, of all the investigated conditions, none yielded any product. During the reactions without solvent (entries 1-3), decomposition of the thienoindole took place, indicated by the formation of graphitic solid and a strong odor of sulfur upon opening of the reaction vial. Characterization of reactions 4-6 after workup only revealed dehalogenated thiophene.

C.2.2.3 Additional reactions

After the successful formation of **12** and **20** bromination was required to yield the CH activation precursors. Thus, an electrophilic substitution with NBS was employed. It was expected, that the electron rich nature of the thiophene rings, with the 2-position being the most activated, would promote a bromination.

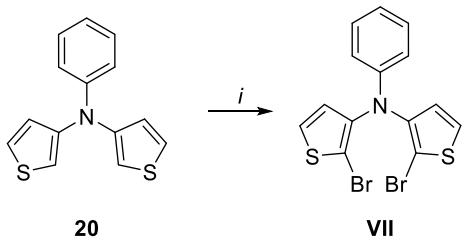


12 **I**

Scheme 18: Bromination of **12**: ***i)*** NBS (1 eq.), DMF, -20 °C.

A first experiment was conducted using **12** and NBS in DMF at -20 °C. The molecule could successfully be brominated at the 2-position of the thiophene ring employing this method. The moderate yield of 59% could be attributed to the formation of small quantities of side product which led to losses during purification. This problem could be minimized by careful reaction control, but an optimization of the reaction was not done during this work.

Employing the same conditions, a bromination was attempted on **20** (Scheme 19).



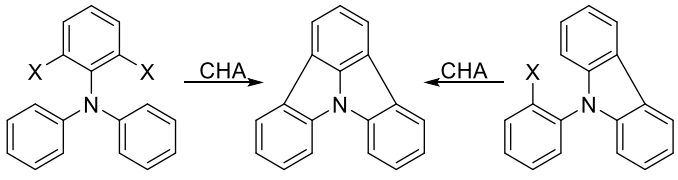
20 **VII**

Scheme 19: Bromination of **20: *i)*** NBS (1 eq.), DMF, -20 °C.

In this case, no formation of side product was observed, and the product **VII** was obtained in quantitative yield.

C.2.3 CH activation

A crucial step in this work was the ring closing step *via* CH activation towards the annulated target molecules. In search of better atom efficiency in cross coupling reactions, the CH activation - a major step towards this goal - has first been reported over 30 years ago and still is a “hot topic” for ongoing research.[31] This method of a C-C bond formation uses two reaction partners of which only one is activated by the introduction of e.g. a halide. Recently, the synthesis of indolo[3,2,1-*jk*]carbazole and derivatives employing CH activation was reported by Lv. et al.[32] In our research group, a modified protocol has been developed, which allows for a more efficient and faster reaction. Furthermore, two-sided reactions can be performed and the scope of substrates could be broadened to chlorinated species (Scheme 20).[12]



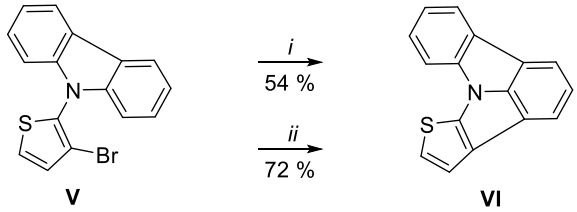
X=Br or Cl

Scheme 20: Possible routes towards ICz employing the CH activation protocol developed in our research group.

This success could be realized using allyl[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]chloropalladium(II) (**36**) as catalyst. Alternatively, the salt of the NHC-ligand can be used together with $Pd(OAc)_2$ to form the catalyst *in situ*. However, this can in some cases result in lower yields. Furthermore, it was discovered, that a water content of 1000 ppm in the

solvent (DMAc) is necessary for the reaction to proceed. Recently, this CH activation protocol was successfully applied in the synthesis of nitrogen containing derivatives of ICz showcasing the tolerance of electron deficient N-heterocycles.[14] In this work, electron rich thiophenes should be investigated to broaden the substrate scope. Furthermore, some limitations of the reactions could be identified as will be discussed below.

A first test reaction was performed using substrate **V** to compare the reactivity in respect to the used catalyst system (Scheme 21).

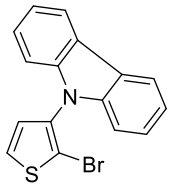
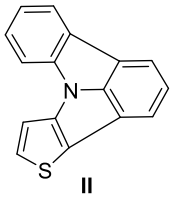
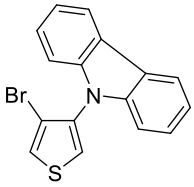
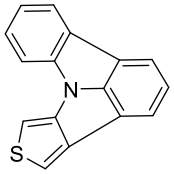
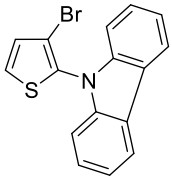
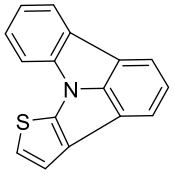


V **VI**

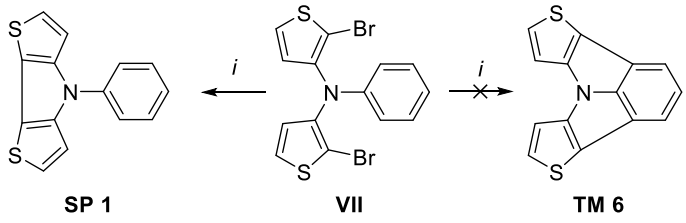
Scheme 21: Comparison of reactivity of ***i)*** $Pd(OAc)_2$ in combination with [NHC]Cl and ***ii)*** Pd[NHC](allyl) catalyst.

In this comparison, the advantage of using the pre-prepared catalyst can be seen as the yield is improved from 54% to 72%, which easily justifies the use. All subsequent CH activation reactions towards SICz systems were performed with the Pd[NHC](allyl) catalyst. The CH activation did work with all the substrates for the SICz moieties without any problems (Table 5).

Table 5: Ring closing CH activation towards SICz moieties. **1-3)** substrate (**I**, **III** or **V**) (1 eq.), K_2CO_3 (2 eq.), Pd[NHC](allyl) (0.05 eq.), DMAc (1000 ppm H_2O), 130 °C, 24 h.

Entry	Substrate	Product	Yield
1	 ***I***	 **II (1SICz)**	72%
2	 ***III***	 **IV (2SICz)**	83%
3	 **V**	 **VI (3SICz)**	72%

For a reaction towards a S_2ICz moiety, only substrate **VII** was available. The CH activation was performed in the same manner as with the SICz precursors. **VII** was dissolved in DMAc together with the Pd-catalyst and K_2CO_3. The reaction was performed at 130 °C for 48 h.

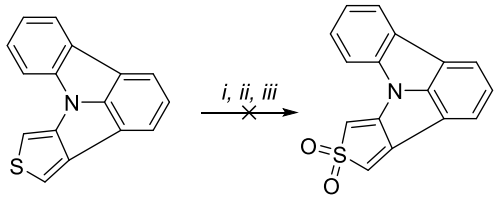


Scheme 22: CH activation towards S_2ICz **TM 6**: ***i)*** **VII** (1 eq.), K_2CO_3 (2 eq.), Pd[NHC](allyl) (0.05 eq.), DMAc (1000 ppm H_2O), 130 °C, 48 h.

During reaction control with GCMS and after workup, no product could be observed. However, a substance, **SP 1**, was isolated in a yield of 62%, which turned out to be the product of a reductive cyclization. It is unclear, why this reaction took place.

C.2.4 Oxidation

The incorporation of sulfur allows for an additional modification of the electronic properties of the building blocks. As sulfur can easily be oxidized to give a sulfoxide or a sulfone, it was attempted to convert the SICz moieties from electron donors to acceptors in just one step by oxidation with *m*-CPBA or DMDO (Scheme 23).



IV **TM 7**

Scheme 23: Oxidation of SICz moiety: ***i)*** *m*-CPBA (2. eq.), anhydrous DCM, rt; ***ii)*** DMDO (2 eq.), anhydrous DCM, rt; ***iii)*** DMDO (2 eq.), $BF_3 \cdot Et_2O$ (3 eq.), anhydrous DCM, rt.

Initially the oxidation was performed using *m*-CPBA in anhydrous DCM. However, under these conditions only degradation of the molecule was observed. The reaction was repeated with DMDO as an oxidizing agent. After addition, the colorless solution became yellow, then red. After 1 h a bright red solid precipitated. The solid was filtered off but could not be dissolved for characterization. The solvent of the filtrate was evaporated leaving a brown residue. Unfortunately, no product could be identified. An additional reaction was performed with DMDO in the presence of $BF_3 \cdot Et_2O$ with the same outcome, leading to the conclusion that the oxidized species is not stable and degrades rapidly.

C.2.5 Characterization

Photophysical and electrochemical characterizations of the target molecules were conducted to determine whether the desired trends for HOMO/LUMO levels as well as UV/Vis absorption/emission could be observed.

C.2.5.1 Absorption, singlet and triplet emission

Absorption and fluorescence measurements were performed in solution with a concentration of 5 nmol/ml in DCM. The solvent was thoroughly degassed with argon since decomposition in solution was observed for the SICz molecules in the presence of oxygen. The optical bandgaps of the molecules were determined from the absorption onset of the UV/Vis absorption spectra.

The triplet energy is of crucial importance for applications in PhOLED devices. To prevent back transfer of triplet excitons from the phosphorescent dye to the host material, the E_T of

the host must be higher than that of the dopant. This is especially challenging for deep blue emitters at the high-energy end of the visible spectrum.[33]

Triplet energies of the target molecules were determined from the phosphorescent emission. To suppress quenching effects the solutions (1 mg/ml in toluene/*i*-PrOH) were degassed thoroughly and measured at 77 K. From the recorded spectra the E_T was determined from the highest energy maximum.

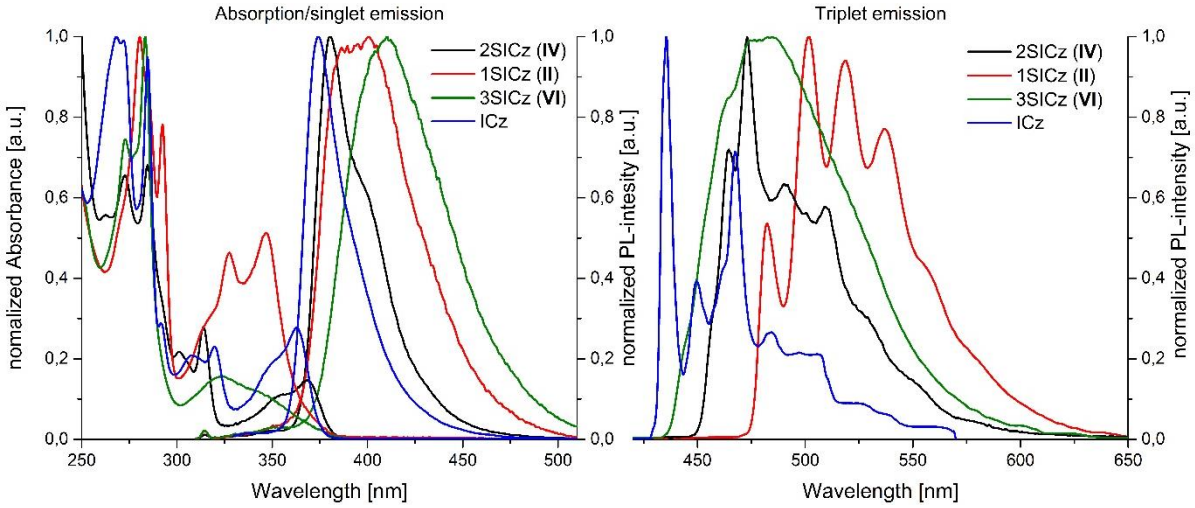


Figure 4: Left: Absorption and singlet-emission spectra of the SICz moieties, recorded in DCM with a concentration of 5 nmol/ml. Right: Phosphorescence spectra of the SICz moieties, recorded in toluene/*i*-PrOH with a concentration of 1 mg/ml at 77 K.

Normalized absorption and singlet-emission spectra of the SICz moieties are depicted in Figure 4. From the absorption spectra it is clear that the position of the sulfur has a significant effect on the electronic properties of the whole molecule. However, the optical bandgap determined by the absorption onset is relatively similar for all three systems. **3SICz** (**VI**) exhibits the smallest bandgap with **3.22 eV**, closely followed by **1SICz** (**II**) and **2SICz** (**IV**) with **3.25 eV** each (compared to **3.30 eV** for **ICz**). This trend towards smaller bandgaps of the investigated molecules indicates a potential application of these building blocks in small molecule donors in organic solar cells. In the region between 270 to 290 nm a similar pattern of two maxima about 10 nm apart can be observed for all three motifs, reminiscent of the absorption spectra of ICz in that area.

2SICz (**IV**) shows emission with maximum intensity at **380 nm**. **1SICz** (**II**) and **3SICz** (**VI**) are red-shifted to **394 nm** and **410 nm**, respectively, while **ICz** emits at a higher energy of **373.5 nm**.

In contrast to its singlet emission, **3SICz** (**VI**) shows the highest E_T with **2.79 eV**. Red shifted by about 13 nm, **2SICz** (**IV**) has an E_T of **2.71 eV**. A substantially lower E_T was determined for **1SICz** (**II**) with **2.57 eV**. Compared to **ICz** with **2.85 eV** the triplet energies are somewhat lower. Nevertheless, these E_T values allow for applications in light blue PhOLEDs (**2SICz** and **3SICz**) and green PhOLEDs (**1SICz**).

C.2.5.2 Electrochemical properties

In modern multi-layered OLED devices, HOMO and LUMO levels are of interest regarding efficiency. By matching the HOMO and LUMO levels of the host material to those of neighboring layers, the charge injection barrier is minimized allowing for a lower driving voltage.[33] Considering this circumstance, the ability to fine tune these energy levels allows for better device design.

The HOMO and LUMO levels of the target molecules were determined by cyclic voltammetry with solutions of the molecules in ACN. From the resulting plots the onsets of oxidation and reduction respectively were determined and related to ferrocene.

The results for the SICz moieties show that, while the bandgaps are relatively similar for all three molecules, the absolute values of the HOMO levels are significantly influenced by the position of the sulfur. The HOMO levels of **1SICz** (**II**), **3SICz** (**VI**) and **2SICz** (**IV**) located at **-5.68 eV**, **-5.56 eV** and **-5.53 eV**, respectively, are higher compared to **ICz** (**-5.82 eV)**. Therefore, better hole injection is expeted. Owing to a smaller bandgap, the LUMO levels of the target molecules (**-2.38 eV**, **-2.28 eV** and **-2.30 eV**) are comparable to **ICz** (**-2.31 eV**). These findings show the successful modulation of the HOMO levels while retaining LUMO levels in comparison to **ICz**. A HOMO level above -5 eV corresponds with facile oxidation under atmospheric conditions and an unfavorable I_{on}:I_{off} ratio in OFETs. While an energy level significantly lower than -5.5 eV results in very good charge carrier transport and I_{on}:I_{off} ratio, the threshold voltage becomes too high.[34]

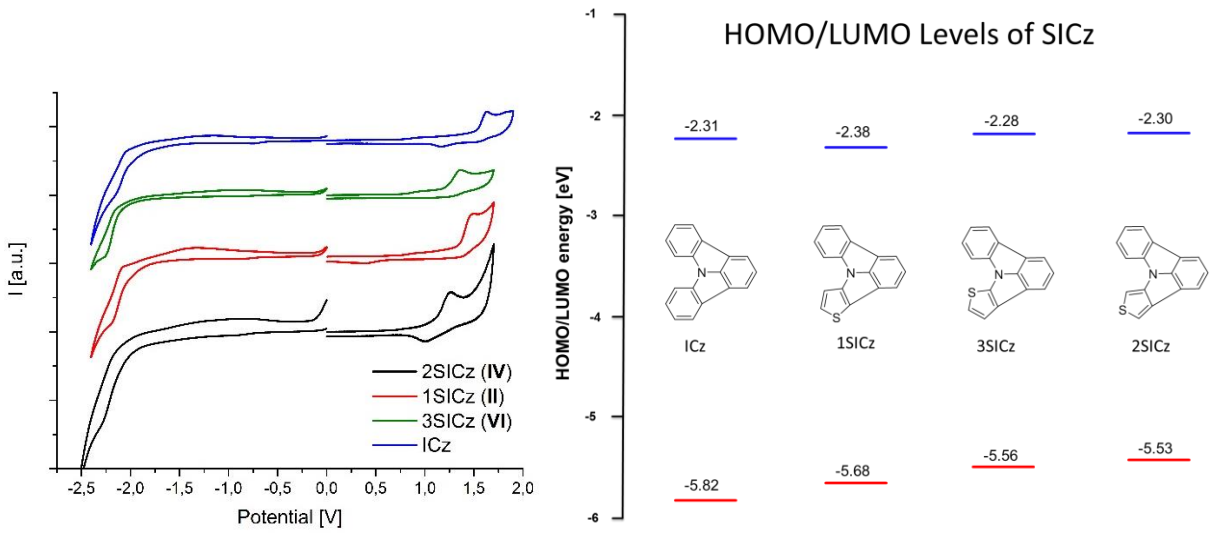
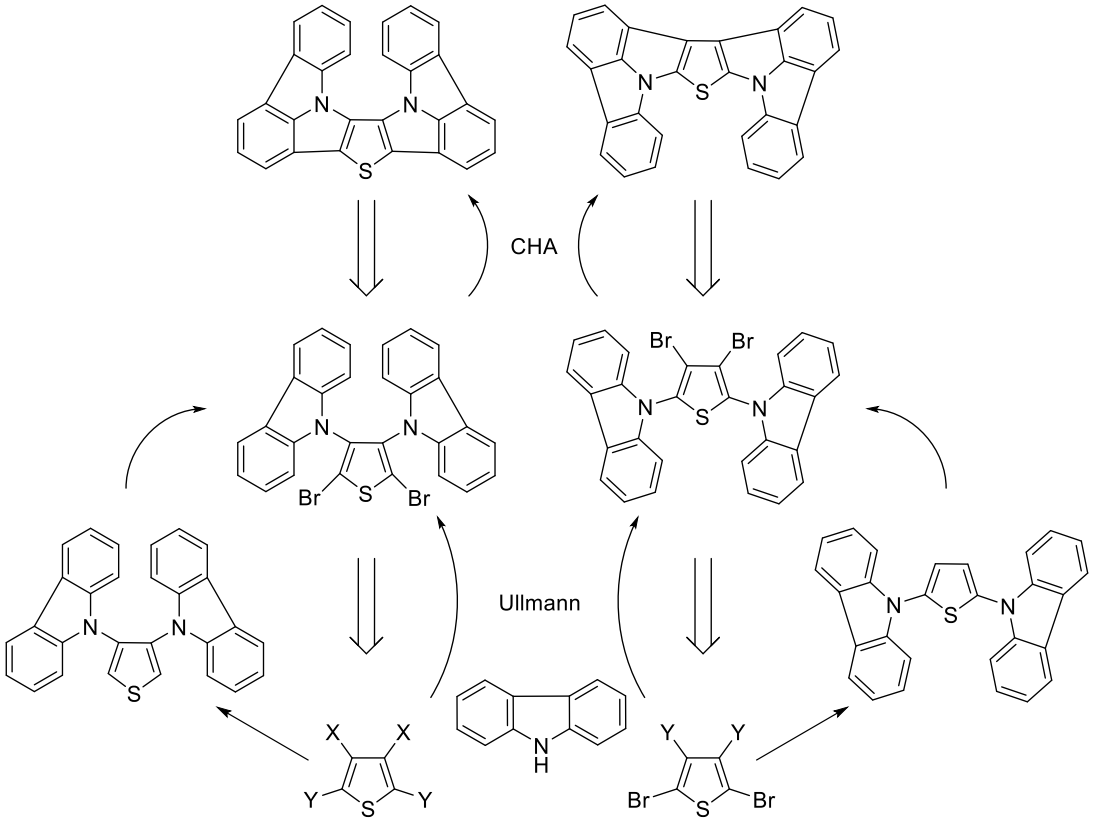


Figure 5: Left: Cyclic voltammetriy plots of oxidation (positive potential) and reduction (negative potential) of SICz motifs and ICz. Right: Visualization of HOMO and LUMO energy levels of the target molecules and ICz.

C.3 Large annulated thiophene linked systems

Highly annulated ring systems, containing the ICz building block, have been studied in our research group in the past and promising electrochemical as well as thermal properties were found.[13] After showcasing the compatibility of sulfur containing systems with the described CH activation method, it was of interest to apply the same reactions to create highly annulated systems comprised of two ICz moieties linked by a thiophene unit. A retrosynthetic analysis of the target molecules resembling the approach towards the SICz systems is given in Scheme 24.

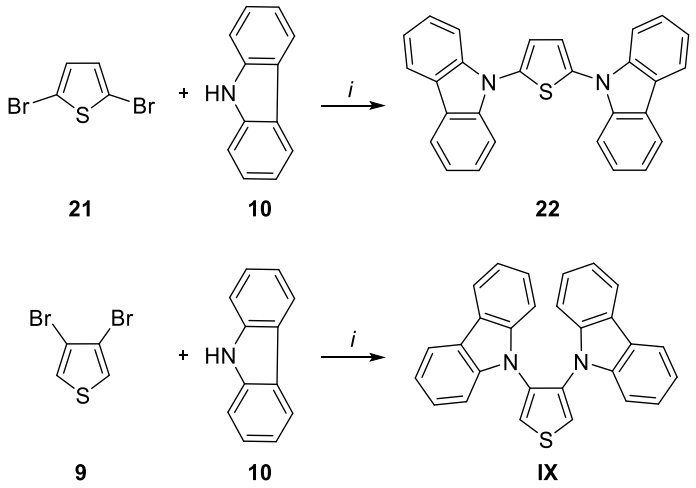


Scheme 24: Retrosynthetic analysis of thiophene linked systems. (X = Br or I; Y = Br or H)

C.3.1 Substrates for CHA

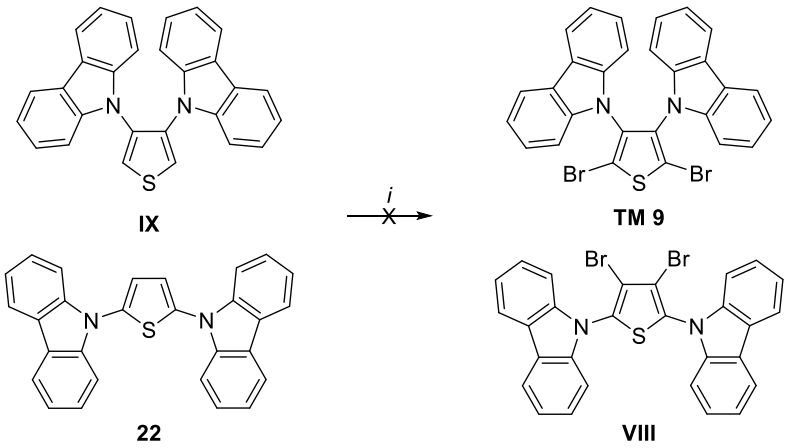
Since the formation of a twofold substituted product using Ullmann condensation with dihalogenated thiophene and carbazole (**10**) has already been observed (Table 3, entry 8), the synthesis of the precursors for the thiophene linked systems was performed using the same procedure with an excess of carbazole and longer reaction times.

Accordingly, thiophenes **21** and **9** were subjected to Ullmann condensation with carbazole (**10**) employing the established protocol. In such a way **22** and **IX** were obtained in 44% and 54% yield (Scheme 25).



Scheme 25: Synthesis towards the precursors for thiophene linked systems **22** and **IX**: ***i)*** **21** or **9** (1 eq.), carbazole (**10**) (2 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (3 eq.), 250 °C.

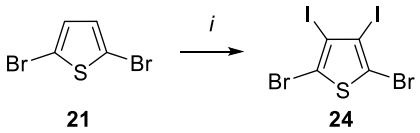
Bromination of the molecules **22** and **IX** were attempted employing the established conditions. However, upon execution of the reactions, it was discovered that, while some desired product was formed, it was accompanied by the formation of side products with various substitution patterns. Due to the very low solubility of these compounds, the separation of the formed products proved to be impossible.



Scheme 26: Bromination towards substrates for CH activation of thiophene linked systems. ***i)*** NBS (2 eq.), DMF, -20 °C.

To overcome the selectivity problems during the bromination reactions, a direct synthesis of the CH activation substrates starting from tetrahalogenated thiophenes was attempted. It was expected, that the higher reactivity of the 2 and 5 positions in the Ullmann condensation would allow the synthesis of **VIII** from tetrabromothiophene **23**. It was then attempted to reverse this reactivity by the implementation of iodine into the 3 and 4 position.

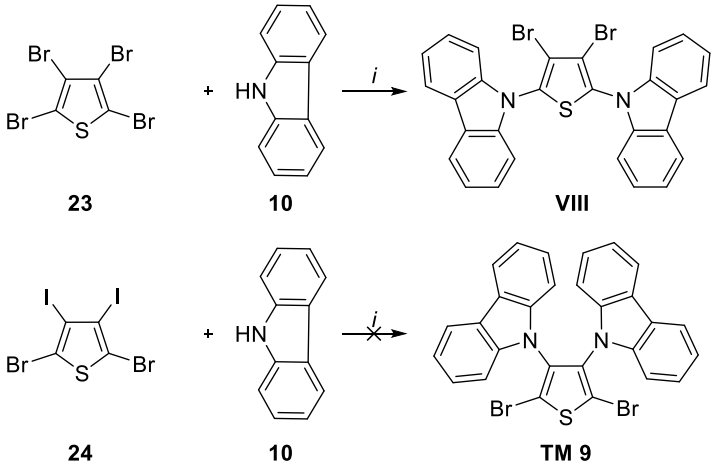
Thus, 2,5-dibromo-3,4-diiodothiophene (**24**) was synthesized according to a protocol by Ayres et al.[35] 2,5-Dibromothiophene (**21**) was dissolved in a mixture of AcOH, H_2O and H_2SO_4 together with periodic acid and I_2. The mixture was heated to 90 °C for 3.5 h, whereby a white solid precipitated. After separation, drying and recrystallization of the solid, the target compound **24** was obtained in a yield of 74%.



21 **24**

Scheme 27: Synthesis of 2,5-dibromo-3,4-diiodothiophene (**24**): ***i***) **21** (1 eq.), periodic acid (0.4 eq.), Iodine (1 eq.), $AcOH/H_2O/H_2SO_4$, 90 °C, 3.5h.

Ullmann condensations were employed in the synthesis of the CH activation precursors (Scheme 28).



23 **10** **VIII**

24 **10** **TM 9**

Scheme 28: Synthesis towards the precursors for thiophene linked system. ***i)*** thiophene (1 eq.), carbazole (**10**) (2 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.), K_2CO_3 (3 eq.), 250 °C.

The crystal structure of **VIII**, as depicted in Figure 6, was obtained from x-ray diffraction of single crystals (recrystallization from DCM), confirming the desired substitution pattern.

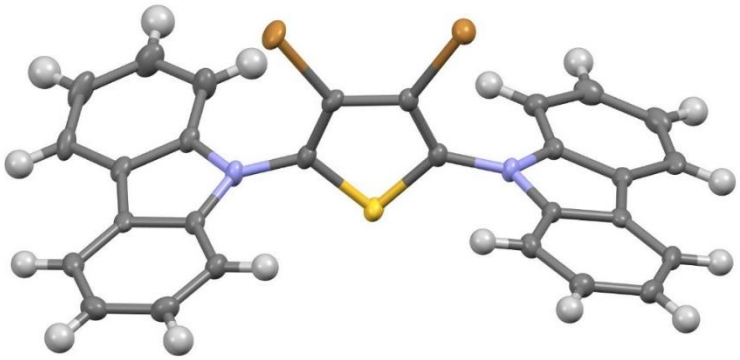
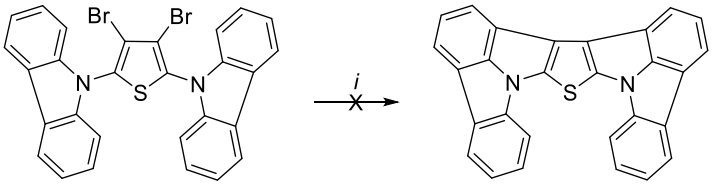


Figure 6: Crystal structure of **VIII**. Single crystals were obtained by recrystallization from DCM. C,N,S,Br atoms are depicted as grey, blue, yellow and orange ellipsoids at 95% probability, H atoms are depicted as white spheres of fixed size.

C.3.2 CH activation

Having demonstrated that the thiophene ring does not hinder the reaction, the same CH activation protocol was tested on the bigger thiophene-linked system. Unfortunately, no product formation could be observed.



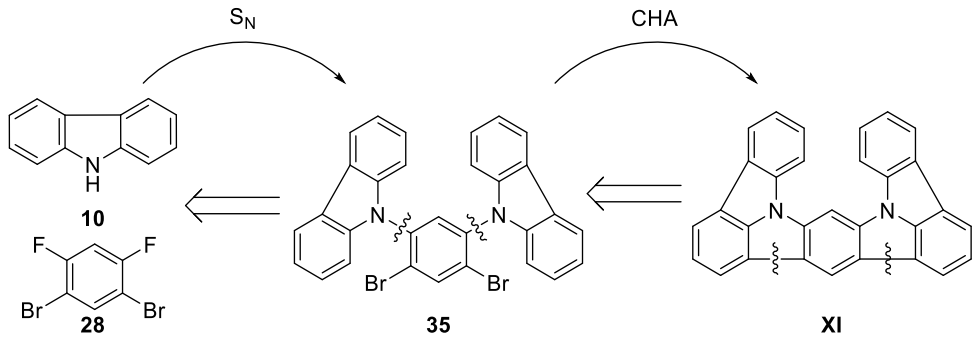
VIII **TM 8**

Scheme 29: CH activation towards thiophene linked system **TM 8**. ***i)*** **VIII** (1 eq.), K_2CO_3 (4 eq.), Pd[NHC](allyl) (0.05 eq.), DMAc (1000 ppm H_2O), 130 °C, 24 h.

C.4 Large annulated benzene linked systems

As the synthesis of the highly annulated thiophene linked systems could not be realized, the investigation of such systems containing a benzene linker were continued.

For these systems, a nucleophilic substitution was chosen as a first step towards the target compounds as exemplarily shown in the retrosynthetic analysis of compound **XI** (Scheme 30).



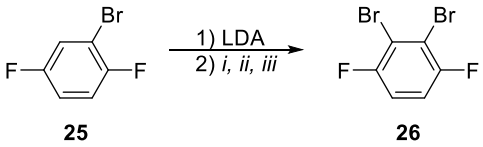
Scheme 30: Retrosynthetic analysis of a benzene linked system.

C.4.1 Precursors

For the S_NAr reactions towards the CH activation substrates, polyhalogenated benzenes were required. More specifically, dibromodifluorobenzenes with different substitution patterns, and in the case of compound **XII** difluorotetrabromobenzene. 1,4-Dibromo-2,5-difluorobenzene (**33**) was acquired commercially, the other halogenated benzenes were synthesized from difluoro species.

C.4.1.1 2,3-Dibromo-1,4-difluorobenzene

Precursor **26** was prepared from 2-bromo-1,4-difluorobenzene (**25**) *via* two steps (Scheme 31). First, **25** was lithiated using LDA in THF. The LDA was prepared from DIPA with *n*-BuLi in THF at -80 °C. Then the starting compound **25** was added to the solution and stirred before the reaction was quenched. Three different reagents were investigated regarding their reactivity. The best results could be achieved with method *iii* using CBr_4, which was dissolved in dichloromethane, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure beforehand. For the quench, the reagent was dissolved in dry THF and added *via* syringe to the reaction mixture resulting in an orange color and a yield of 63% after workup and purification. While reagents F_2Br_2C and Br_2 did also yield some product, the amount of side products (mostly over-brominated species) and the low yield (approximately 10%) rendered them far inferior compared to method *iii*.

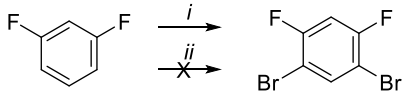


25 **26**

Scheme 31: Synthesis of **26:** 1) LDA (freshly prepared from DIPA and *n*-BuLi), THF, -80 °C;2) -80 °C, ***i*)** F_2Br_2C ***ii*)** Br_2 ***iii*)** CBr_4.

C.4.1.2 1,5-Dibromo-2,4-difluorobenzene

A first attempt towards the synthesis of **28** (using a protocol by Nishina and Takami[36]) using Fe_2O_3 on zeolite and Br_2 did only yield monobrominated product. The synthesis was successfully performed according to a protocol by Manka et al.[37] Fe-powder was suspended in a solution of **26** in DCM and Br_2 was slowly added with a dropping funnel. In this way, $FeBr_3$ is created *in situ* and acts as a catalyst for the bromination. The product could be isolated with an excellent yield of 91%.

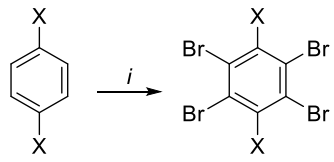


26 **28**

Scheme 32: Synthesis of **28: *i*)** Br_2, Fe-powder, DCM, reflux; ***ii*)** Br_2, Fe_2O_3 on zeolite, DCM.

C.4.1.3 Tetrabromo precursor

Furthermore, hexasubstituted benzenes were synthesized. Since there were no literature references for a feasible synthesis towards compound **32**, the dichloro species **31** was prepared initially, according to a protocol by Harada et al.[38] However, this moiety showed no reactivity in the subsequent S_NAr reaction (see Scheme 37). Using the same method, the difluoro precursor **31** was successfully synthesized with a satisfying yield of 69%.



29: X=Cl
30: X=F

31: X=Cl
32: X=F

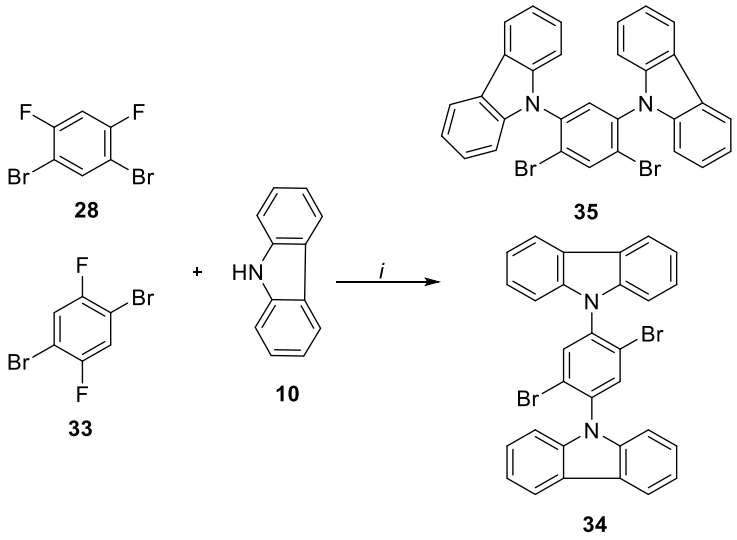
Scheme 33: Synthesis of **31** and **32: *i*)** Fe-powder, I_2, Br_2, fuming sulfuric acid.

C.4.2 Substrates for CH activation

The substrates for the benzene linked systems were derived *via* S_NAr reactions employing different conditions.

In contrast to the electron rich thiophenes, the polyhalogenated benzenes are rather electron deficient and can undergo nucleophilic substitution. According to the element effect the reactivity of halogens in a S_NAr reaction is: F>Cl~Br>I. This order can be attributed to numerous factors. For example, the polarity of the C-F bond is significantly higher compared to the other halogens. But influences on the transition state must be considered as well. A polarity reversal of the C-X bond, that can be observed with Cl and Br, leads to a higher activation barrier of the nucleophilic substitution and is absent for F. Also a stabilization by negative hyperconjugation is most prominent with fluorine substrates.[39]

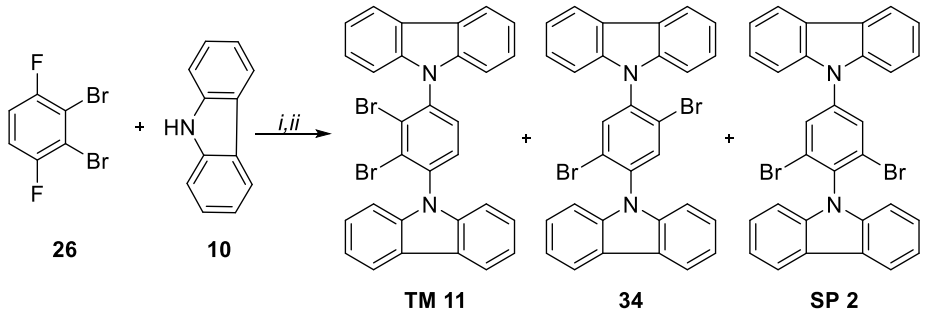
The synthesis of molecules **34** and **35** was done according to Kautny,[40] employing Cs_2CO_3 as a base in anhydous DMSO (Scheme 34).



Scheme 34: Synthesis of **34** and **35** via S_NAr: ***i)*** carbazole (**10**) (2 eq.), Cs_2CO_3 (2.2 eq.), DMSO, 120 °C

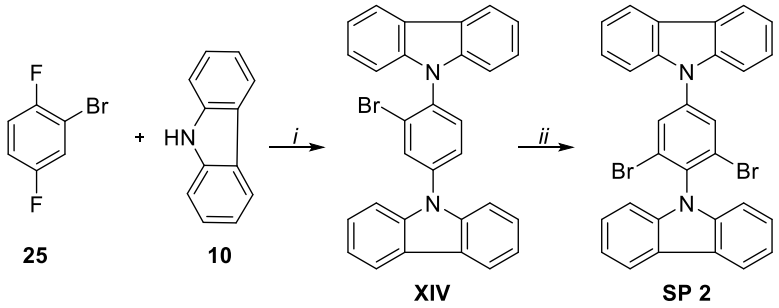
When the same reaction conditions were applied to 2,3-dibromo-1,4-difluorobenzene (**26**), the nucleophilic substitution took place. However, a side reaction occurred. A bromine atom migrated to give significant amounts of the two other possible substitution patterns (Scheme 35). The ratio of product to the two side products was determined *via* NMR to be roughly 1:1:1. Every attempt to separate the molecules using column chromatography and recrystallization from various solvents failed. A second reaction employing NaH as a base in DMF and lower temperatures to prevent halogen migration only resulted in a minor

improvement. The ratio could be altered to 2.5:1:1, but purification still proved to be impossible.



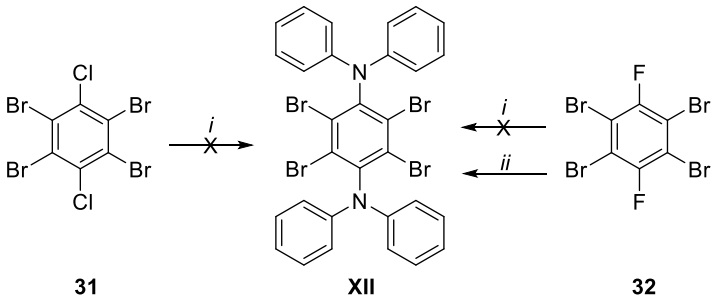
Scheme 35: Nucleophilic substitution of **26**: ***i)*** **26** (1 eq.), carbazole (**10**) (2 eq.), Cs_2CO_3 (2.2 eq.), DMSO, 120 °C; ***ii)*** **26** (1 eq.), carbazole (**10**) (2 eq.), NaH (2 eq.), DMF, 80 °C

To circumvent the bromine migration during the S_NAr reaction, a different route was explored (Scheme 36). 2-Bromo-1,4-difluorobenzene (**25**) was reacted with carbazole (**10**) using the established conditions and subsequently brominated by treatment with LDA and quenching with CBr_4 as described for the synthesis of **26**. However, in this reaction the formation of the side product **SP 2** was strongly favored with a ratio of 1:1:11.



Scheme 36: S_NAr reaction with subsequent bromination yielding the wrong product **SP2**. ***i)*** carbazole (**10**) (2 eq.), Cs_2CO_3 (2.2 eq), DMSO, 120 °C; ***ii)*** 1) LDA (freshly prepared from DIPA and *n*-BuLi), THF, -80 °C; 2) -80 °C, CBr_4.

For the synthesis towards **XII** a first experiment using the established conditions was performed using the dichloro species **31** with diphenylamine (**40**). With this method no product could be obtained, which was assumed to be due to the lower reactivity of the chlorine substrate. Thus, the reaction was repeated employing the difluoro species **32** and again, no product formation was observed. **XII** was finally synthesized using NaH in DMF starting from **32** in a yield of 40%.

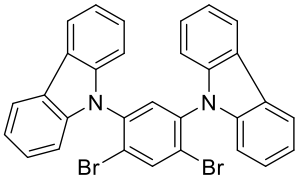
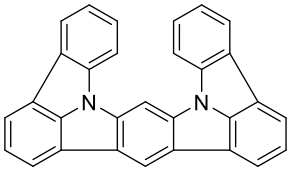
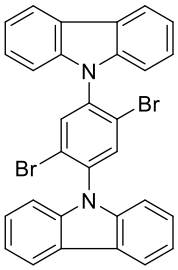
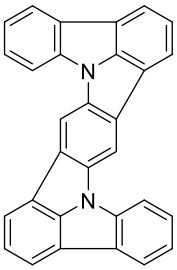
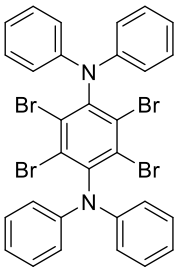
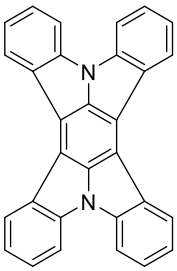


Scheme 37: Synthesis towards **XII**: ***i)*** diphenylamine (**40**) (2 eq.), Cs_2CO_3 (2.2 eq.), DMSO, 120 °C; ***ii)*** diphenylamine (**40**) (2 eq.), NaH (2 eq.), DMF, 80 °C.

C.4.3 CH activation

The final synthesis of the benzene linked systems starting from precursors **34**, **35** and **XII** was performed using $Pd(OAc)_2$ and the NHC-ligand to form the catalyst *in situ*. A summary of the reaction condition and yields is given in Table 6. While substrates **34** and **35** could be converted with excellent to good yields, the tetrabromo species **XII** did not yield any product. The reaction was repeated using the preprepared catalyst with the same outcome.

Table 6: Ring closure *via* CH activation towards the benzene linked systems. **1-3)** Substrate (**34**, **35** or **XII**) (1 eq.), K_2CO_3 (4 eq.), (8 eq. for **XII**), $Pd(OAc)_2$ (0.02 eq.), [NHC]Cl (0.02 eq), DMAc (1000 ppm H_2O), 130 °C, 24 h.

Entry	Substrate	Product	Yield
1	 **35**	 **XI** (***m*-ICz-B-ICz**)	91%
2	 **34**	 **X** (***p*-ICz-B-ICz**)	68%
3[a]	 **XII**	 **TM 13**	-

[a] Reaction repeated with preprepared catalyst Pd[NHC](allyl).

In conclusion, it can be noted that overall the CH activation reactions did work satisfyingly with only two exceptions. A closer look on these failed attempst reveals, that there is an *ortho* substitution pattern of the bromine atoms with respect to each other. The same observation was made with the thiophene linked system. Since the exact mechanism of the CH activation reaction is not yet fully understood, one can only speculate, but one reasonable explanation could be a steric hindrance of a transition state caused by the second bromine atom. Obviously, a sample size of two is not sufficient for any definite conclusions, but further investigations with similarly substituted substrates as well as with smaller chlorine substituents could potentially help to shed light on the reaction mechanism and transition states involved.

C.4.4 Characterization

C.4.4.1 Absorption, singlet and triplet emission

Absorption and singlet-emission of ***p*-ICz-B-ICz** (**X**) and ***m*-ICz-B-ICz** (**XI**) in solution were recorded (depicted in Figure 7). Applying the same procedure as for the SICz molecules, the triplet energies for the benzene linked systems were determined.

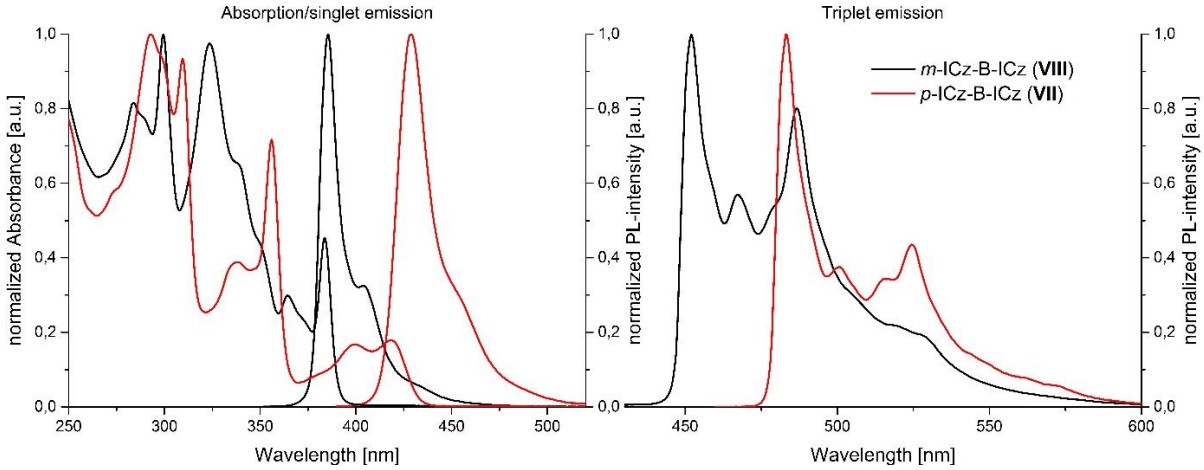


Figure 7: Left: Absorption and singlet-emission spectra of benzene linked systems, recorded in DCM with a concentration of 5 nmol/ml. Right: Phosphorescence spectra of benzene linked systems, recorded in toluene/*i*-PrOH with a concentration of 1 mg/ml at 77 K.

Distinct differences in the photophysical properties can be observed based on the different substitution patterns. The bandgap increases from 2.86 eV for ***p*-ICz-B-ICz** (**X**) to 3.17 eV for ***m*-ICz-B-ICz** (**XI**). While ***p*-ICz-B-ICz** (**X**) exhibits very narrow deep blue emission with a maximum at 429 nm, ***m*-ICz-B-ICz** (**XI**) has an even narrower, blue shifted emission at 385 nm.

Analogously, variations of the triplet energies, associated with the different substitution patterns were observed for the benzene linked systems. ***m*-ICz-B-ICz** (**XI**) exhibits vibronically resolved emission with a maximum at 452 nm corresponding to an E_T of 2.74 eV. A very similar, albeit red shifted emission is observed for ***p*-ICz-B-ICz** (**X**) with the maximum at 483 nm corresponding to 2.57 eV.

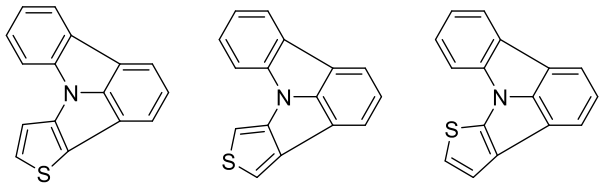
While the bandgaps unfortunately are too large to consider OFET applications, the very narrow and deep blue emission of the molecules is quite promising. Together with the relatively high E_T it could be possible to implement the molecules **X** and **XI** in hybrid OLEDs. In such a device, the blue light is emitted *via* singlet emission while the green, yellow and red light originates from phosphorescence. Using such an approach, devices can be fabricated

featuring the advantages of PhOLEDs while circumventing the current difficulties with deep blue phosphorescent emitters.

C.5 Conclusion, summary and outlook

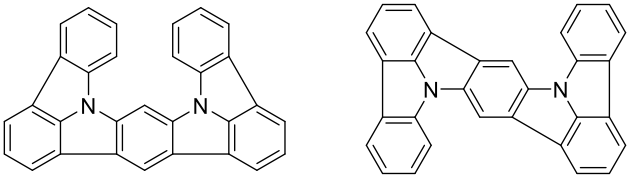
In the course of this work, the scope and applicability of a previously refined CH activation protocol was further increased to sulfur containing moieties as well as large annulated systems. The synthesis of these target molecules could be achieved with good to excellent yields in reasonably short reaction times. Failed attempts of the CH activation suggest a possible limitation of the reaction. *Ortho* substituted dibromo species seem unreactive towards ring closure using this protocol. Further investigations with different substrates and other halides could shed more light on the actual reaction mechanism involved.

Comprehensive synthetic strategies towards new building blocks for applications in organic electronics were developed. Three electron rich, sulfur containing, planar molecules based on the indolo[3,2,1-*jk*]carbazole scaffold were successfully synthesized and characterized to reveal desirable photophysical and electrochemical properties. The incorporation of electron rich thiophenes not only increases the donor strength, but also allows for fine tuning of the HOMO levels *via* the positioning of the sulfur. Due to high triplet energies these building blocks are promising candidates for applications in blue OLED devices.



Scheme 38: Electron rich building blocks based on the ICz scaffold.

Large annulated systems comprised of multiple ICz subunits were synthesized successfully and characterized. High triplet energies and extraordinarily narrow and deep blue emissions hint at potential applications as emitters in OLEDs.



***m*-ICz-B-ICz** **p-ICz-B-ICz**

Scheme 39: Large annulated, benzene linked systems.

Future work will focus on the derivatization of SICz and incorporation of building blocks in hostmaterials, as well as the investigation of the large, annulated benzene linked systems in OLEDs.

D Experimental part

D.1 General remarks

Unless explicitly mentioned otherwise, all reagents from commercial suppliers were used without further purification. Anhydrous solvents were absolutized by the PURESOLV-system from Innovative Technology Inc. Other anhydrous solvents were purchased from commercial suppliers. The commercially available lithiation reagent *n*-BuLi was used without additional quantitative analyses, using the declared value.

D.2 Chromatographic Methods

D.2.1 Thin layer chromatography

Thin layer chromatography (TLC) was performed using TLC-aluminum foil (Merck, silica gel 60 F254).

D.2.2 Column chromatography

Preparative column chromatography was performed using a *Büchi SepacoreTM Flash system* which was equipped with the following components:

Pump-system:	2 *Büchi* pump modules C-605
	Büchi pump manager C-615
Detector:	*Büchi* UV photometer C-635
Fraction collector:	*Büchi* fraction collector C-660

The appropriate PP-cartridges were packed with silica gel (Merck, 40-63 µm).

D.3 Microwave

Reactions under microwave irradiation were performed using a *BIOTAGE Initiator EXP EU 355301*.

D.4 Analytical methods

D.4.1 GC-MS measurements

GC-MS measurements were conducted using a GC-MS interface from Thermo Scientific:

- TRACE 1300 Gas Chromatograph with a Restek Rxi-5Sil MS column (l=30 m, ID=0.25 mm, 0.25 µm film, achiral).
- ISQ LT Single Quadrupole Mass Spectrometer (electron ionization).

D.4.2 NMR-spectroscopy

NMR spectra were recorded using a *Bruker Avance DPX-200 MHz* (200 MHz for ^{1}H) or a *DRX-400 MHz* (400 MHz for ^{1}H; 100 MHz for ^{13}C) Fourier transform spectrometer. ^{1}H- and ^{13}C-spectra are given as stated: chemical shift in parts per million (ppm) referenced to the according solvent (^{1}H: $CDCl_3$ δ=7.26 ppm, CD_2Cl_2 δ=5.32 ppm, DMSO-d6 δ=2.50 ppm; ^{13}C: $CDCl_3$ δ=77.0 ppm, CD_2Cl_2 δ=54.0 ppm, DMSO-d6 δ=39.5 ppm) with tetramethylsilane (TMS) at δ=0 ppm. Multiplicities of the signals are given as: ^{1}H: s=singlet, d=doublet, dd=doublet on doublet, ddd=doublet on doublet on doublet, dt=doublet on triplet t=triplet and m=multiplet.

D.4.3 Single crystal diffraction

Single crystal structures were determined in collaboration with Dr. Berthold Stöger and the X-ray centre. All data were collected on an APEX II diffractometer with κ geometry, equipped with a CCD detector using Mo *Kα* irradiation at 100 K in a dry stream of nitrogen.

D.4.4 Cyclic voltammetry

Cyclic voltammetry was performed using a three-electrode configuration consisting of a Pt working electrode, a Pt counter electrode and a Ag/AgCl reference electrode and a PGSTAT128N potentiostat provided by Metrohm Autolab B.V. Measurements were carried out in a 0.5 mM or saturated (for poorly soluble substances) solution in anhydrous ACN with Bu_4NBF_4 (0.1 M) as supporting electrolyte. The solutions were purged with nitrogen for 15 min prior to measurement. HOMO and LUMO energy levels were calculated from the onset of oxidation and reduction, respectively. The onset potential was determined by the intersection of two tangents drawn at the background and the rising of oxidation or reduction peaks. Ferrocene was used for calibration.

D.4.5 Absorption spectroscopy

Absorption spectra were recorded on a *Thermo Scientific NanoDrop Onec Microvolume* UV-Vis spectrophotometer in degassed DCM solution (5 µM).

D.4.6 Fluorescence and phosphorescence spectroscopy

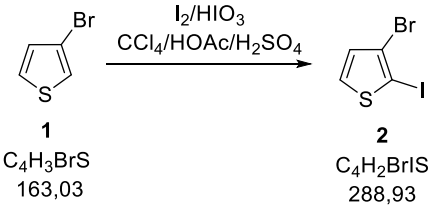
Fluorescence and phosphorescence spectra were recorded on a *PerkinElmer LS 55* fluorescence spectrometer. For fluorescence measurements 5 µM degassed solutions in DCM were used. Phosphorescence spectra of 1 mg/ml solutions in degassed toluene:*i*PrOH were recorded at 77 K.

D.5 Synthesis and characterization of the compounds

Detailed experimental procedures for the synthesis of each compound as well as their characterization are presented in the following chapter.

D.5.1 Synthesis towards SICz and S_2ICz Systems

D.5.1.1 3-Bromo-2-iodothiophene (2)



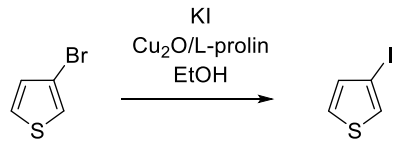
1
C_4H_3BrS
163,03

2
C_4H_2BrIS
288,93

Iodine (5.28 g, 20.8 mmol, 0.4 eq.) and HIO_3 (1.83 g, 10.4 mmol, 0.2 eq.) were put in a 500 ml flask equipped with a reflux condenser. The solids were suspended in a mixture of H_2O, AcOH and CCl_4 (1:2:2, 212 ml). 3-Bromothiophene (**1**) (8.48 g, 52 mmol, 1 eq.) was added *via* a syringe and while stirring H_2SO_4 (conc.) (5.2 ml) was added and the mixture was heated to 60 °C for 5 h whereby a change of color to orange could be observed. After cooling to rt, stirring was continued for an additional 24 h. The reaction mixture was poured onto H_2O and extracted three times with $CHCl_3$. The combined organic phases were washed with $NaHCO_3$, dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. 14.57 g of crude product were purified by vacuum distillation to yield 11.71 g, 78% product **2** as a red liquid.

^{1}H NMR (400 MHz, $CDCl_3$, FID DOB48/70) δ 7.41 (d, *J* = 5.6 Hz, 1H), 6.90 (d, *J* = 5.6 Hz, 1H). Reaction number: DOB48

D.5.1.2 3-Iodothiophene (3)



1
C_4H_3BrS
163,03

3
C_4H_3IS
210,03

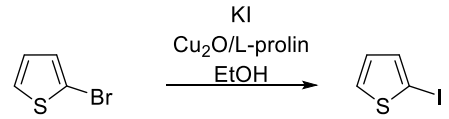
The synthesis of **3** was performed according to Feng et al.[16]

KI (35.86 g, 216 mmol, 3 eq.), Cu_2O (1.03 g, 7.2 mmol, 0.1 eq.) and L-prolin (1.66 g, 14.4 mmol, 0.2 eq.) were suspended in degassed EtOH (215 ml) in a round bottom flask. 3-Bromothiophene (**1**) (11.74 g, 72 mmol, 1 eq.) was added *via* a syringe and the reaction mixture was heated to reflux for three days (reaction control with GCMS). The mixture was

cooled to rt and the solvent removed under reduced pressure. The residue was dissolved in Et_2O and washed with water and brine. The organic phase was dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The curde product was distilled to give 4.12 g of **3** as a colorless liquid in a yield of 27%.

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB49/20) δ 7.41 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.20 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.11 (dd, *J* = 5.0, 1.2 Hz, 1H). Reaction number: DOB49

D.5.1.3 2-Iodothiophene (6)



5
C_4H_3BrS
163,03

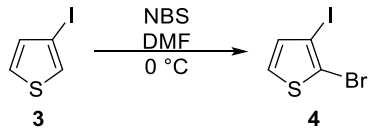
6
C_4H_3IS
210,03

The synthesis of **6** was performed according to Feng et al.[16]

KI (35.86 g, 216 mmol, 3 eq.), Cu_2O (1.03 g, 7.2 mmol, 0.1 eq.) and L-prolin (1.66 g, 14.4 mmol, 0.2 eq.) were suspended in degassed EtOH (215 ml) in a round bottom flask. 2-Bromothiophene (**5**) (11.74 g, 72 mmol, 1 eq.) was added *via* a syringe and the reaction mixture was heated to reflux for four days (reaction control with GCMS). The mixture was filtered over a plug of celite® and the solvent removed under reduced pressure. The residue was dissolved in Et_2O and washed with water and brine. The organic phase was dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was distilled (15 mbar, 67 °C) to give pure **6** in a yield of 3.97 g (26%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB51/20) δ 7.36 (dd, *J* = 5.4, 1.3 Hz, 1H), 7.25 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.81 (dd, *J* = 5.4, 3.6 Hz, 1H). Reaction number: DOB51

D.5.1.4 2-Bromo-3-iodothiophene (4)



3
C_4H_3IS
210,03

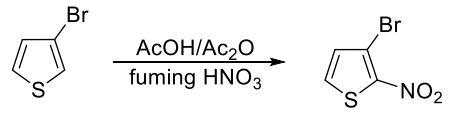
4
C_4H_2BrIS
288,93

3-Iodothiophene (**3**) (3.36 g, 16 mmol, 1 eq.) was dissolved in 64 ml DMF and cooled to 0 °C using a NaCl/ice bath. NBS (3.13 g, 17.6 mmol, 1.1 eq.) was added slowly while stirring. After complete addition the solution was warmed to rt and stirred overnight. The reaction mixture was poured onto water and extracted three times with DCM. The combined organic phases were washed with water, dried over Na_2SO_4, filtered and the solvent removed under

reduced pressure. The crude product was purified by column chromatography (LP) to yield **4** 3.45 g, 75%.

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB107/20) δ 7.23 (d, *J* = 5.7 Hz, 1H), 6.96 (d, *J* = 5.7 Hz, 1H) ppm. Reaction number: DOB107

D.5.1.5 3-Bromo-2-nitrothiophene (7)



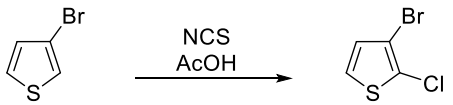
1
C_4H_3BrS
163,03

7
$C_4H_2BrNO_2S$
208,03

Fuming HNO_3 (2.32 ml) was added dropwise to 28.83 ml of acetic acid at 5 °C. To that mixture a solution of 3-bromothiophene (**1**) (7.83 g, 48 mmol, 1 eq.) in 16.3 ml acetic anhydride was added dropwise keeping the temperature below 5 °C. After complete addition the reaction mixture was stirred for 2 h at a temperature below 10 °C. The solution was poured onto ice, the precipitate was filtered off and thoroughly washed with water and LP. The product was dried under reduced pressure to yield **7** as a yellow solid (3.11 g, 31%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB135/10) δ 7.49 (d, *J* = 5.5 Hz, 1H), 7.11 (d, *J* = 5.5 Hz, 1H) ppm. Reaction number: DOB135

D.5.1.6 3-Bromo-2-chlorothiophene (8)



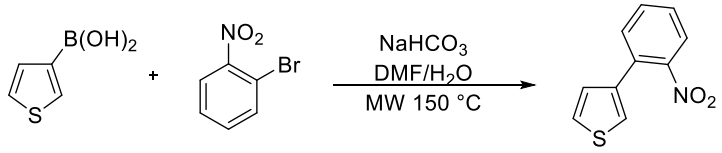
1
C_4H_3BrS
163,03

8
C_4H_2BrClS
197,47

3-Bromothiophene (**1**) (2.45 g, 15 mmol, 1 eq.) was dissolved in 20 ml of acetic acid and NCS (2.00 g, 15 mmol, 1 eq.) was added slowly. After complete addition the solution was heated to reflux for 2 h. After cooling to rt the solution was poured onto water and extracted three times with DCM. The combined organic phases were washed with water, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude product was purified by distillation (15 mbar at 75 °C) to yield **8** as a colorless liquid (2.72 g, 77%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB100/40) δ 7.12 (d, *J* = 5.8 Hz, 1H), 6.91 (d, *J* = 5.8 Hz, 1H). Reaction number: DOB100

D.5.1.7 3-(2-Nitrophenyl)thiophene (15)



13
$C_4H_5BO_2S$
127,95

14
$C_6H_4BrNO_2$
202,01

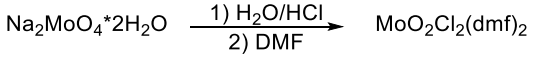
15
$C_{10}H_7NO_2S$
205,23

The synthesis of **15** was performed according to Appukkuttan et al.[18]

A microwave vial was charged with boronic acid **13** (832 mg, 6.5 mmol, 1.3 eq.), 1-Bromo-2-nitrobenzene (**14**) (1.01 g, 5 mmol, 1 eq.), $NaHCO_3$ (1,26 g, 15 mmol, 3 eq.) and $Pd(PPh_3)_4$ (289 mg, 0.25 mmol, 0.05 eq.). The vial was flushed with argon, 15 ml of degassed solvent (DMF/H_2O 1:1) was added and the vial was sealed. The reaction was performed in the microwave oven for 15 min at 150 °C. The reaction mixture was poured onto water and extracted three times with DCM. The combined organic phases were washed with water and brine, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude product was purified *via* column chromatography (LP/DCM 25%) to yield the product (**15**) as a colorless oil (949 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB146/30) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.59 (td, *J* = 7.6, 1.3 Hz, 1H), 7.47 (m, 2H), 7.39 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.09 (d, *J* = 5.0 Hz, 1H) ppm. Reaction number: DOB146

D.5.1.8 $MoO_2Cl_2(dmf)_2$ (38)



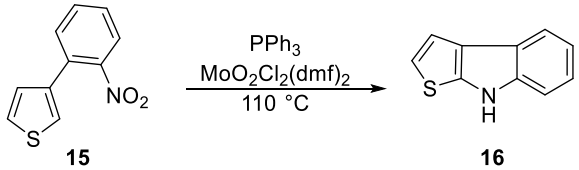
37
$H_4MoNa_2O_6$
241,97

38
$H_{14}C_6N_2Cl_2MoO_4$
436,66

The synthesis of the catalyst **38** was performed according to Sanz et al.[20]

$Na_2MoO_4 \cdot 2H_2O$ (**37**) (4.84 g, 20 mmol, 1 eq.) was dissolved in 10 ml of H_2O and conc. HCl (14 ml) was added while stirring. The solution was extracted with Et_2O whereby a color change to a bright yellow was observed. The organic phase was dried over Na_2SO_4, filtered and DMF (3.26 ml) was slowly added. The yellow precipitate was filtered off and washed with Et_2O. The product was dried under reduced pressure to yield **38** as a yellow powder (4.59 g, 61%). Reaction number: DOB153

D.5.1.9 Thieno[2,3-*b*]indole (16)



15
$C_{10}H_7NO_2S$
205,23

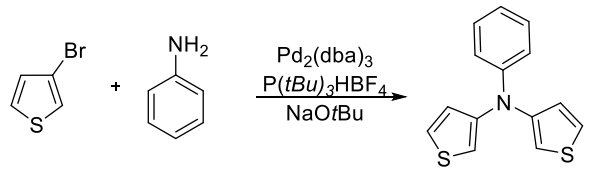
16
$C_{10}H_7NS$
173,23

The synthesis of **16** was performed according to Baert et al.[19]

Thiophene-precursor **15** (1.560 g, 7.65 mmol, 1 eq.) was dissolved in anhydrous toluene and the solution was degassed with argon. PPh_3 (4.82 g, 18.37 mmol, 2.4 eq.) and $MoO_2Cl_2(dmf)_2$ (144 mg, 0.38 mmol, 0.05 eq.) were added under argon counterflow and the reaction mixture was heated to 110 °C. After 24 h, 4 ml DMSO and additional 27 mg of the catalyst were added and the solution was stirred at 110 °C for another hour. After completion the solvent was removed under reduced pressure and the crude product was purified *via* column chromatography (toluene/LP 2:3). The product **16** was yielded as a white solid (830 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB157/20) δ 8.20 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.32 – 7.15 (m, 2H), 6.90 (d, *J* = 5.3 Hz, 1H) ppm. Reaction number: DOB157

D.5.1.10 *N*-Phenyl-di-3-thiophenamine (20)



1
C_4H_3BrS
163,03

17
C_6H_7N
93,13

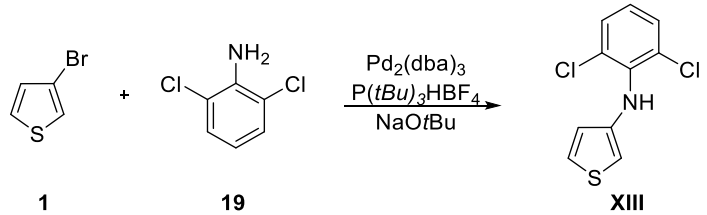
20
$C_{14}H_{11}NS_2$
257,37

A round bottom flask was charged with $Pd_2(dba)_3$ (71 mg, 0.078 mmol, 0.02 eq.), P(*t*Bu)$_3$·HBF_4 (113 mg, 0.39 mmol, 0.1 eq.), NaO*t*Bu (937 mg, 9.75 mmol, 2.5 eq.) and flushed with argon three times. The apparatus was assembled under argon flux. 3-Bromothiophene (**1**) (1.59 mg, 9.75 mmol, 2.5 eq.), aniline (**17**) (363 mg, 3.9 mmol, 1 eq.) and 25 ml of anhydrous toluene were added *via* syringe under argon counterflow. The reaction mixture was heated to reflux and stirred overnight. After GCMS revealed incomplete conversion 1 eq. of 3-bromothiophene (**1**) was added and stirring at reflux was continued for 5 h. Another eq. of **1** was added and stirring at reflux continued for another 24 h. After cooling to rt the solution was poured onto water and extracted three times with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and the

solvent removed under reduced pressure. The crude product was purified by column chromatography (LP/DCM 3%) to yield target compound **20** (624 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB115/20) δ 7.30 – 7.20 (m, 4H), 7.14 – 7.06 (m, 2H), 7.04 – 6.95 (m, 1H), 6.89 (dd, *J* = 6.5, 5.3 Hz, 2H), 6.67 (s, 2H) ppm. Reaction number: DOB115

D.5.1.11 *N*-(2,6-Dichlorophenyl)-3-thiophenamine (XIII)



1
C_4H_3BrS
163,03

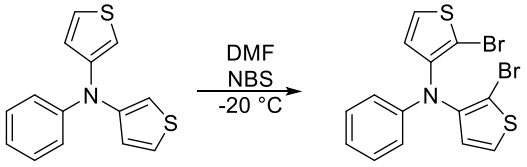
19
$C_6H_5Cl_2N$
162,01

XIII
$C_{10}H_7Cl_2NS$
244,13

A reaction vial was charged with 2,6-dichloroaniline (**19**) (162 mg, 1 mmol, 1 eq.), $Pd_2(dba)_3$ (18 mg, 0.02 mmol, 0.02 eq.), P(*t*Bu)$_3$·HBF_4 (29 mg, 0.1 mmol, 0.1 eq.) and NaO*t*Bu (105 mg, 1.1 mmol, 1.1 eq.). The vial was flushed with argon three times and 3-bromothiophene (**1**) (163 mg, 1 mmol, 1 eq.) and 5 ml of anhydrous toluene were added under argon counterflow. The vial was sealed and put on a heating block at 120 °C for 24 h. After that time, GCMS showed incomplete conversion and another 0.5 eq. of (**1**) was added and the mixture was stirred for another 24 h at 120 °C. After cooling to rt the mixture was taken up in DCM and washed three times with water. The organic phase was dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude product was purified *via* column chromatography (LP/DCM 3%). The target compound **XIII** was isolated in a yield of 78 mg (32%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB105/20) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 5.2 Hz, 1H), 6.99 (t, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 5.1 Hz, 1H), 6.26 (s, 1H) ppm. NH not detected. Reaction number: DOB105

D.5.1.12 2,2´-Dibromo-*N*-phenyldi-3-thiophenamin (VII)



20
$C_{14}H_{11}NS_2$
257,37

VII
$C_{14}H_9Br_2NS_2$
415,16

20 (118 mg, 0.46 mmol, 1 eq.) was dissolved in 5 ml DMF and cooled to -20 °C using a NaCl/ice bath. NBS (163 mg, 0.92 mmol, 2 eq.) was added slowly while stirring. After

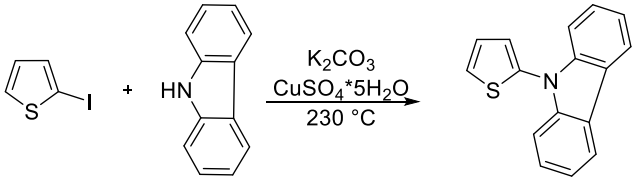
complete addition the solution was heated to rt and stirred overnight. The reaction mixture was poured onto water and extracted three times with DCM. The combined organic phases were washed with water, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to yield **VII** (189 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB112/10) δ 7.25 (d, *J* = 5.9 Hz, 2H), 7.23 – 7.19 (m, 2H), 6.97 – 6.88 (m, 1H), 6.81 (d, *J* = 5.8 Hz, 2H), 6.80 – 6.76 (m, 2H) ppm. Reaction number Dob112.

D.5.1.13 General procedure for Ullmann reactions GP1

A reaction vial equipped with a small stirring bar was charged with K_2CO_3 (1.5 eq.), $CuSO_4 \cdot 5H_2O$ (0.05 eq.) and carbazole (**10**) (1 eq.) and flushed with argon three times. The corresponding thiophene precursor (1.5 eq.) was added and the vial was flushed with argon once more and sealed. The reaction mixture was put in a preheated heating block at 250 °C until completion. After cooling to rt, the reaction mixture was dissolved in DCM and H_2O, the phases were separated and the aqueous phase was extracted two times with DCM. The combined organic phases were washed two times with water and once with brine and then dried over Na_2SO_4, filtered and the solvent removed under reduced pressure.

D.5.1.14 9-(2-Thienyl)-*9H*-carbazole (11)



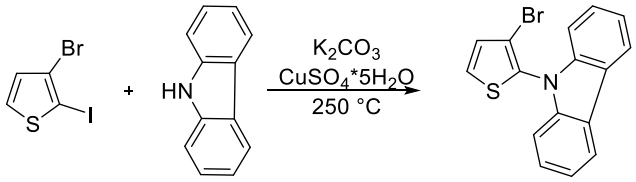
6 C_4H_3IS 210,03 | **10** $C_{12}H_9N$ 167,21 | **11** $C_{16}H_{11}NS$ 249,33

The preparation of **11** was performed according to GP1.

$CuSO_4 \cdot 5H_2O$ (12 mg, 0.05 mmol, 0.05 eq.), K_2CO_3 (207 mg, 1.5 mmol, 1.5 eq.), carbazole (**10**) (334 mg, 2 mmol, 2 eq.) and 2-iodothiophene (210 mg, 1 mmol, 1 eq.) were reacted at 230 °C to give the product **11** after workup in a yield of 139 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB67/20) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.39 (dd, *J* = 5.5, 1.5 Hz, 1H), 7.31 (ddd, *J* = 8.1, 6.1, 2.1 Hz, 2H), 7.23 – 7.16 (m, 2H). Reaction number: DOB67

D.5.1.15 9-(3-Bromo-2-thienyl)-9*H*-carbazole (V)



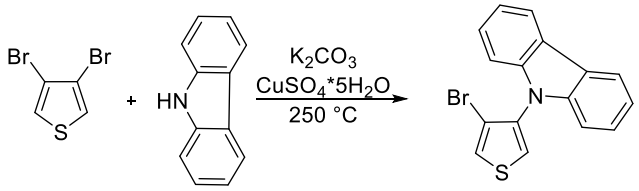
2 C_4H_2BrIS 288,93 | **10** $C_{12}H_9N$ 167,21 | **V** $C_{16}H_{10}BrNS$ 328,23

The synthesis of **VI** was performed according to general procedure GP1.

3-Bromo-2-iodothiophene (**2**) (866 mg, 3 mmol, 1,5 eq.), carbazole (**10**) (334 mg, 2 mmol, 1 eq.), K_2CO_3 (415 mg, 3 mmol,1.5 eq.) and $CuSO_4 \cdot 5H_2O$ (24 mg, 0.1 mmol, 0.05 eq.) were reacted at 250 °C for 1 h. After workup the crude product was purified *via* column chromatography (LP/DCM 3%) yielding 169 mg (26%) of **V**.

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB88/20) δ 8.12 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.32 (ddd, *J* = 7.7, 7.2, 1.1 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.19 (d, *J* = 5.9 Hz, 1H). Reaction number: DOB88

D.5.1.16 9-(4-Bromo-3-thienyl)-9*H*-carbazole (III)



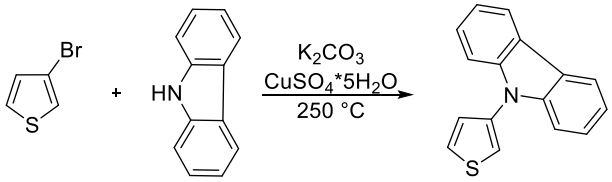
9 $C_4H_2Br_2S$ 241,93 | **10** C12H9N 167,21 | **III** $C_{16}H_{10}BrNS$ 328,23

The synthesis of **III** was performed according to general procedure GP1.

3,4-Dibromothiophene (**9**) (1.06 g, 4.4 mmol, 1.1 eq.), carbazole (**10**) (669 mg, 4 mmol, 1 eq.), K_2CO_3 (608 mg, 4.4 mmol, 1.1 eq.) and $CuSO_4 \cdot 5H_2O$ (50 mg, 0.2 mmol, 0.05 eq.) were reacted at 250 °C for 2.5 h. After workup the crude product was purified *via* column chromatography (LP/DCM 3%). The product **III** was obtained as an off-white solid (654 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB127/20) δ 8.13 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.42 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.30 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H). Reaction numbers: DOB116/127

D.5.1.17 9-(3-Thienyl)-9*H*-carbazole (12)



1
C_4H_3BrS
163,03

10
$C_{12}H_9N$
167,21

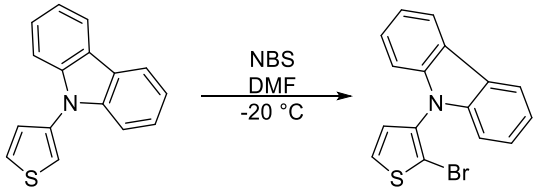
12
$C_{16}H_{11}NS$
249,33

The synthesis of **12** was performed according to general procedure GP1.

3-Bromothiophene (**1**) (2.35 g, 14.4 mmol, 1.2 eq.), carbazole (**10**) (2.71 g, 12 mmol, 1 eq.), K_2CO_3 (2.49 g, 14.4 mmol, 1.2 eq.) and $CuSO_4 \cdot 5H_2O$ (150 mg, 0.6 mmol, 0.05 eq.) were reacted at 250 °C for 2.5 h. After workup the crude product was purified *via* column chromatography (LP/DCM 3%). **12** was obtained in a yield of 2.134 g (71%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB117/20) δ 8.14 (d, *J* = 7.7 Hz, 2H), 7.56 (dd, *J* = 5.1, 3.2 Hz, 1H), 7.50 – 7.40 (m, 5H), 7.36 – 7.27 (m, 3H). Reaction numbers: DOB111/117

D.5.1.1 9-(2-Bromo-3-thienyl)-9*H*-carbazole (I)



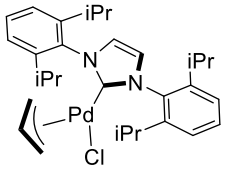
12
$C_{16}H_{11}NS$
249,33

I
$C_{16}H_{10}BrNS$
328,23

12 (249 mg, 1 mmol, 1 eq.) was dissolved in DMF (12 ml) and cooled to -20 °C with an ice/NaCl bath. While stirring, NBS (178 mg, 1 mmol, 1 eq.) was added slowly, keeping the temperature at -20 °C. After complete addition the solution was warmed to rt and stirred overnight. The reaction mixture was poured onto water and extracted three times with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. Purification of the crude product was done by column chromatography (LP/DCM 3%) to yield the product **I** as an off white solid. (193 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB113/20) δ 8.14 (ddd, *J* = 7.7, 1.3, 0.8 Hz, 2H), 7.51 (d, *J* = 5.8 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 5.7 Hz, 1H). Reaction number: DOB113

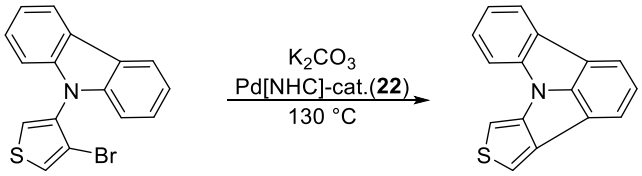
D.5.1.2 General procedure for CH activation GP2



36
$C_{30}H_{41}ClN_2Pd$
571,52

A round bottom flask was charged with the precursor (1 eq.), K_2CO_3 (4 eq.), NHC-catalyst **36** (0.05 eq.) and flushed with argon three times and the apparatus was assembled under argon counterflow. DMAc with a water content of 1000 ppm was degassed with argon and added to the reaction apparatus under argon counterflow. The mixture was heated to 130 °C and stirred until completion. The reaction mixture was cooled to rt and poured onto saturated NaCl solution. The precipitate was filtered off, thoroughly washed with water and dried under reduced pressure.

D.5.1.3 Thieno[3´,4´:4,5]pyrrolo[3,2,1-*jk*]carbazole (IV)



III
$C_{16}H_{10}BrNS$
328,23

IV
$C_{16}H_9NS$
247,32

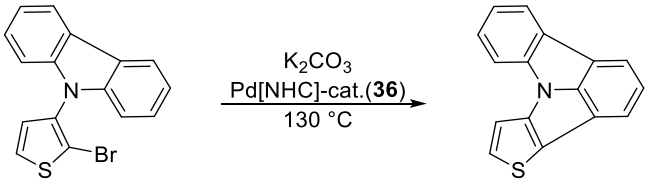
The synthesis of **IV** was performed according to general procedure GP2.

III (581 mg, 1.77 mmol, 1 eq.), K_2CO_3 (489 mg, 3.54 mmol, 2 eq.) and the Pd[NHC]-catalyst **36** (51 mg, 0.089 mmol, 0.05 eq.) were suspended in 75 ml DMAc (1000 ppm H_2O) and reacted at 130 °C for 24 h. After workup, the crude product was dissolved in DCM, filtered over silica and the solvent removed to give a brown solid. The product was further purified *via* HPLC (*n*-heptane/*i*-PrOH 0.02% for 1 min to 0.1% over 10 min.) to yield **IV** as a white solid (282 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB128/70) δ 8.13 – 8.09 (m, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.73 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.53 (ddd, *J* = 8.1, 7.4, 1.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.33 (ddd, *J* = 7.8, 7.3, 1.1 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$ FID DOB128/71) δ 151.7, 140.9, 138.3, 137.7, 128.5, 126.6, 123.0, 122.6, 121.2, 119.6, 119.0, 118.7, 116.3, 113.9, 111.6, 96.6 ppm. Reaction number: DOB128

D.5.1.4 Thieno[2´,3´:4,5]pyrrolo[3,2,1-*jk*]carbazole (II)



I
$C_{16}H_{10}BrNS$
328,23

II
$C_{16}H_9NS$
247,32

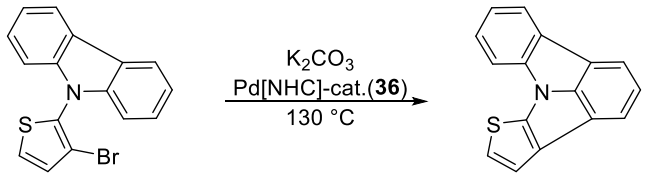
The synthesis of **II** was performed according to general procedure GP2.

Thiophene-precursor **I** (799 mg, 2.43 mmol, 1 eq.), K_2CO_3 (672 mg, 4.86 mmol, 2 eq.) and the catalyst **36** (70 mg, 0.122 mmol, 0.05 eq.) were suspended in 105 ml DMAc (1000 ppm H_2O) and reacted at 130 °C for 2 h. After workup the crude product was purified *via* column chromatography (LP/DCM 4%). The product was further purified by recrystallization from cyclohexane and *via* HPLC (*n*-heptane/*i*-PrOH 0.02% for 1 min to 0.1% over 10 min.) to yield **II** as a white solid (474 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB129/80) δ 8.10 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 1H), 7.94 (dd, *J* = 7.4, 0.5 Hz, 1H), 7.84 (dd, *J* = 7.6, 0.5 Hz, 1H), 7.75 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.59 – 7.46 (m, 4H), 7.33 (td, *J* = 7.6, 1.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$ FID DOB129/81) δ 145.3, 141.2, 138.7, 129.6, 128.1, 126.9, 124.1, 123.2, 123.1, 121.8, 119.9, 118.4, 117.8, 117.5, 111.8, 111.5 ppm. Reaction number: DOB129

D.5.1.5 Thieno[3´2´:4,5]pyrrolo[3,2,1-*jk*]carbazole (V)



IV
$C_{16}H_{10}BrNS$
328,23

V
$C_{16}H_9NS$
247,32

The synthesis of **V** was performed according to general procedure GP2.

IV (488 mg, 1.49 mmol, 1 eq.), K_2CO_3 (412 mg, 2.98 mmol, 2 eq.) and the catalyst **36** (42 mg, 0.074 mmol, 0.05 eq.) were suspended in 65 ml DMAc (1000 ppm H_2O) and reacted

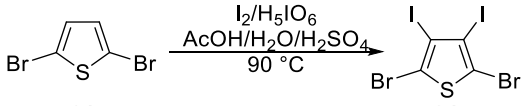
at 130 °C for 4 h. After workup the crude product was purified *via* column chromatorgraphy (LP/DCM 4%). The product was further purified by recrystallization from cyclohexane and *via* HPLC (*n*-heptane/*i*-PrOH 0.02% for 1 min to 0.1% over 10 min.) to yield **V** as a white solid (255 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB130/50) δ 8.10 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 1H), 7.92 (dd, *J* = 7.4, 0.5 Hz, 1H), 7.87 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.70 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.58 – 7.45 (m, 3H), 7.35 (td, *J* = 7.6, 1.0 Hz, 1H), 7.08 (d, *J* = 5.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$ FID DOB130/51) δ 146.5, 138.9, 138.2, 131.3, 130.0, 126.9, 123.3, 123.2, 122.2, 119.3, 119.2, 119.1, 118.6, 117.8, 117.4, 111.7 ppm. Reaction number: DOB130

D.5.2 Synthesis towards large annulated thiophene linked systems

D.5.2.1 2,5-Dibromo-3,4-diiodothiophene (24)



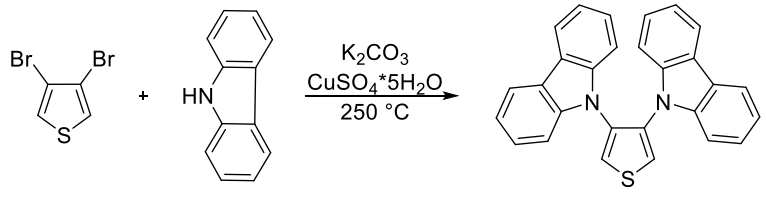
21
$C_4H_2Br_2S$
241,93

24
$C_4Br_2I_2S$
493,72

The Synthesis of **24** was performed according to Ayres et al.[35]

A three necked flask equipped with a reflux condenser was charged with periodic acid (0.97 g, 4.25 mmol, 0.425 eq.), I_2 (2.54 g, 10 mmol, 1 eq) and a mixture of $AcOH/H_2O/H_2SO_4$ (6 ml/1.5 ml/0.2 ml). 2,5-Dibromothiophene (2.42 g, 10 mmol, 1 eq.) was added *via* a syringe and the solution was heated to 90 °C while stirring. The dark red solution became lighter colored with the consumption of iodine and a white solid precipitated. After 3.5 h the solution was decolorized, and the reaction mixture cooled to rt. An aqueous solution of Na_2SO_3 (~8 ml) was added and it was stirred vigorously for 10 minutes. The solid was filtered and washed with cold water. The crude product was dried in vacuum and purification was accomplished by recrystallization from EtOH. The product was obtained as colorless needles in a yield of 3.66 g (74%). Characterization *via* GCMS. Reaction number: DOB161

D.5.2.2 9,9´-(3,4-Thiophendiyl)bis[9*H*-cabazole] (IX)



9
$C_4H_2Br_2S$
241,93

10
$C_{12}H_9N$
167,21

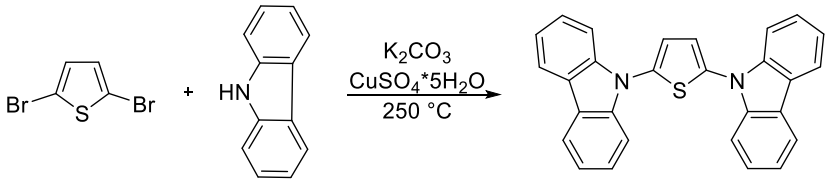
IX
$C_{28}H_{18}N_2S$
414,53

The synthesis of **IX** was performed according to general procedure GP1.

3,4-Dibromothiophene (**9**) (968 mg, 4 mmol, 1 eq.), carbazole (**10**) (1.34 g, 8 mmol, 2 eq.), K_2CO_3 (1.11 g, 8 mmol, 2 eq.) and $CuSO_4 \cdot 5H_2O$ (50 mg, 0.2 mmol, 0.05 eq.) were reacted at 250 °C for 8 h. After workup the crude product was recrystallized from toluene to give **IX** as a white solid in a yield of 897 mg (54%).

^{1}H NMR (400 MHz, DMSO-d_6 FID DOB121/30) δ 8.27 (s, 2H), 7.94 (d, *J* = 7.6 Hz, 4H), 7.23 (d, *J* = 8.2 Hz, 4H), 7.13 (ddd, *J* = 8.2, 7.1, 1.4 Hz, 4H), 7.06 (td, *J* = 7.4, 1.1 Hz, 4H). Reaction number: DOB121

D.5.2.3 9,9´-(2,5-Thiophenediyl)bis[9*H*-carbazole] (22)



21
$C_4H_2Br_2S$
241,93

10
$C_{12}H_9N$
167,21

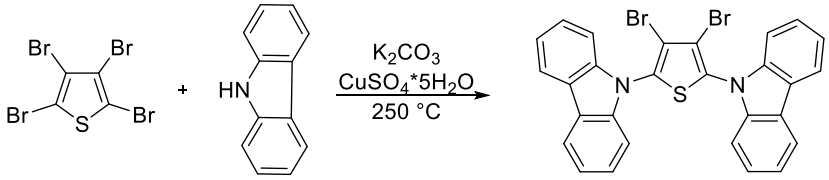
22
$C_{28}H_{18}N_2S$
414,53

The synthesis of **22** was performed according to general procedure GP1.

2,5-Dibromothiophene (**21**) (968 mg, 4 mmol, 1 eq.), carbazole (**10**) (1.34 g, 8 mmol, 2 eq.), K_2CO_3 (1.11 g, 8 mmol, 2 eq.) and $CuSO_4 \cdot 5H_2O$ (50 mg, 0.2 mmol, 0.05 eq.) were reacted at 250 °C for 8 h. After workup the crude product was purified *via* column chromatography (LP/DCM 20%) yielding **22** as a white solid (768 mg, 44%).

^{1}H NMR (400 MHz, DMSO-d_6 FID DOB122/30) δ 8.26 (d, *J* = 7.8 Hz, 4H), 7.67 (d, *J* = 8.2 Hz, 4H), 7.59 (s, 2H), 7.54 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 4H), 7.36 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 4H). Reaction number: DOB122

D.5.2.4 9,9´-(3,4-Dibromo-2,5-thiophenediyl)bis[9*H*-carbazole] (VIII)



23
C_4Br_4S
399,72

10
C12H9N
167,21

VIII
$C_{28}H_{16}Br_2N_2S$
572,32

The synthesis of **VIII** was performed according to general procedure GP1.

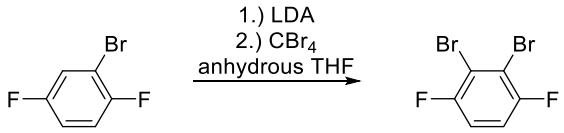
1,2,3,4-Tetrabromothiophene (**23**) (1.12 g, 2.8 mmol, 1 eq.), carbazole (**10**) (936 mg, 5.6 mmol, 2 eq.), K_2CO_3 (774 mg, 5.6 mmol, 2 eq.) and $CuSO_4 \cdot 5H_2O$ (35 mg, 0.14 mmol, 0.05 eq.) were reacted at 250 °C for 2 h. After workup the crude product was purified *via* column chromatography (LP/DCM 4% - 30%) yielding **VIII** as a white solid (234 mg, 15%).

^{1}H NMR (400 MHz, DMSO-d_6 FID DOB126/40) δ 8.28 (d, *J* = 7.7 Hz, 4H), 7.63 (d, *J* = 8.2 Hz, 4H), 7.55 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 4H), 7.39 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 4H).

^{13}C NMR (101 MHz, Methylene Chloride-d_2 FID DOB126/71) δ 141.3, 133.7, 127.0, 124.4, 121.8, 120.9, 114.5, 110.9. Reaction number: DOB126

D.5.3 Syntheis towards large annulated benzene linked systems

D.5.3.1 2,3-Dibromo-1,4-difluorobenzene (26)



25
$C_6H_3BrF_2$
192,99

26
$C_6H_2Br_2F_2$
271,89

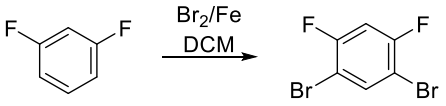
The synthesis of **26** was performed according to Diemer et al.[41]

DIPA (0.71 g, 7 mmol, 1 eq.) was dissolved in anhydrous THF (15 ml) and cooled to -80 °C with an acetone/N_2 bath. *n*-BuLi (2.5 M in hexane) (2.8 ml, 7 mmol, 1 eq.) was added dropwise with a syringe, not exceeding -80 °C. The mixture was stirred for 30 min at -80 °C before **25** (1.35 g, 7 mmol, 1 eq.) was added dropwise and the solution was stirred for 2 h at -80 °C. CBr_4 (2.79 g, 8.4 mmol, 1.2 eq.) was dissolved in 5 ml anhydrous THF and added to the reaction mixture *via* a syringe (color change to orange). The solution was stirred for 30 min at -80 °C before it was heated to rt and stirred overnight. 20 ml H_2O were added and the mixture was extracted with Et_2O and 1N HCl. The combined organic phases were dried

over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was purified using column chromatography (LP) to give **26** as an off-white solid in a yield of 1.19 g (63%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB56/20) δ 7.10 (dd, *J* = 5.9, 1.7 Hz, 2H). Reaction number: DOB 56

D.5.3.2 1,5-Dibromo-2,4-difluorobenzene (28)



27
$C_6H_4F_2$
114,09

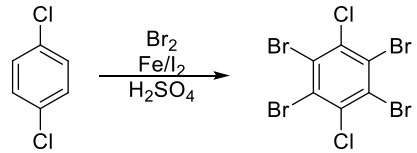
28
$C_6H_2Br_2F_2$
271,89

28 was synthesized according to Manka et al. [37]

meta-Difluorobenzene (**27**) (2.05 g, 18 mmol, 1 eq.) and Fe-powder (281 mg) was suspended in 10 ml DCM. Br_2 (6.33 g, 39.6 mmol, 2.2 eq.) dissolved in 10 ml DCM was added dropwise over a period of 1.5 h at reflux. The reaction mixture was kept at reflux for an additional hour (reaction control with GCMS). After completion the solution was poured onto saturated Na_2SO_3 solution (100 ml) and extracted with DCM/H_2O. the combined organic phases were washed with brine and dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was purified using flash chromatography (LP) to yield 4.45 g (91%) of **28** as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB57/20) δ 7.76 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 8.1 Hz, 1H). Reaction number: DOB57

D.5.3.3 1,2,4,5-Tetrabromo-3,6-dichlorobenzene (31)



29
$C_6H_4Cl_2$
147,00

31
$C_6Br_4Cl_2$
462,58

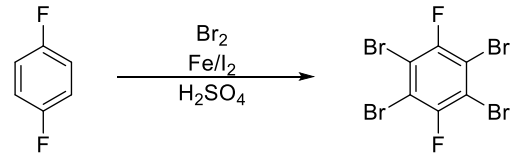
The synthesis of **31** was performed according to Harada et al.[38]

A round bottom flask was charged with Fe-powder (50 mg), I_2 (50 mg) and *para*-dichlorobenzene (**29**) (1.62 g, 11 mmol, 1 eq.) together with fuming sulfuric acid (20 ml). Br_2 (7.03 g, 44 mmol, 4 eq.) was added dropwise. After complete addition the mixture was heated to 60 °C for 1 h. The solution was poured on ice, the precipitate was filtered off and

washed with water. The crude product was recrystallized from toluene to yield **31** (2.73 g, 54%) as a white solid.

Calculated *m/z*: 458 [M⁺]. Found MS (EI): *m/z:* 459.65 [M⁺] Reaction number: DOB52

D.5.3.4 1,2,4,5-Tetrabromo-3,6-difluorobenzene (32)



30
$C_6H_4F_2$
114,09

32
$C_6Br_4F_2$
429,68

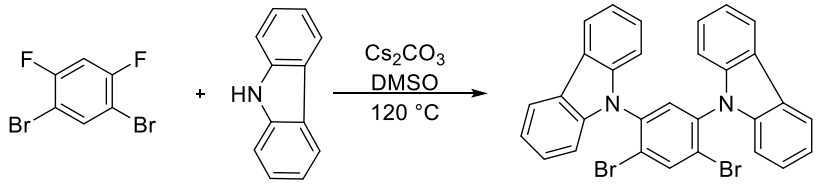
The synthesis of **32** was performed according to Harada et al.[38]

A round bottom flask was charged with Fe-powder (50 mg), I_2 (50 mg) and *para*-difluorobenzene (**30**) (1.26 g, 11 mmol, 1 eq.) together with fuming sulfuric acid (20 ml). Br_2 (7.21 g, 45.1 mmol, 4.1 eq.) was added dropwise. After complete reaction (1 min, GCMS) the mixture was poured onto ice and extracted wit DCM. The combined organic phases were washed with aqueous Na_2SO_3, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. A solution of the crude product was filtered over silica to give 3.28 g (69%) of **32** as a white solid after evaporation of the solvent.

^{13}C NMR (101 MHz, $CDCl_3$ FID DOB60/81) δ 153.72 (dd, *J* = 248.0, 4.7 Hz), 113.56 – 113.14 (m).

^{19}F NMR (376 MHz, $CDCl_3$ FID DOB60/74) δ -88.55 (s). Reaction numbers: DOB60/69

D.5.3.5 9,9'-(4,6-Dibromo-1,3-phenylene)bis[9*H*-carbazole] (35)



28
$C_6H_2Br_2F_2$
271,89

10
$C_{12}H_9N$
167,21

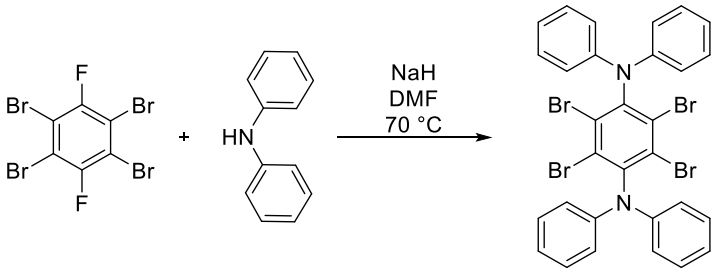
35
$C_{30}H_{18}Br_2N_2$
566,30

28 (952 mg, 3.5 mmol, 1 eq.) and carbazole (**10**) (1171 mg, 7 mmol, 2 eq.) were dissolved in DMSO (90 ml) in a flask which was purged with argon. Cs_2CO_3 (2.5 g, 7.7 mmol, 2.2 eq.) was added while stirring and the reaction mixture was heated to 120 °C. After 24 h the solution was cooled to rt, poured on H_2O (500 ml) and extracted with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and the solvent removed

under reduced pressure. The crude product was purified by column chromatography (LP/DCM 10% - 50%) yielding **35** (1.43 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB59/30) δ 8.39 (s, 1H), 8.13 (dd, *J* = 7.8, 1.3 Hz, 4H), 7.66 (s, 1H), 7.45 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 4H), 7.32 (ddd, *J* = 7.5, 1.0 Hz, 4H), 7.19 (d, *J* = 8.2 Hz, 4H). Reaction number: DOB59

D.5.3.6 2,3,5,6-Tetrabromo-*N*¹,*N*¹,*N*⁴,*N*⁴-tetraphenylbenzene-1,4-benzenediamine (XII)



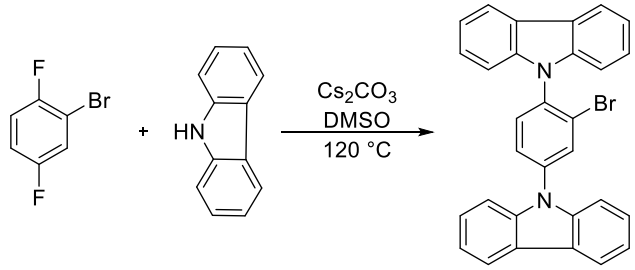
32 $C_6Br_4F_2$ 429,68 + **40** $C_{12}H_{11}N$ 169,23 → **XII** $C_{30}H_{20}Br_4N_2$ 728,12

NaH (72 mg, 3 mmol, 2 eq.) was suspended in anhydrous DMF (40 ml) in a round bottom flask under argon atmosphere. The mixture was degassed with argon and a solution of diphenylamine (**40**) (508 mg, 3 mmol, 2 eq.) in 10 ml DMF was added dropwise while stirring. After complete addition the solution was stirred for 1 h at rt. When no further gas formation could be detected, **32** (645 mg, 1.5 mmol, 1 eq.) dissolved in 10 ml DMF was added. The reaction was stirred at 70 °C overnight and the solution turned from blue to red. The solvent was removed under reduced pressure, the residue dissolved in DCM and washed with water and brine. The organic phase was dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude product was purified using column chromatography (LP/DCM 15% - 40%) yielding 437 mg (40%) of **XII**.

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB72/50) δ 7.33 – 7.27 (m, 8H), 7.07 – 7.00 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$ FID DOB72/61) δ 144.4, 144.1, 131.7, 129.3, 122.6, 120.7. Reaction number: DOB72

D.5.3.7 9,9´(2-Bromo-1,4-phenylene)bis[*9H*-carbazole] (XIV)



25
$C_6H_3BrF_2$
192,99

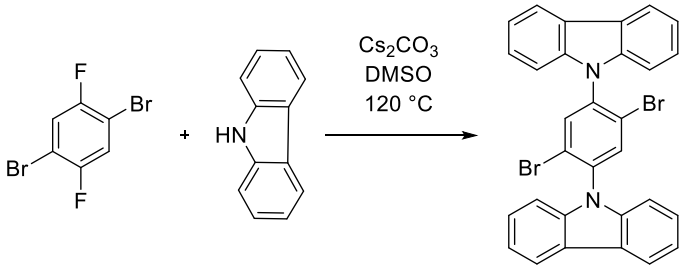
10
$C_{12}H_9N$
167,21

XIV
$C_{30}H_{19}BrN_2$
487,40

25 (1.16 g, 6 mmol, 1 eq.) and carbazole (**10**) (2.01 g, 12 mmol, 2 eq.) were dissolved in 160 ml DMSO and degassed with argon. Cs_2CO_3 (4.30 g, 13.2 mmol, 2.2 eq.) was added and the reaction mixture was heated to 120 °C overnight under argon atmosphere. The solution was cooled to rt and poured on brine. The precipitate was filtered off and thoroughly washed with water. The crude product was purified *via* column chromatography (LP/DCM 20%) to yield **XIV** (776 mg, 27%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB140/30) δ 8.19 (m 4H), 8.14 (d, *J* = 2.3 Hz, 1H), 7.80 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.61 (dt, *J* = 8.3, 0.9 Hz, 2H), 7.50 (m 4H), 7.40 – 7.32 (m, 4H), 7.28 – 7.20 (m, 2H) ppm. Reaction number: DOB140

D.5.3.8 9,9´(2,5-Dibromo-1,4-phenylene)bis[*9H*-carbazole] (34)



33
$C_6H_2Br_2F_2$
271,89

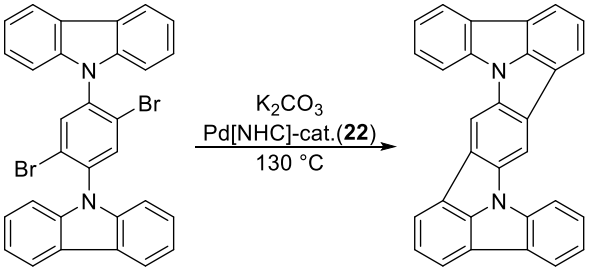
10
$C_{12}H_9N$
167,21

34
$C_{30}H_{18}Br_2N_2$
566,30

33 (1.09 g, 4 mmol, 1 eq.) and carbazole (**10**) (1.34 g, 8 mmol, 2 eq.) were dissolved in 100 ml DMSO and degassed with argon. Cs_2CO_3 (2.86 g, 8.8 mmol, 2.2 eq.) was added and the reaction mixture was heated to 120 °C overnight under argon atmosphere. The solution was cooled to rt and poured on brine. The precipitate was filtered off and thoroughly washed with water. The crude product was recrystallized from toluene to give **34** in a yield of 824 mg (36%).

^{1}H NMR (400 MHz, $CDCl_3$ FID DOB77/20) δ 8.19 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 4H), 8.01 (s, 2H), 7.51 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 4H), 7.37 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 4H), 7.26 (d, *J* = 8.2 Hz, 4H). Reaction number: DOB 77

D.5.3.9 Benzo[1˝,2˝:4,5;4˝,5˝:4′,5′]dipyrrolo[3,2,1-*jk*;3′,2′,1′-*j′k′*]dicarbazole (X)



34
$C_{30}H_{18}Br_2N_2$
566,30

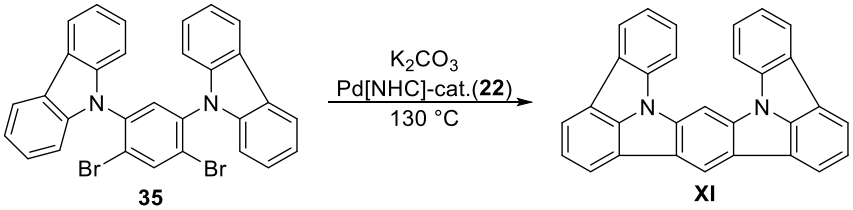
X
$C_{30}H_{16}N_2$
404,47

The synthesis of **X** was performed according to general procedure GP2.

Precursor (**34**) (327 mg, 0.58 mmol, 1 eq.), K_2CO_3 (321 mg, 2.32 mmol, 4 eq.) and the Pd[NHC]-catalyst (**36**) (17 mg, 0.03 mmol, 0.05 eq.) were suspended in 20 ml DMAc (1000 ppm water content) and reacted at 130 °C for 24 h. After workup the crude product was washed with EtOH and Et_2O to yield the target compound **X** as a bright yellow solid (159 mg, 68%).

^{1}H NMR (400 MHz, DMSO-d_6 FID DOB79/10) δ 9.29 (s, 2H), 8.51 (d, *J* = 8.1 Hz, 2H), 8.35 (m, 4H), 8.27 (d, *J* = 7.3 Hz, 2H), 7.78 – 7.69 (m, 4H), 7.51 – 7.42 (m, 2H). Reaction number: DOB79

D.5.3.10 Benzo[1˝,2˝-4,5:5˝,4˝-4′5′]dipyrrolo[3,2,1-*jk*:3′,2′,1′-*j′k′*]dicarbazole (XI)



35
$C_{30}H_{18}Br_2N_2$
566,30

XI
$C_{30}H_{16}N_2$
404,47

The synthesis of **XI** was performed according to general procedure GP2.

Precursor **35** (566 mg, 1 mmol, 1 eq.), K_2CO_3 (553 mg, 4 mmol, 4 eq.) and the Pd[NHC]-catalyst **36** (29 mg, 0.05 mmol, 0.05 eq.) were suspended in 20 ml DMAc (1000 ppm water

content) and reacted at 130 °C for 24 h. After workup the crude product was washed with EtOH and Et_2O to yield the target compound **XI** as a grey solid (368 mg, 91%).

^{1}H NMR (400 MHz, DMSO-d_6 FID DOB80/10) δ 9.19 (s, 1H), 9.08 (s, 1H), 8.87 (d, *J* = 8.1 Hz, 2H), 8.34 (d, *J* = 7.6 Hz, 2H), 8.28 (d, *J* = 7.3 Hz, 2H), 8.21 (d, *J* = 7.4 Hz, 2H), 7.78 – 7.66 (m, 4H), 7.49 (td, *J* = 7.6, 1.0 Hz, 2H). Reaction number: DOB 80

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