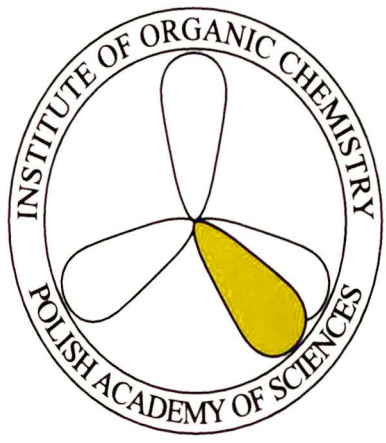

DISSERTATION

Dyads and triads bearing corrole as models for energy- and electron-transfer studies

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Supervisor:
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This PhD dissertation covers the work, accomplished in group 10 in years 2006–2011

WARSAW 2011

I would like to thank my supervisor Prof. Daniel T. Gryko for help in choosing interesting research topic, for support and inspiration during my doctorate. I am grateful to my colleagues Beata Koszarna, Mariusz Tasior and Michał Gałęzowski for introducing me into chemistry of porphyrinoids. It was great pleasure to work in one lab with such (undoubtedly famous in the future) people as Aśka Piechowska, Jasiek Lewtak and Janek Klajn. Many thanks to all members of group 10 for a fun time spent together and for pleasant atmosphere during work time.

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My warmest gratitude is addressed to my family
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Mariusz Tasior, Roman Voloshchuk, Yevgen M. Poronik, Tomasz Rowicki and Daniel T. Gryko, Corroles bearing diverse coumarin units – synthesis and optical properties. *J. Porphyrins Phthalocyanines*, **2011**. – *in the press*

Contents

1 Introduction

One of the most fascinating scientific topics is the conversion of sunlight into chemical energy in natural photosynthesis. [1] Chemistry can contribute to this field of research in two ways, one is by synthesis and spectroscopic characterization of model systems for the natural counterparts, [2] another is by application of the acquired knowledge to derive 'biomimetic' photovolatic devices. [3] In nature two subsystems are required to achieve efficient photosynthesis which consists of the well-characterized reaction centers and the much larger light-harvesting systems that incorporate up to hundreds of dyes. Electron transfer (eT) which occurs in reaction center is the elementary event of electron flow between two molecules. The first widely accepted theory of this process was developed by Rudolph A. Marcus. [4] Energy transfer (EnT) dominates in antenna and has a role to harvest photon from entire visible spectrum. Photosynthetic systems occurring in the nature are extremely complex and arose as a result of billions years of evolution. For this reason so-called "artificial photosynthesis" is developing much slower than one could expect.

There are, however, great number of successful attempts to mimic behavior of separate stages of natural systems, which in the future can finally lead to mastering of one of the most promising energy sources.

Due to excellent properties and availability of porphyrins, they have constituted for several decades the most used components of models for light energy collection and conversion. However, the need to improve the performance and increase the variety of such molecular systems encouraged the use of other porphyrinoids. Between those corroles – one carbon shorter analogs of porphyrins – had some success since they possess the right properties, namely intense light absorption throughout the visible spectral range, singlet excited state lifetime in the nanosecond range, high luminescence yield and high radiative rate constants,

strong absorption feature of the excited state, good photostability in most solvents and relative ease of oxidation. However, construction of corrole-based systems displaying long life time of charge-separated state (τ_{CS}) and efficient light harvesting of whole solar spectrum have not been achieved yet.

Corroles' scaffold is known since 1964, but these compounds became readily accessible only after the discovery of one-pot procedure for their synthesis in 1999. [5] Further improvements allowed to optimize the synthetic procedures and to obtain virtually any substitution pattern in corroles. [6]

Mariusz Tasior from Gryko's group was the first one to introduce *meso*-substituted corroles as alternative building blocks in construction of multichromophoric arrays. [7] This approach turned out to be very promising and many dyads possessing interesting properties were efficiently prepared though typical τ_{CS} were not too long.

In compliance with current state of research in the field, main goals of my work can be delineated as follows:

- Preparation of corrole-based triad possessing electron-acceptor and secondary electron donor (expecting τ_{CS} elongation).
- Investigation of dyads comprising of corrole and previously unknown electron acceptor.
- Investigation of dyads comprising of corrole and alternative energy donor.

During my work I planned to step out of classical chromophores used in artificial synthesis and to try heterocyclic compounds which although generally known were never tried before in this context. In order to accomplish the plan certain degree of methodological development was required in the chemistry of such compounds like aromatic imides, coumarins, acridins, diketopyrrolopyrroles etc. Obviously, during realization of these goals many interrelated trends occurred.

The synthesis of more complicated, three-component system was started from careful design of the final molecule under close collaboration with photophysics expert Prof. Lucia Flamigni* and followed by tailoring of corresponding building blocks.

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Combining of above mentioned chromophores with corrole was aimed towards preparation of multichromophoric arrays able to display the ability to collect and/or transfer light energy, to convert it *via* photoinduced electron transfer into charge separated state. These systems are important for light energy conversion applications and for the production of photo-responsive molecular structures. During the research, attention was paid to corrole stability and in most cases electron-withdrawing substituents were employed.

2 Literature review

2.1 Introduction

There is a sharp increase in the interest in aromatic imides observed within the last few years. The number of papers is steadily increasing, so is the range of possible structural modifications. Especially perylene bisimides and naphthalene imides are objects of intense studies aiming at modification of their optical and electronic properties.

Aromatic imides are one of the typical electron acceptors used in the construction of multi-chromophoric arrays. This is due to their low reduction potential and ability to form radical anions with distinguished "spectral signature". In most cases perylene bisimides are used due to their overall good combination of properties. Their intense absorption in the green part of the visible spectrum complements absorption of porphyrins and chlorins but may cause problems due to the competitive EnT process.

This overview will cover aromatic cyclic imides which core consists of one or more fused benzene rings, excluding, however, higher rylene dyes family. The chemistry and properties of rylene dyes were very recently covered in two comprehensive reviews[8,9] (and in many other published earlier), due to their popularity in many areas of research. Synthetic aspects and physicochemical properties of imides will be emphasized while their application will be mentioned only briefly. Such distribution of accents is caused by the fact, that there are already several application-aimed reviews (for example about naphthalene diimides) published during the period of interest.[10] The overwhelming amount of material combined with size limitations of this chapter caused, that review will focus on results, reported during the last decade (2000–2011).

2.2 Imides based on a single benzene unit

The simplest member of this group is phthalimide (Figure 2.1). By increasing the number of imide moieties, one can move to benzene-1,2:4,5-tetracarboxydiimide (pyromellitic) and benzene-1,2:3,4:5,6-hexacarboxytriimide (mellitic). All these compounds posses five-membered imide rings.

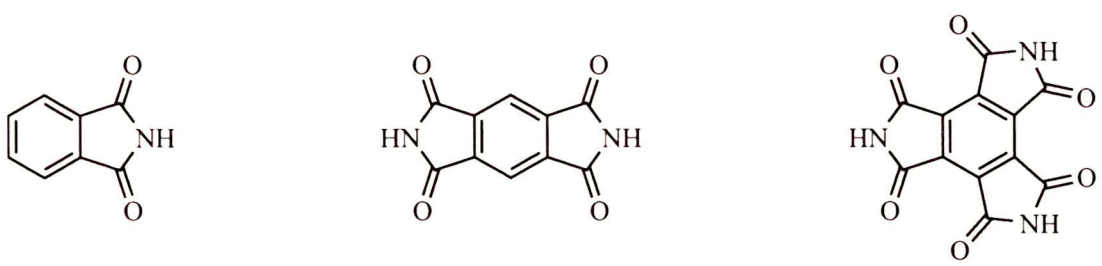


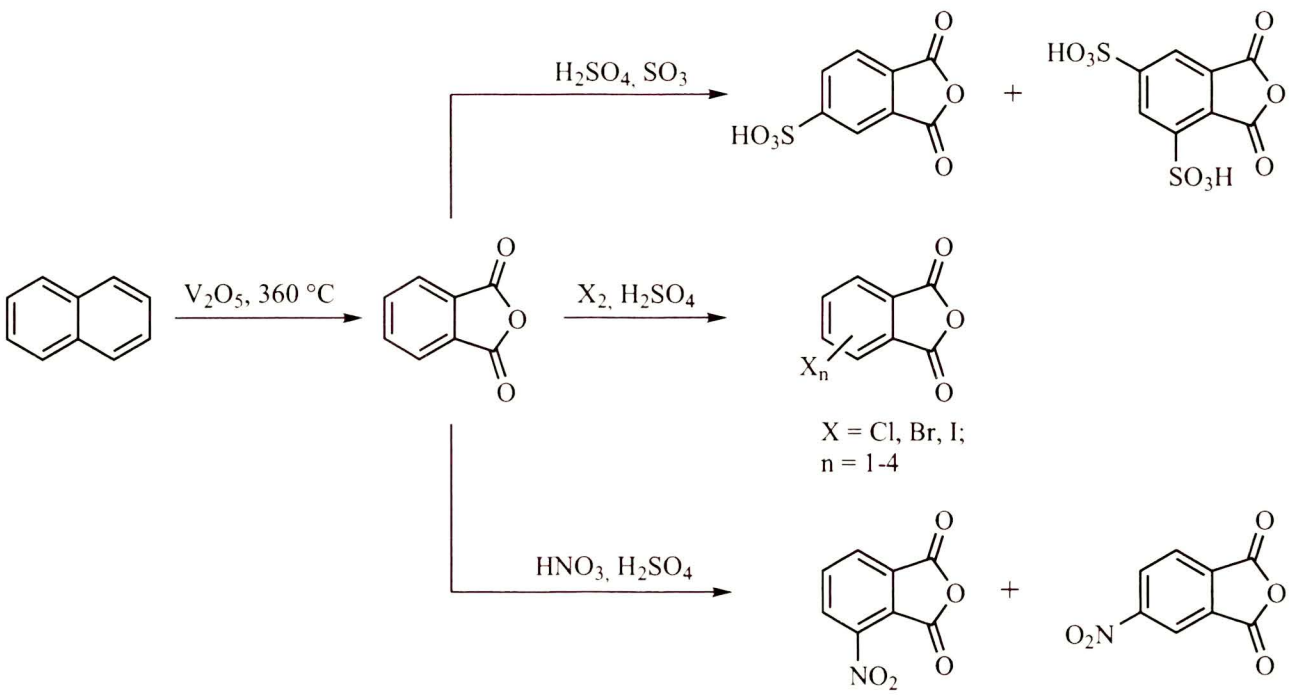
Figure 2.1

Proximity of two carbonyl groups at benzene ring make them interacting strongly and mutually enhance their electron-withdrawing effect. Furthermore, nitrogen atom located in between is showing strong electron deficiency and hence, high acidity of N-H bond ($pK_a = 8.3$, comparing to the value 15.1 for acetamide).

The key precursor for phthalimides is phthalic anhydride. It is a readily available chemical and its industrial production is based on catalytic oxidation of naphthalene and *ortho*-xylene (Gibbs phthalic anhydride process). There are many methods available for its derivatization, such as halogenation,[11] nitration,[12] and sulfonation[13] (Scheme 2.1).

The conventional methods of halogenation as well as nitration suffer from the lack of selectivity and often tedious purification is required. Luckily, there are alternative routes towards specific isomers, such as stepwise hydrodechlorination[14] or appropriate choice of substituted starting material (naphthalene or xylene) for oxidation reaction.[15]

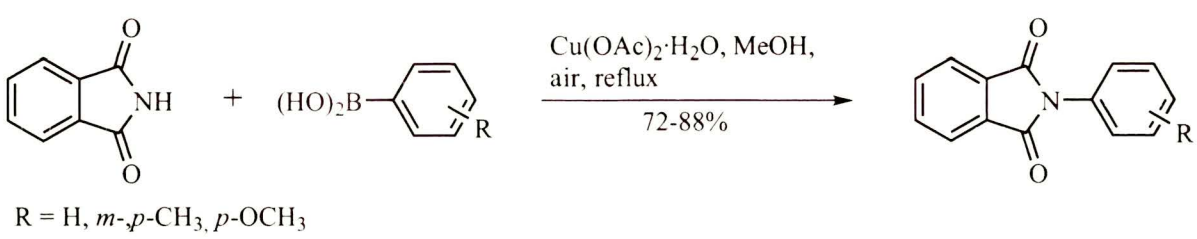
Classical synthesis of phthalimides involves dehydrative condensation of phthalic anhydride with primary amines at high temperatures with or without addition of Lewis acid. When primary amine is not readily accessible, an another option is to start from *N*-unsubstituted imide and alkylate it with alcohol (Mitsunobu reaction) or alkyl halide (Gabriel synthesis). Even the synthesis of sim-



Scheme 2.1

ple *N*-unsubstituted phthalimides experiences constant improvements, involving nitrogen source diversification,[16] developing of microwave variants of classical procedures[17] etc.

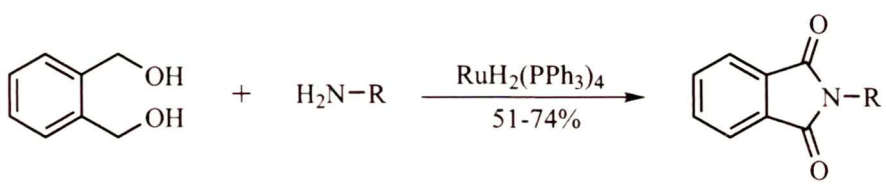
When aromatic substituent, directly attached to nitrogen atom is required, the matter complicates even more, due to the reduced nucleophilicity of anilines. For such cases prolonged heating of anhydrides with corresponding anilines has been developed as classical conditions. This led, however, to severe limitation of starting materials which can be used. Recently, few another approaches have been developed,[18] which later were improved by Lan *et al.*,[19] opening access to wide variety of *N*-aryl substituted five-membered imides. It was shown, that catalytic amount of simple copper salt can efficiently catalyze *N*-arylation reaction of imide with arylboronic acid without any base or ligands (Scheme 2.2).



Scheme 2.2

Among recent advances in rare transition metal-catalyzed imide synthesis the

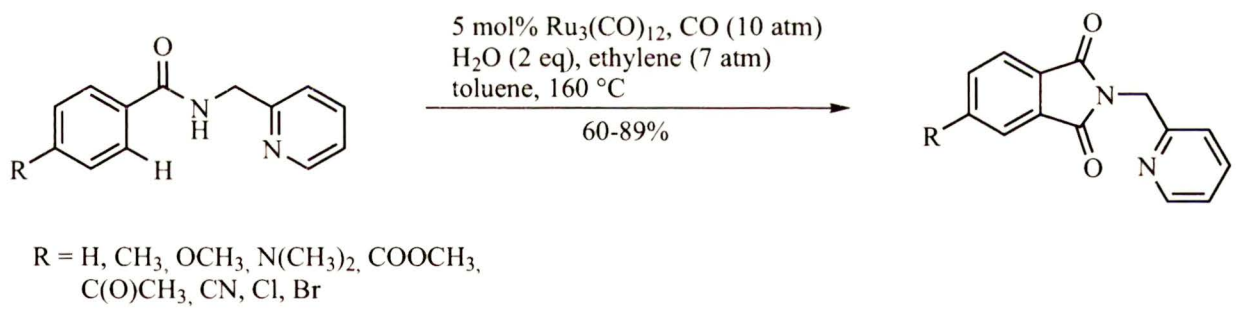
method towards cyclic imides from simple diols can be mentioned. Zhang and co-workers[20] made an endeavor to perform direct oxidative coupling of diols with primary amines in the presence of ruthenium catalyst to obtain corresponding imides (Scheme 2.3).



Scheme 2.3

The idea was to oxidize diol to aldehyde first, which then will form hemiaminal with amine. Subsequent extraction of four hydrogen atoms should lead to the desired product. The method works both for aliphatic and aromatic diols but yields are usually moderate. The fact that xylene-based diols are usually prepared reducing carboxylic acid derivatives (esters, cyclic anhydrides) together with the cost of catalyst makes this protocol of little practical interest.

An another example is ruthenium-catalyzed carbonylation of *ortho*-CH bond in aromatic amides[21] (Scheme 2.4).



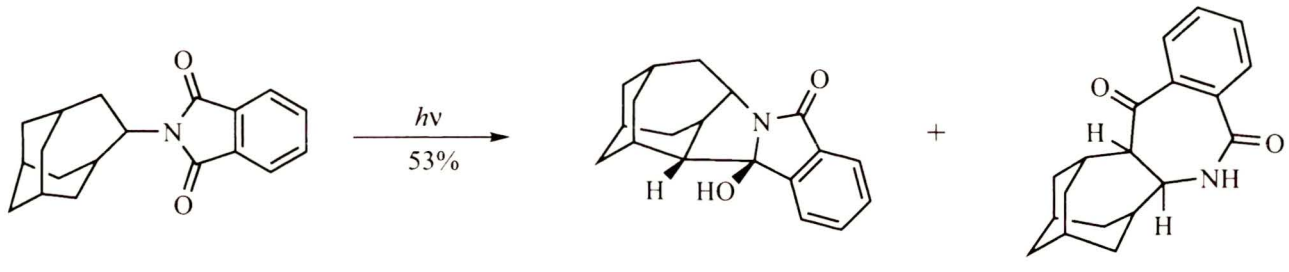
Scheme 2.4

The key feature of this chelation-assisted transformation is the presence of pyridyl moiety. Together with amide group it forms bidentate ligand coordinating catalyst strongly. This induces unprecedented regioselectivity of CH activation and carbonylation.

The commercial availability of phthalic acid derivatives and virtually countless number of available amines in combination with constantly growing arsenal of synthetic tools, gives an opportunity for the synthesis of myriad of different imides.

Along with many phthalimides' preparation methods and their variants, its chemistry expands even further by the reactivity of the imide group. Core-unsubstituted phthalimides are probably the most studied compounds in this regard. One among extensively developing directions is photochemistry of phthalimides. Simple *N*-alkyl phthalimides are weakly fluorescent and main deactivation channel of first excited singlet state is intersystem crossing, resulting in population of triplet state.[22] Consequently, the photochemistry of phthalimides originates mostly from the excited triplet states.

Cindro and co-workers[23] recently described photochemical reaction of *N*-(4-homoadamantyl)phthalimide (Scheme 2.5).



1 **2** *syn*- and *anti*-

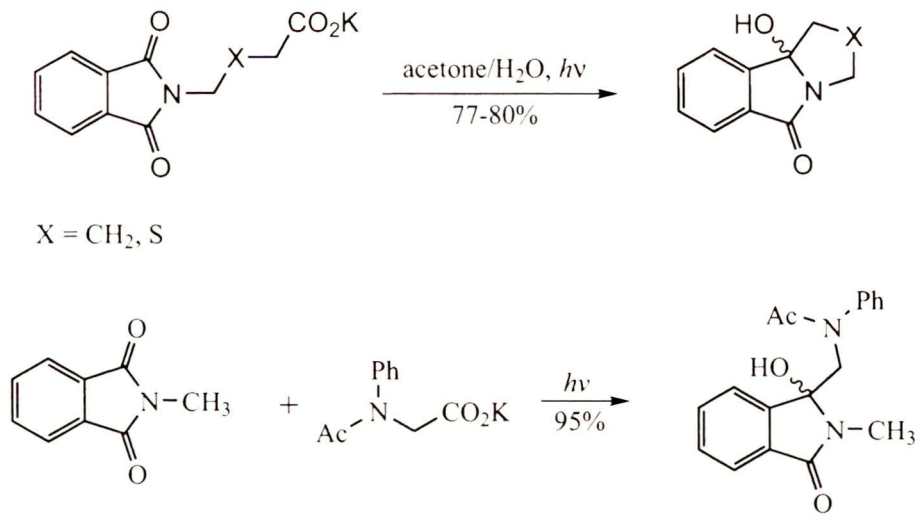
Scheme 2.5

After excitation of compound **1** with UV light, the abstraction of hydrogen atom from homoadamantane takes place. 1,5-Biradical formed in such a way undergoes stereoselective cyclization furnishing the major product **2**.

Thus, the intramolecular or intermolecular hydrogen extraction followed by photoreduction, cyclization, cleavage or decarboxylation[24] can give product of great complexity in one photochemical step (Scheme 2.6). Detailed discussion on photochemistry of phthalimides can be found in recently published review.[25]

An another interesting feature of imide group is possibility of insertion of Ni(0) complex into C−N bond. Such intermediate after decarbonylation can undergo several transformations, like for example coupling with organozinc reagents,[26] insertion of dienes and acetylenes[27] (Scheme 2.7).

Benzimidazole derivatives, formed by condensation of cyclic aromatic anhydrides with arylene-1,2-diamines, are compounds of importance in pigment and dye chemistry[28] and organic electronics.[29] Typical conditions used for the condensation reaction of diamines with carboxylic acid anhydrides involve heating under



Scheme 2.6

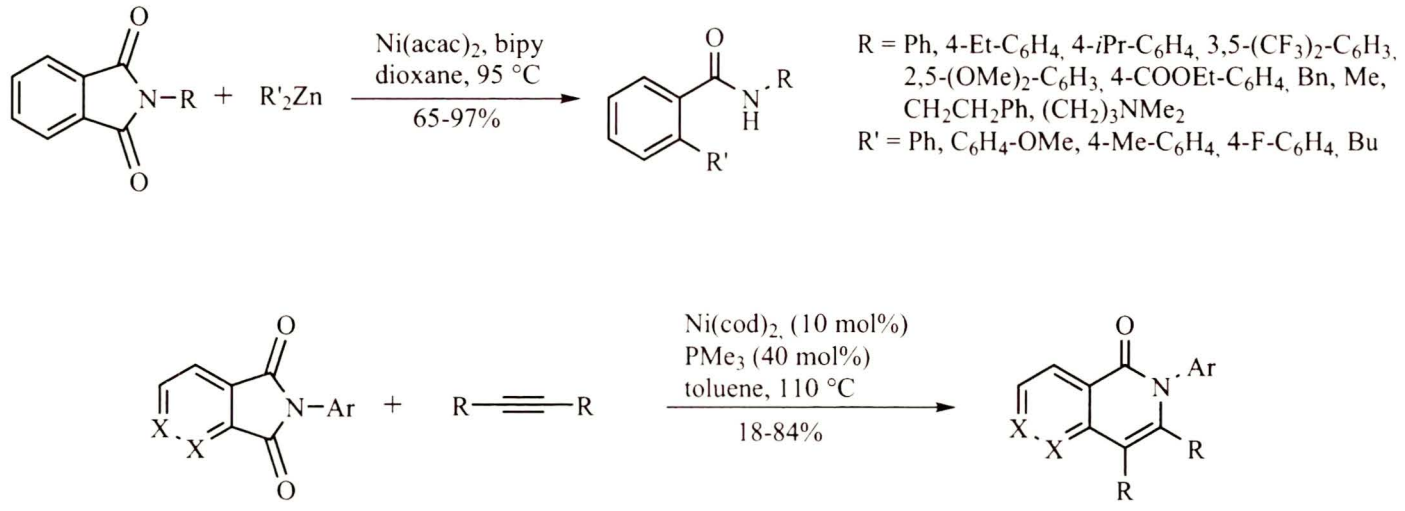
reflux in AcOH[30] and in case of higher rylene dyes even more harsh conditions are required to overcome reactivity and solubility issues.

Recently, Anzenbacher with co-workers[31] reported improved protocol with accent on "green" chemistry. They found that optimal condensation reaction conditions for 1,8-naphthalic anhydride and *o*-phenylenediamine (neat, $Zn(OAc)_2$) gave mixture of products in case of phthalic anhydride. Reaction, however, proceeds cleanly in water, giving a mixture **3** of two intermediates, precipitating from reaction mixture, which then dehydrated smoothly during purification by train sublimation, giving **4** of excellent purity (Scheme 2.8). This method is quite general and can be used successfully for more complex imides.

After formal addition of imide function to phthalimide one can obtain pyromellitic diimide. Corresponding benzene-1,2,4,5-tetracarboxylic acid was prepared for the first time by Otto Linné Erdmann in 1851 during heating mellitic acid. Its cyclic dianhydride is even more reactive comparing to phthalic due to combined electron-withdrawing effect of all substituents on single benzene core.

Pyromellitic imides are known, among other applications, as segments of highly insulating polyimide dielectrics. Probably due to this fact until recently no attempt was made to fabricate organic thin film transistors from them, serving as n-channel semiconductor. Zheng *et al.*[32] synthesized series of diimides by heating pyromellitic dianhydride with polyfluorinated amines in DMF (Scheme 2.9).

Fluorinated substituents at the nitrogen atoms are crucial in order to protect



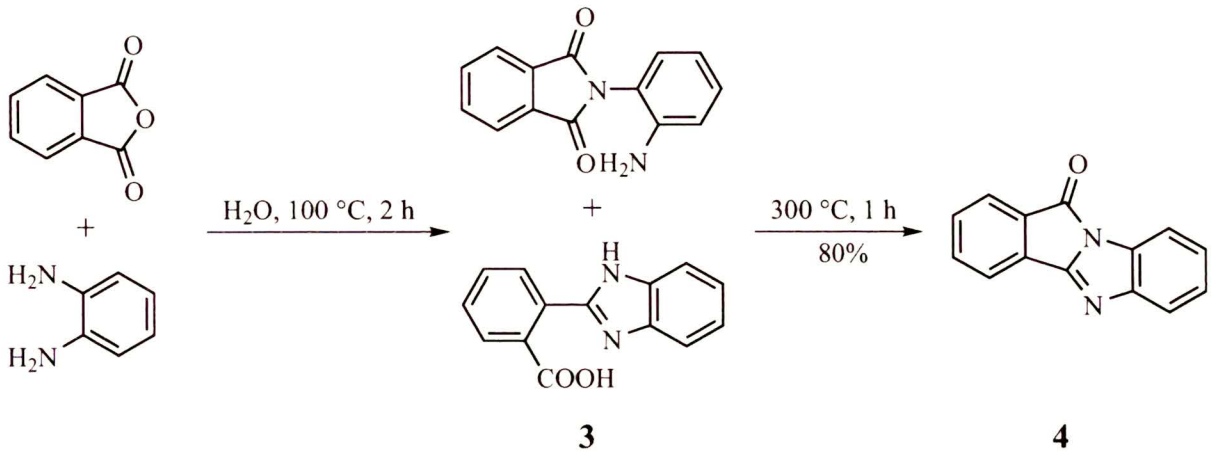
Scheme 2.7

charge carriers from being trapped by ambient molecules such as O_2 and H_2O. The crystallinity of thin layer appeared to influence greatly the charge carriers mobility which highest level (for compound **5**, $0.074\,cm^2\,V^{-1}\,s^{-1}$ was obtained for a device deposited at 70 °C and with OTS surface treatment.*

When substituents on the nitrogen atom are replaced with triarylamine moieties, the behavior of such imides is completely different. [33]

While in a bulk, there is three-dimensional crystalline structure which is vanished entirely when material is deposited on a silicone plate by spin coating. One can expect ambipolar (n- and p-type) behavior from the combination of diimide and triarylamine in one molecule since constituents have comparable hole and electron mobilities. In the case of compound **10**, however, field effect was observed only in p-channel configuration with mobility of $2.5 \times 10^{-5}\,cm^2\,V^{-1}\,s^{-1}$. Taking into account the ionization potential of triarylamine fragment (which is slightly higher than 5 eV) compound **10** can be considered as a candidate for the fabrica-

*to facilitate self-organization and increase crystallinity which result in grain size enlargement



3 **4**

Scheme 2.8

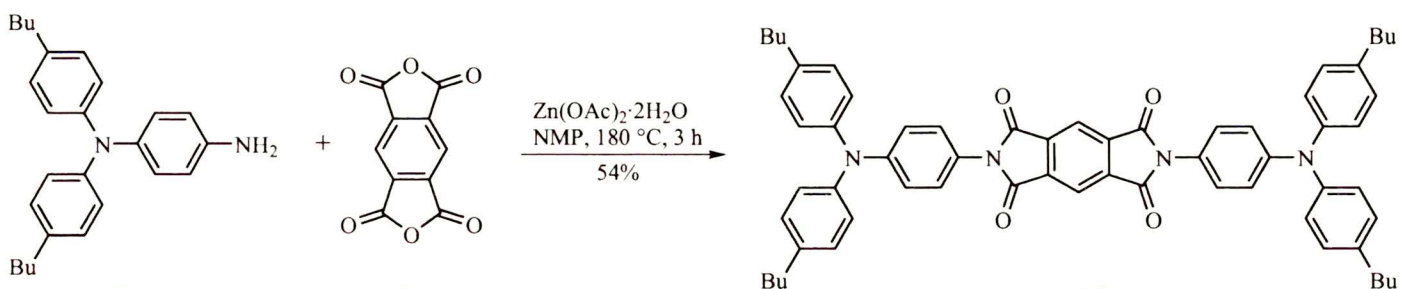
5 **6** **7**

Scheme 2.9

tion of air-operating p-channel OFETs.

One can imagine that when bisanhydrides react with diamines, polymers of various length's can be easily prepared. Indeed, working on molecular wires and two-dimensional arrays for conjugated organic molecules, Dong with co-workers [34] designed and synthesized the pyromellitic diimide-based polymer (Figure 2.2).

Additional benzene rings were necessary to drive self-organization of polymer chains and maintain strong interaction between layers. Such well-defined structures have potential as a scaffolds for second order NLO chromophores (which



8 **9** **10**

Scheme 2.10

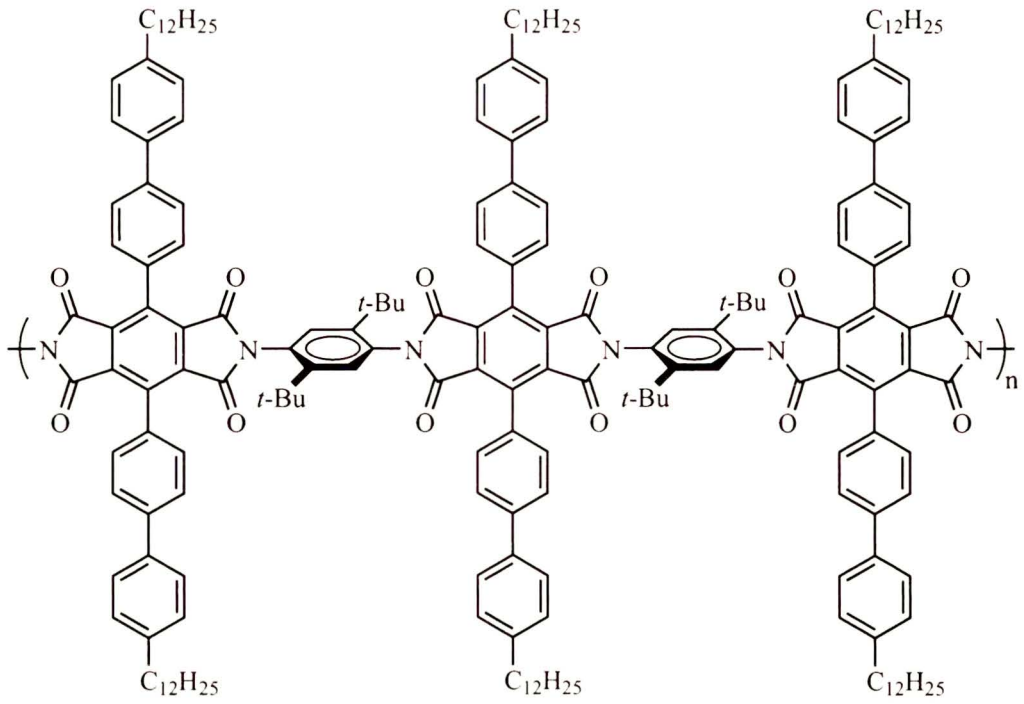


Figure 2.2

typically require poling), for studying intermolecular energy migration which is most efficient in molecular ordered films or aggregates. In the close future, such ordered layers of insulator can separate the parts of molecular electronic circuits.

Kato *et al.*[35] recently reported the synthesis and characterization of interesting pyromellitic diimide derivatives with π-expanded conjugation system (Figure 2.3).

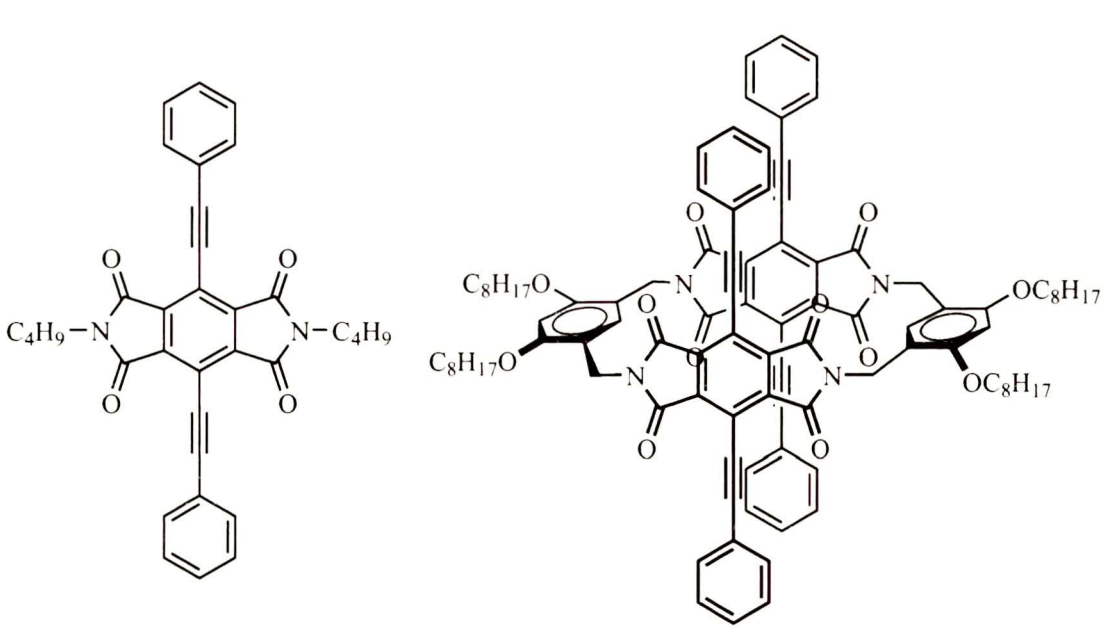
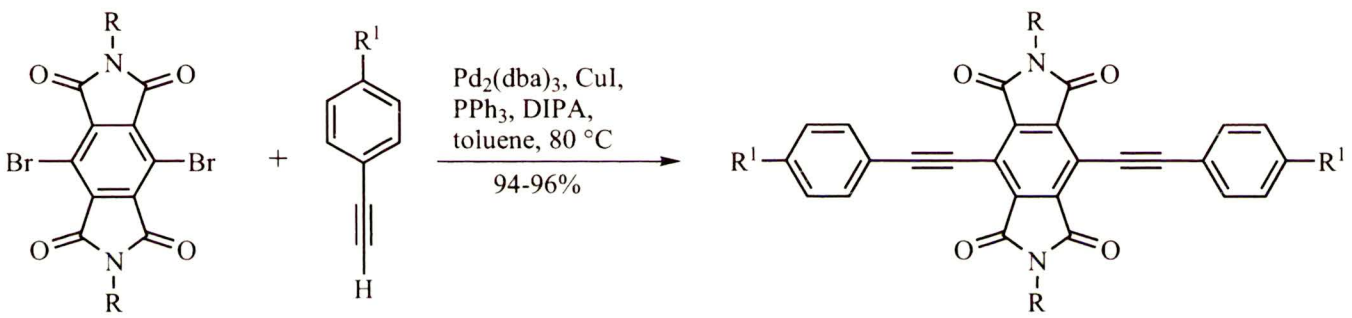


Figure 2.3

By the introduction of two phenylethynyl substituents to the benzene core

of pyromellitic diimide the absorption maxima was shifted bathochromically for 70 nm and molar absorptivity increased significantly comparing to unsubstituted analogue. Structural analysis reveals formation of highly ordered crystals with some interesting features. Such kind of compounds have potential as an n-type organic semiconductors.

Guo and Watson[36] recently reported results of the study of the influence of electron-donating arylethynyl substituents located at positions 3 and 6 of pyromellitic diimide on the optical properties. They observed decrease of luminescence along with increasing donating power of substituent, explaining this by growing possibility of intramolecular charge separation. The color of solids varied from yellow through orange to red (**11** $\longrightarrow$ **13**) reflecting bathochromic shift of absorption maxima. It is noteworthy, that electronic gaps are also decreased from **11** to **13** (Scheme 2.11).

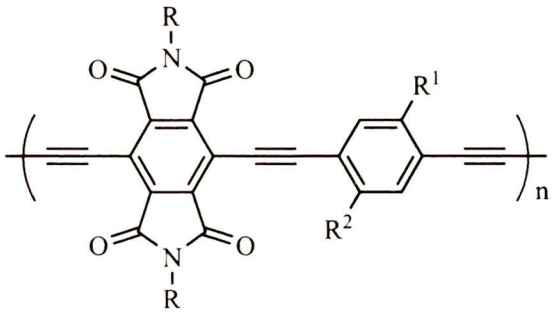


R = 2-ethylhexyl

R^1 = H (**11**), OCH_3 (**12**), $N(CH_3)_2$ (**13**)

Scheme 2.11

Encouraged by those results authors synthesized polymer consisting of alternating pyromellitic diimide and arylene fragments connected by ethynylene linkers (Figure 2.4).



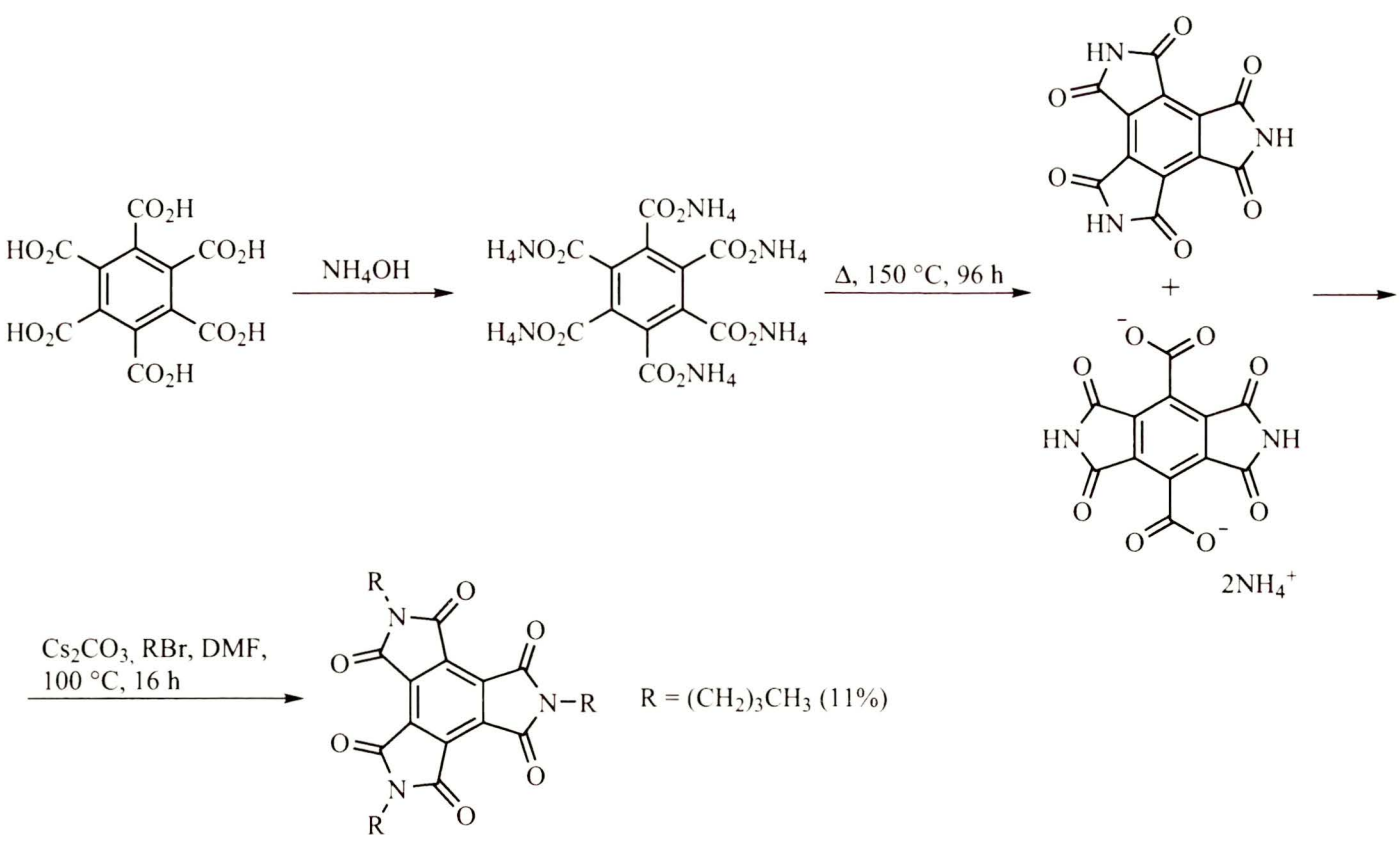
	R^1	R^2
14	3,7-dimethyloctyl	
15	2-ethulhexyloxy	
16	di(*n*-octyl)amino	H
17	2-buthyloctylamino	H
18	di(*n*-octyl)amino	

Figure 2.4

The absorption maxima shifts had similar trend as for model compounds occupying the range from 490 to 591 nm. Strikingly, absorption maximum of **17** was unevenly red-shifted. This fact authors explained by hydrogen bond formation of phenylene fragment with imide group, increasing coplanarity in this way.

Fully substituted benzene based triimide (mellitic triimide) did not found application due to problematic synthesis and extremely low solubility. The parent hexacarboxylic acid (mellitic acid or graphitic acid) has been known for over 200 years, having been obtained from the unusual "organic" mineral mellite (honeystone, formula $Al_2[C_6(COO)_6] \cdot 12\,H_2O$) by Klaproth in 1799. This simple, flat, and highly symmetric core is an attractive structural element in supramolecular chemistry and due to electron-deficient character derivatives of mellitic acid can form colored intermolecular CS complexes. The logical way towards triimide is to prepare trianhydride first and then condense it with amine. However, despite the fact that mellitic anhydride was first obtained by Meyer and Steiner almost century ago, there is no reports in the literature confirming this synthetic strategy.

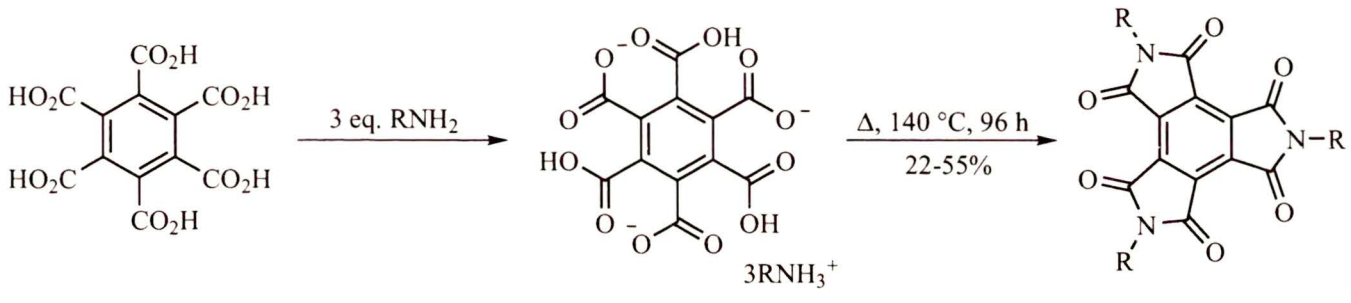
It was not until 2001 when McMenimen and Hamilton presented their results [37] on preparation of mellitic triimide from ammonium mellate (Scheme 2.12). They



Scheme 2.12

were not able to isolate mellitic triimide in pure state and after alkylation of crude product under Mitsunobu conditions, corresponding trialkyltriimide was isolated after painstaking purification in 11% overall yield. The product appeared to have flat structure (triimide core) and electrochemical investigations revealed the ability of delocalization of up to three electrons which is quite unusual for such a small molecule.

In 2008 the refined synthesis of mellitic triimides was published by the same group.[38] The strategy was surprisingly simple – preparation of a triammonium salt of mellitic acid, followed by solid-state thermal dehydration to the triimide (Scheme 2.13).



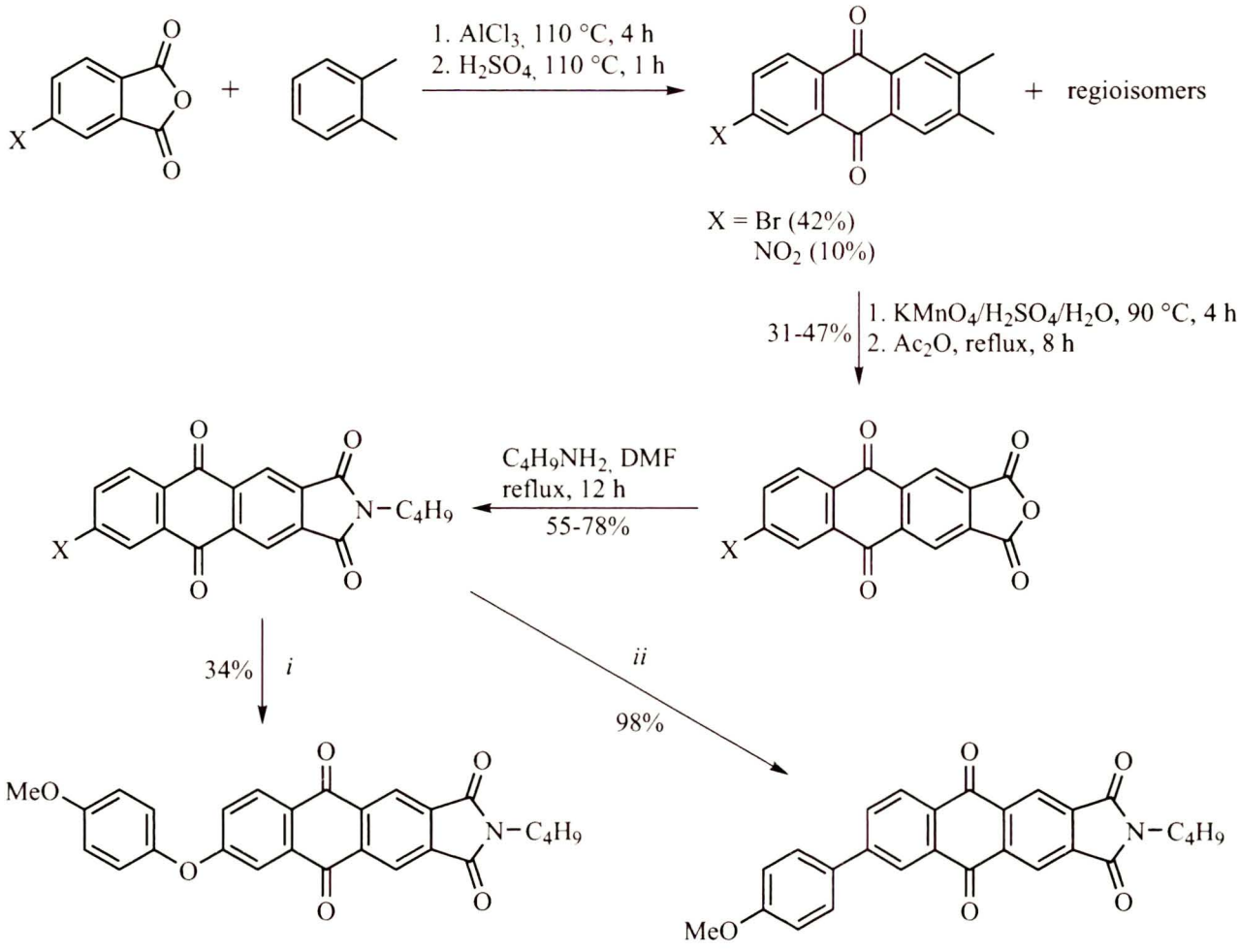
R-NH_2: aliphatic and aromatic amines, O-protected aminoacids

Scheme 2.13

In this way the scope of amines used was expanded to alkylamines, aminoacid esters and anilines (albeit in lower average yields), opening access to a broad family of C3-symmetric organic electron acceptors.

Standing apart examples of benzene-based imides, which can be formally ascribed to this group, are anthraquinone imides (AQI). Normally, carbonyl groups act as electronic insulator, dividing two benzene nuclei into separate, non-conjugated electronic systems. Thus, absorption spectra of AQIs differ insignificantly from those of phthalimides (300–350 nm). However, under electrochemical reduction their electronic structure undergoes tremendous changes resulting in extremely bathochromic shifted absorption maximum. Their properties making them potentially useful for NIR electrochromic materials in various applications.

Qiao *et al.* published recently[39] the synthesis and characterization of several novel AQI-based chromophores (Scheme 2.14). Nitro- and bromosubstituted AQIs were successfully prepared by multistep synthesis, first step, however, produced

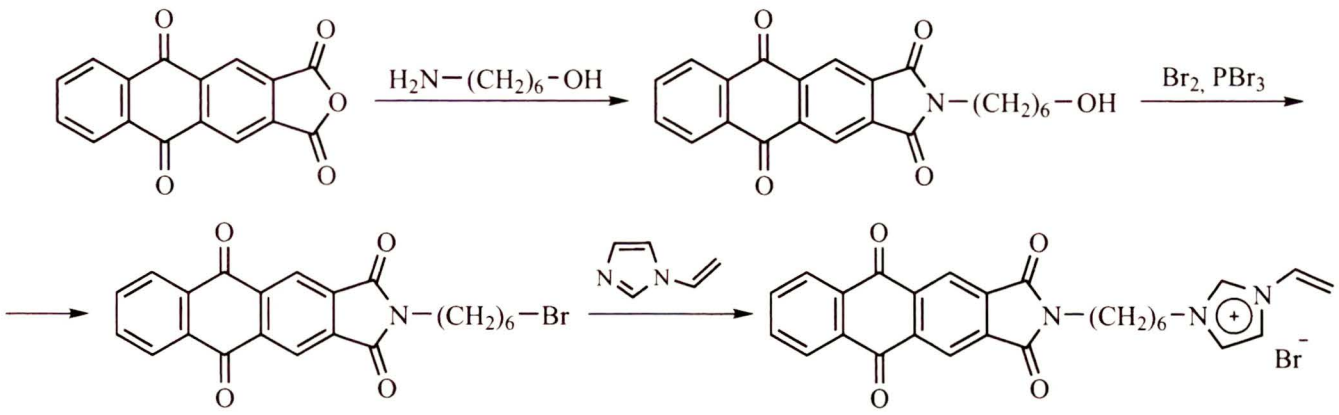


i. sodium *p*-methoxyphenolate, DMF, 120°C, 15 min; *ii*. 4-(hexyloxy)phenylboronic acid, benzene, H_2O, EtOH, DMF, $Pd(PPh_3)_4$, reflux, 30 min

Scheme 2.14

mixture of compounds which was difficult to separate. In terms of optical properties, compounds fulfiled authors' expectations, demonstrating strong absorption of reduced forms (600–1600 nm). By changing the substituent on anthraquinone core authors were able to trace the dependence of λ_{max} position on substituent nature (electron deficiency and conjugation expansion favors red-shifting).

Usually electrochromic devices require miltilayer structure and methods for their simplification are of interest. It was shown recently,[40] that by supporting AQIs on polymer bearing ionic moieties the need of using of separate electrolitic component can be eliminated (Scheme 2.15).



Scheme 2.15

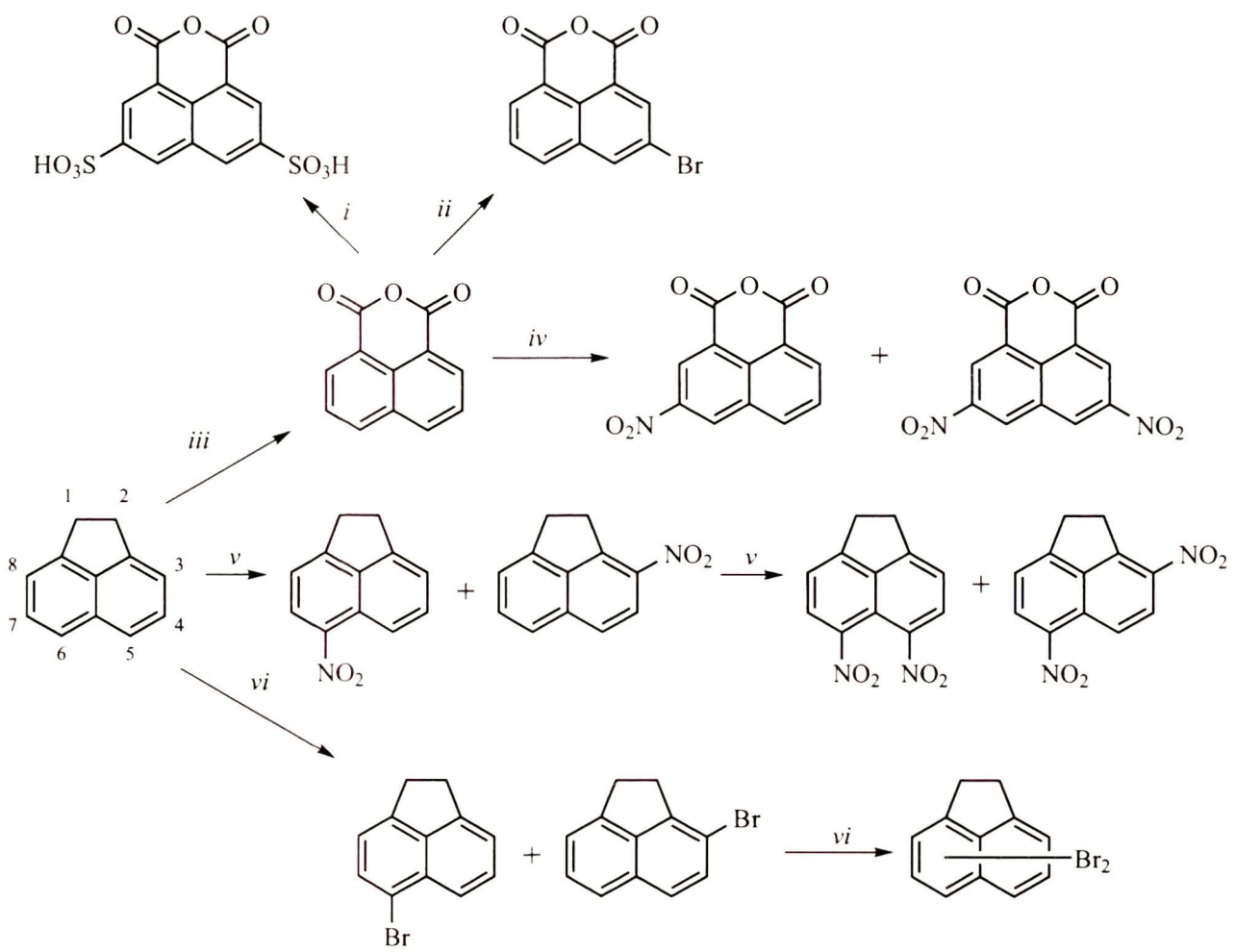
2.3 Imides based on a naphthalene core

There are three possible regioisomers in naphthalene monoimides family. 1,8-Naphthalimide is a most popular platform due to availability of corresponding anhydride (prepared on the large scale from acenaphthene). Many anhydrides with different substitution patterns on naphthalene core are commercially available. This abundance can be explained by the possibility of directing electrophilic aromatic substitution as shown on the scheme 2.16.

1,8-Naphthalenedicarboxylic acid anhydride (prepared by oxidation of acenaphthene) undergoes electrophilic aromatic substitutions at positions 3 and 6. Reaction is relatively easy controlled due to deactivation of aromatic system by the presence of anhydride function. However, behavior of its parent compound – acenaphthene – is completely different. Positions 5 and 6 (which are *para* to the bridge) are most active, followed by positions 3 and 8. Based on comparable activity, often mixtures of products arise, and the place of second substitution is even less predictable (especially in the case of halogenations).

Due to larger aromatic system and only one imide group, 1,8-naphthalimides do not show so pronounced electron-acceptor properties and after introducing alkylamino substituent into the naphthalene core they can even act as electron donors, when located in an appropriate environment.

Although classical method of imide synthesis is based on condensation of 1,8-naphthalic anhydride with amines, the reaction conditions often become harsh and addition of Lewis acid is required (especially in the case of aromatic amines). There is, however, the need to perform these condensation on substrates possessing

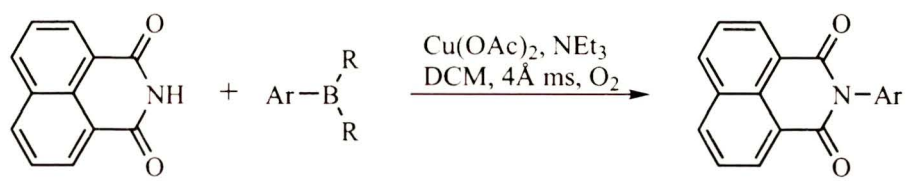


i. H_2SO_4, SO_3; *ii*. Br_2, H_2SO_4; *iii*. $Na_2Cr_2O_7$; *iv*. HNO_3, H_2SO_4; *v*. HNO_3, Ac_2O; *vi*. Br_2, AcOH

Scheme 2.16

sensitive functional groups. That is why mild methods of imide formation are of interest.

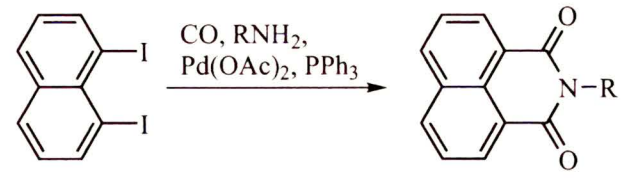
Similarly to procedure elaborated for five-membered imides,[19] Chernick and co-workers published cost-effective conditions[41] allowing to couple six-membered cyclic imides with arylboronic esters using copper(II) acetate (Scheme 2.17).



Ar = Ph, *p*-NO_2-Ph

Scheme 2.17

Somewhat exotic method of imides synthesis was proposed by Tkács *et al.*[42] (Scheme 2.18).



R = *t*-Bu, Ph, CH_2Ph, CH_2COOCH_3, $CH(CH_3)COOCH_3$

Scheme 2.18

1,8-Diiodonaphthalene was shown to undergo aminocarbonylation in the presence of primary amine and palladium catalyst. Such conditions tolerate various functional groups and give high yields of imides from both aromatic and aliphatic amines, bearing sterically hindered substituents. Based on variety of possible 1,8-dinitronaphthalenes which can be transformed through amines into corresponding iodides by Sandmeyer reaction, this protocol is of importance, complementing classical methods of imides synthesis.

Combination of intense absorption in UV region with suitable electrochemical properties of 1,8-naphthalenedicarboximides can be exceptionally useful in the systems for energy and electron transfer studies.

Interesting example of molecular switch was demonstrated by Wallin *et al.*[43] The triad, consisting of zinc porphyrin, naphthalene diimide and naphthalimide acceptors, showed unique ability to selectively direct electron transfer depending on excitation energy (Figure 2.5).

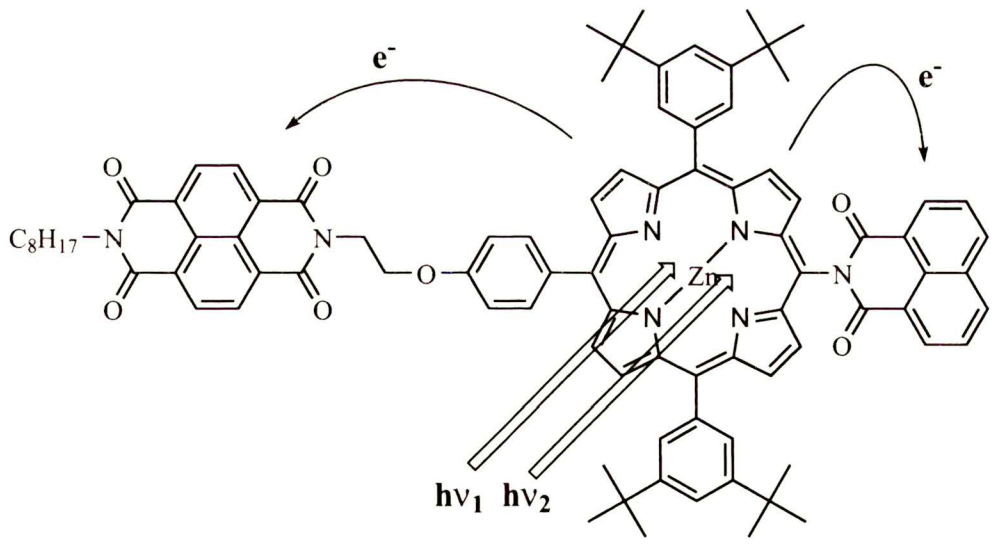


Figure 2.5

The excitation of porphyrin moiety to S1 level (Q-band excitation) would give electron transfer to the naphthalene diimide unit, while excitation to the higher

S2 state (Soret-band excitation) would give electron transfer to the naphthalimide unit. Interesting pattern of back and forward electron transfers reducing the energy of system gradually to S0 was observed after excitation of porphyrin to S2 state.

The donating ability of properly modified naphthalene-1,8-diimide was demonstrated Miller *et al.*[44] on relatively simple molecule, possessing naphthalene-based donor and acceptor connected by phenylene bridge (Figure 2.6).

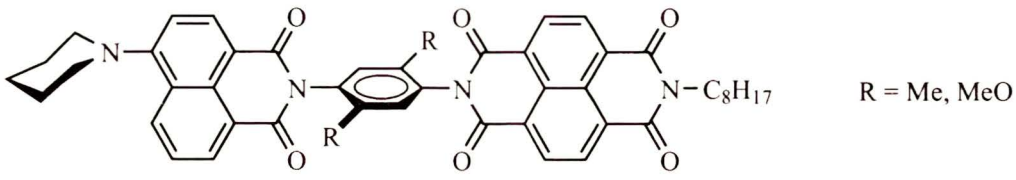
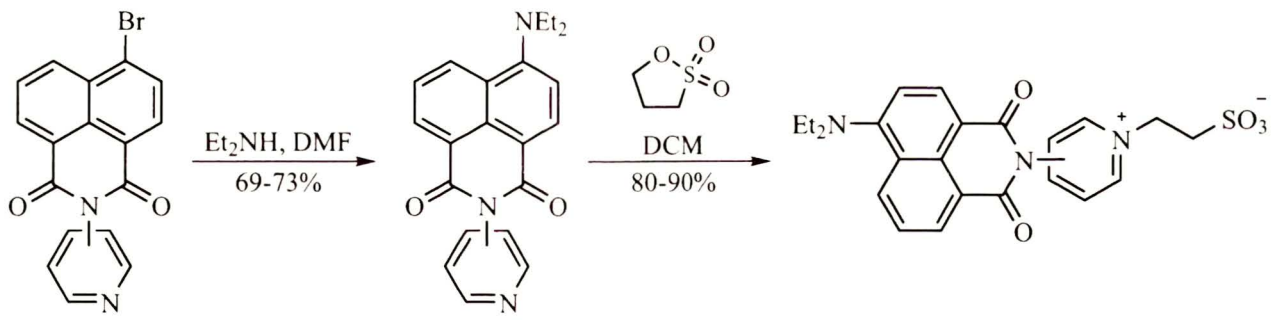


Figure 2.6

The substituents on bridging phenylene moiety showed pronounced effect on the speed of charge transfer processes (i.e. introducing of electron-releasing MeO groups considerably accelerates charge separation and recombination). There are also speculations about mechanism of double electron-transfer where π-orbitals of the bridge are also involved in the process.

Recently, Nandhikonda *et al.*[45] showed that it is possible to polarize 4-alkylaminonaphthalene-1,8-diimide even stronger by positive charge generation on N-aryl substituent (Scheme 2.19).



Scheme 2.19

Authors observed significant bathochromic shift of both absorption and emission bands after quaternization of pyridine moiety.

In order to study different electron transfer pathways Lukas with co-workers[46] designed and synthesized rigid molecule combining different types of imides into the well defined spatial arrangement (Figure 2.7).

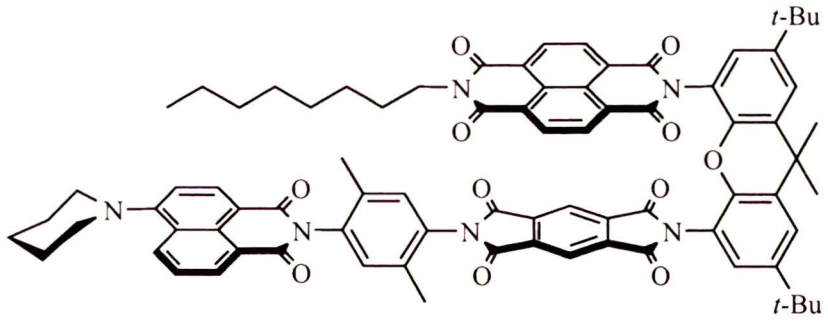
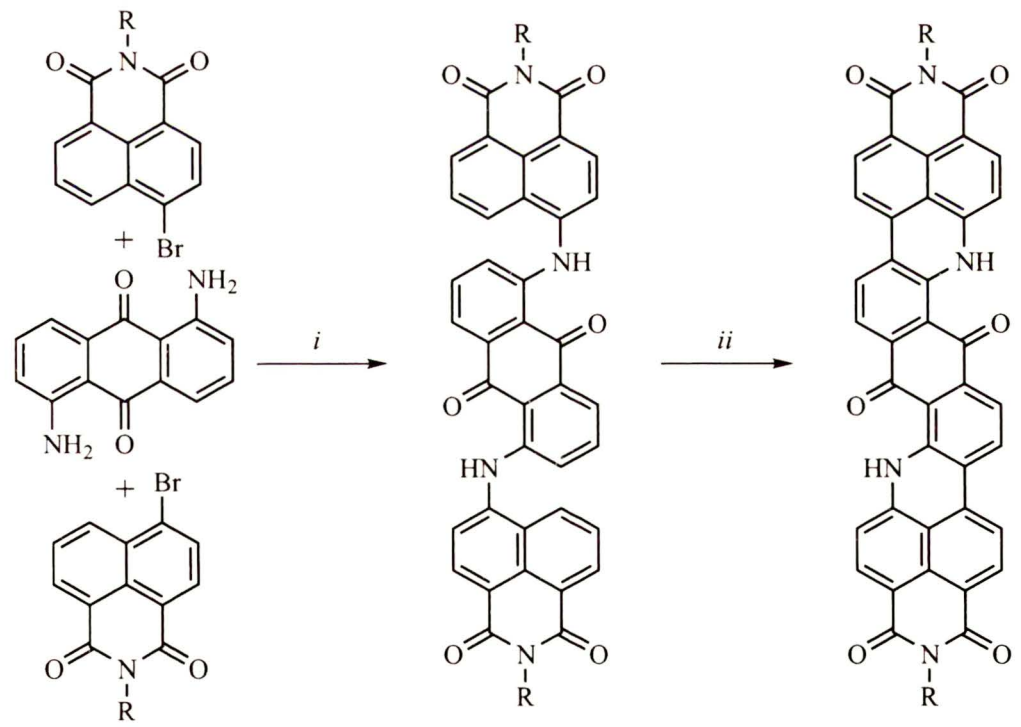


Figure 2.7

Authors were interested mainly in the non-bonded superexchange interactions that include contributions from both the n$-C_8H_{17}$ substituent on the NI acceptor and nearby solvent molecules. Based on the analysis of series of models it was shown that in properly designed rigid systems mediation of electron transfer by non-bonded interactions can compete effectively with electron transfer via bonded pathways.

Kohl *et al.*[47] introduced a hitherto unknown class of dyestuff compounds by an elegant and efficient two step synthesis from simple precursors (Scheme 2.20).



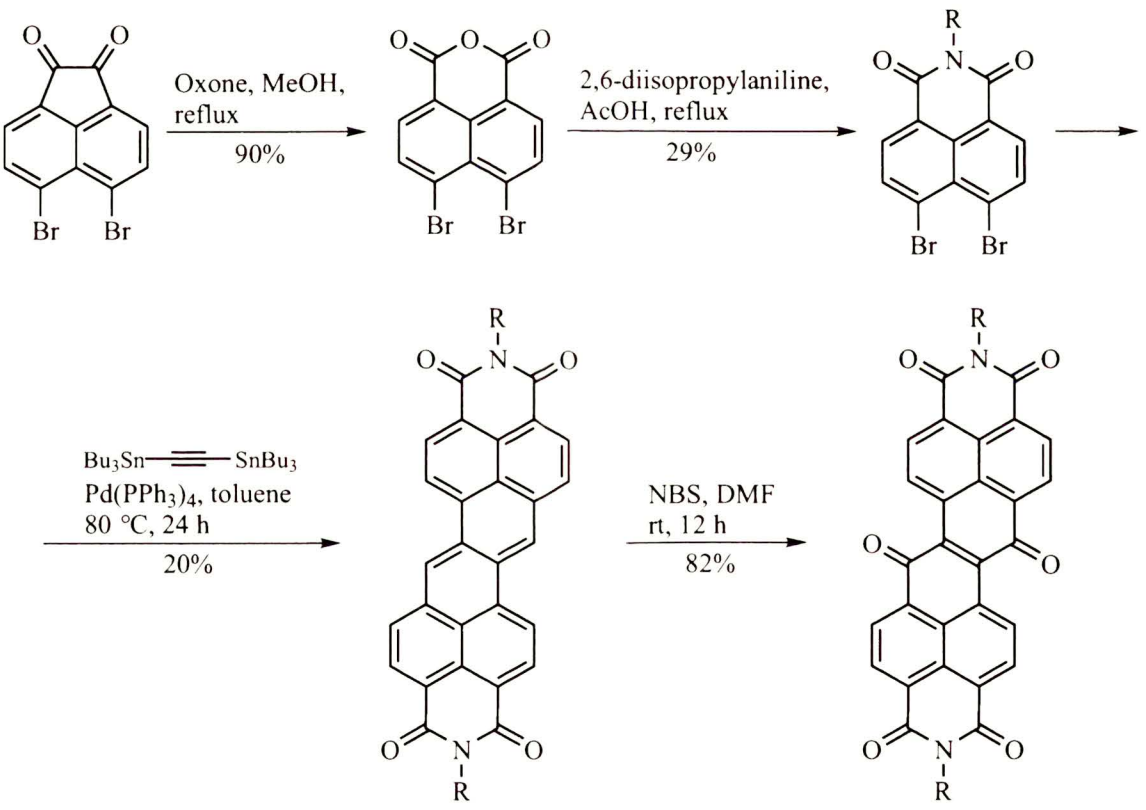
R = 2,6-diisopropylphenyl;
i. BINAP, $Pd_2(dba)_3$, NaO*t*Bu, toluene, 80 °C, overnight (>90%); *ii*. K_2CO_3, ethanolamine, 130 °C, 5d.

Scheme 2.20

The product has green color as a result of a wide absorption band in red and NIR region (with maximum near 750 nm). Subsequently, authors mentioned that

role of lone electron pair of nitrogen (which have to be involved in delocalization) along with intramolecular hydrogen bond formation are crucial features for gaining such photophysical properties. Dye showed good solubility and processability and, most important, excellent photostability. Unfortunately, electrochemical studies were not performed. Anthraquinone-based core with adjacent nitrogen atoms can give interesting picture of electrons delocalization after single electron reduction. It is terrifying to think how the absorption can shift, when in the case of simple anthraquinone imides the difference between electroneutral molecule and anion radical was about 800 nm.

Encouraged by recent successful syntheses of stable zethrene derivatives, [48] Sun and co-workers[49] synthesized zethrenediimide starting from dibromosubstituted 1,8-naphthalene diimide (Scheme 2.21).

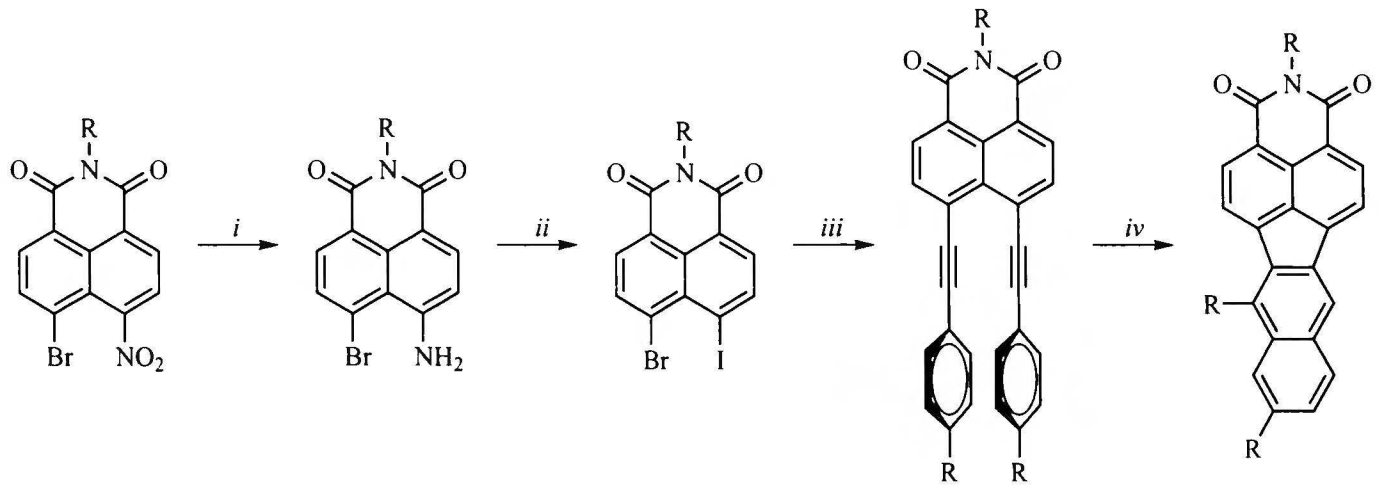


Scheme 2.21

Although experimental data and *in silico* studies of zethrene shed light on its structural features (central butadiene moiety flanked by two naphthalene rings and the central butadiene unit shows significant bond length alternation, 1.368 and 1.468 Å), its diimide derivative exhibit considerable larger red shift compared

to combination of simple naphthalene units. This can be imputed to stronger A−D−A interaction between imide moieties and central butadiene fragment. Interestingly, the attempt of bromination of positions 7 and 14 with NBS yielded unexpectedly oxidized product **20**. The NIR absorption, good solubility and photostability make these compounds promising in various applications.

Duan *et al.*[50] were able to perform photoinitiated cyclization of 4,5-bis(arylethynyl)-1,8-naphthalenediimide yielding NIR-emitting dye (Scheme 2.22).



i. $SnCl_2 \cdot 2H_2O$, AcOH, HCl (g), rt, 90%; *ii*. $NaNO_2$, HCl, KI, 0-5 C, 48%; *iii*. arylacetylene, $Pd(PPh_3)_4$, CuI, Et_3N, N_2, reflux, 85%; *iv*. $h\nu$, 30%.

R=OCH_3 (**21**)
$N(CH_3)_2$ (**22**)

R=OCH_3 (**23**)
$N(CH_3)_2$ (**24**)

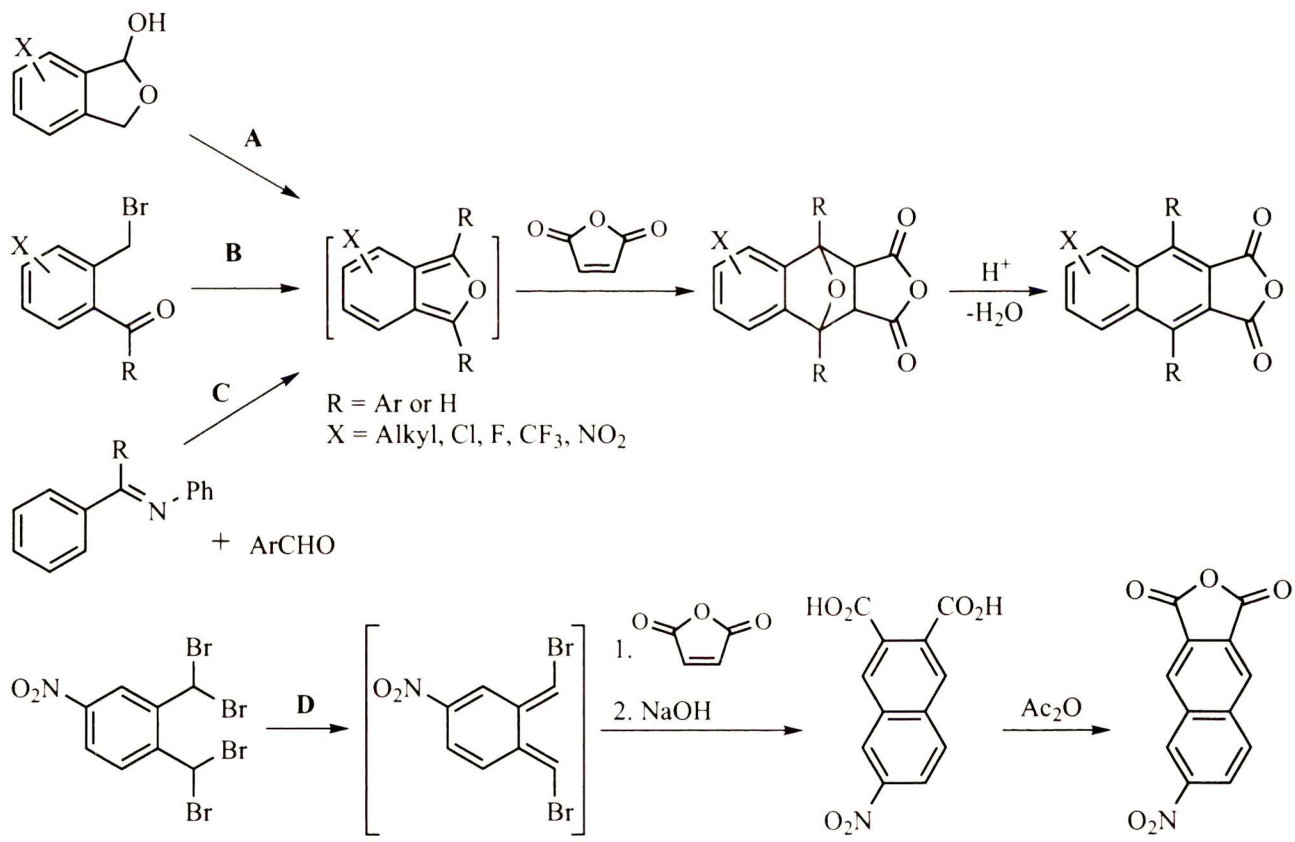
Scheme 2.22

In this photochemical reaction process, authors speculated that 3-hydrocyclohexa-1,2,4-triene intermediate formed first through photochemical cycloaromatization, followed by a very rapid radical-induced 1,3-hydrogen transfer and thus resulted in a stable phenyl ring. Cell uptake experiments with fluorescence images underlined the potential of the dye **24** as a NIR fluorescence imaging agent.

2,3-Naphthalimides are not so popular objects of research as 1,8-substituted analogs mainly because of lack of inexpensive natural precursors. However, they can found interesting applications due to their electron accepting and spectroscopic properties. Derivatives of 2,3-naphthalenedicarboxylic acid, similarly to phthalic acid, can form π-expanded phthalocyanines which are considered as good candidates for Single-Molecule "Logic Switch".[51] The desire to be able to study a relationship between the structure of substituted 2,3-naphthalimides and their photophysical properties forced scientists to discover new synthetic methods.

Leaving aside scanty examples of oxidizing 2,3-substituted naphthalenes or "burning" fused rings of higher hydrocarbons it was Cava[52] and Rickborn[53] who laid the fundation of 2,3-naphthalenedicarboxylic anhydride synthesis starting either from $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene or 1-ethoxy-1,3-dihydroisobenzofuran. In many variants derived from oxygen containing substrates the pivotal step is isobenzofuran formation, which then can be trapped with reactive dienophiles in Diels-Alder reaction. In case of tetrabromoxylenes the intermediate is dibromo-*o*-quinodimethane.

The key precursors for 2,3-naphthalimides are corresponding cyclic anhydrides. There are several reports appeared recently (Scheme 2.23) utilizing above strategies to synthesize various substituted 2,3-naphthalenedicarboxylic acid anhydrides.[54]

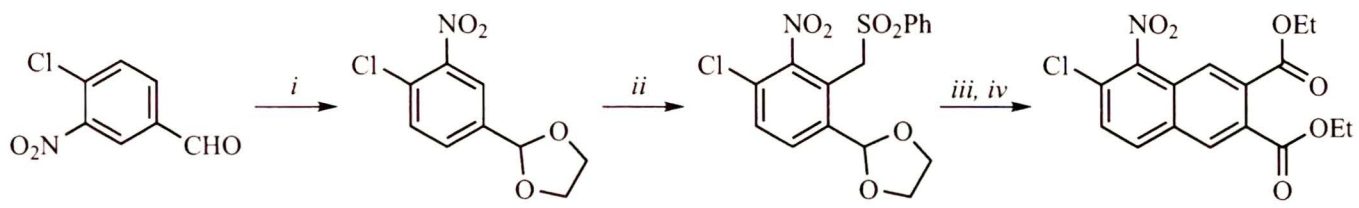


Scheme 2.23

While routes **A** and **D** can be easily traced back to classical syntheses, routes **B** and **C** represent the variant, allowing to prepare 2,3-naphthalic anhydrides with aryl substituent in positions 1 and 4. Route **C** requires rhenium catalyst and the reaction proceeds via selective C−H bond activation (coordination on ketimine),

insertion of an aldehyde, intramolecular nucleophilic cyclization, elimination of aniline and Diels-Alder cycloaddition.

Slightly different reaction pathway[55] is presented on scheme 2.24.



i. ethylene glycol, toluene, reflux, overnight, 95%; *ii*. dry DMSO, KOH, $ClCH_2SO_2Ph$, rt, overnight, 75%; *iii*. $AcOH/H_2O$, reflux, 6 h; *iv*. diethyl maleate, 18-crown-6, K_2CO_3, CH_3CN, reflux, 6 h, 70%.

Scheme 2.24

Here, the key step was the introducing of one-carbon synthon by vicarious nucleophilic substitution of aromatic hydrogen. Subsequent aldehyde deprotection triggered elimination and cyclization and in the presence of dienophile desired naphthalene derivative was formed.

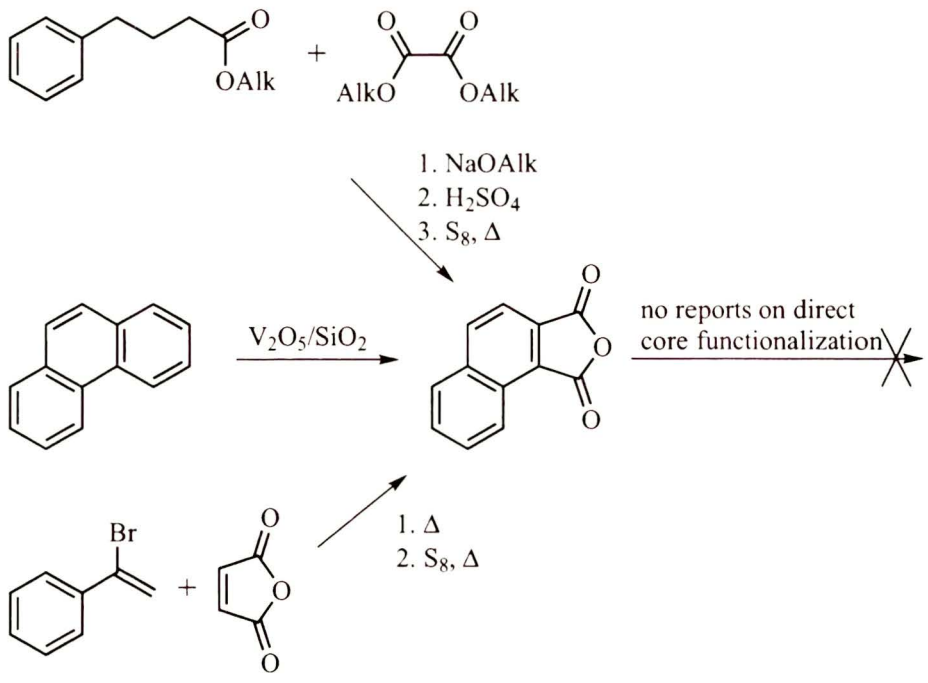
It is not surprisingly that optical and electrochemical properties of 2,3-naphthalimides with aryl substituents are not discussed[54b,54d] since there is, probably, minimal conjugation of substituents with naphthalene core.

On the other hand, relatively simple derivatives with various substituents in positions 5–8 revealed range of breathtaking properties such as unusually large Stokes shift, dual fluorescence and solvatochromism.[54a,55]

The synthesis of third regioisomer – 1,2-naphthalic anhydride – is even more complicated. There is limited number of synthetic methods toward unsubstituted 1,2-naphthalic anhydride which boils down to oxidation of corresponding hydrocarbons such as phenanthrene (where it is usually a minor product), cyclization of γ-phenylbutyric acid esters with alkyl oxalates (Bougault r-n) and Diels-Alder cycloaddition of α-bromostyrene to maleic anhydride.[56–58] The latter latter two methods require intermediate oxidation under harsh conditions (Scheme 2.25). It is noteworthy, that there are no reports on direct modification of the core of anhydride.

Some methods towards substituted 1,2-naphthalic anhydrides are summarized on the scheme 2.26.

The cyclization based on γ-arylbutyric acid esters[59] can be considered as a



Scheme 2.25

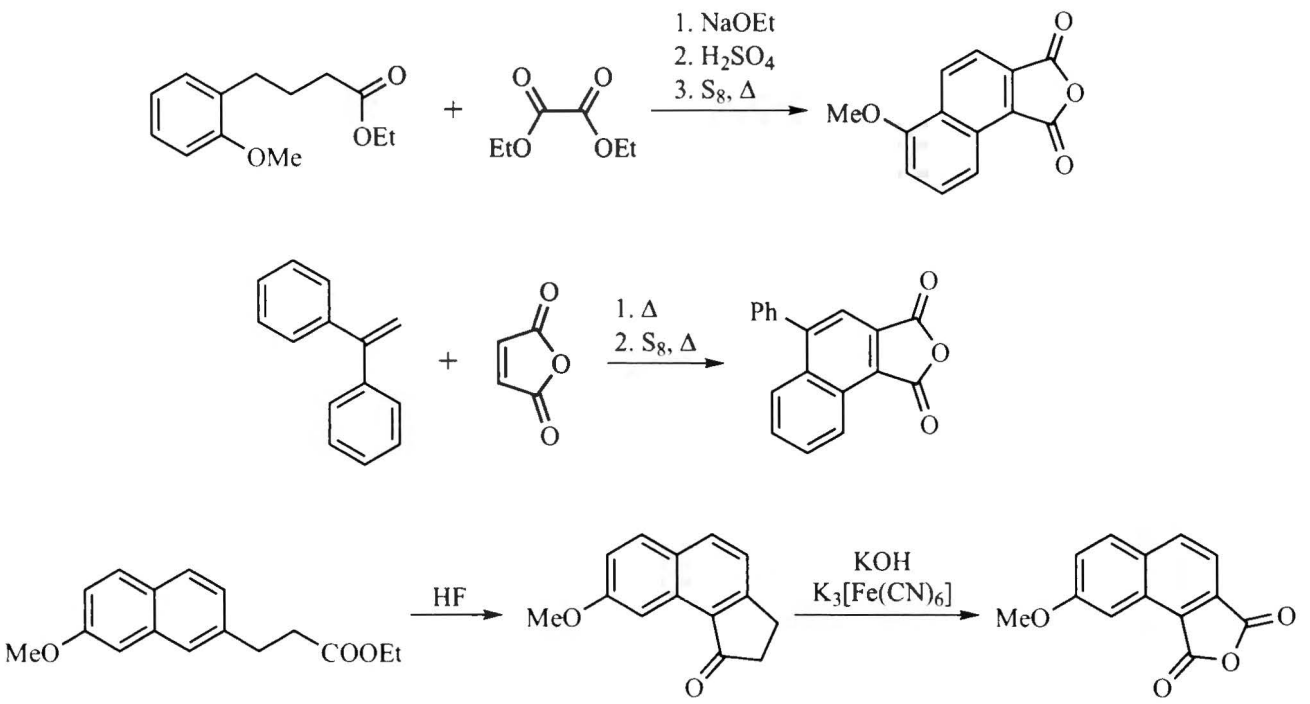
quite general method due to the accessibility of starting material. The cycloaddition of maleic anhydride to 1,1-diphenylethylene (Warner-Jaugger reaction) is limited to electron-donating or neutral substituents.[60] Both methods, however, suffer from harsh oxidation conditions. Another example is oxidation of cyclic ketones[61] which did not found broader application, though.

Mizuno and Yamano[62] recently reported efficient and mild "one pot" method toward 1,2-naphthalimides (Scheme 2.27). The authors found by accident that aromatization step occurs simultaneously with imidation, which allows to avoid inefficient sulfur-based oxidation.

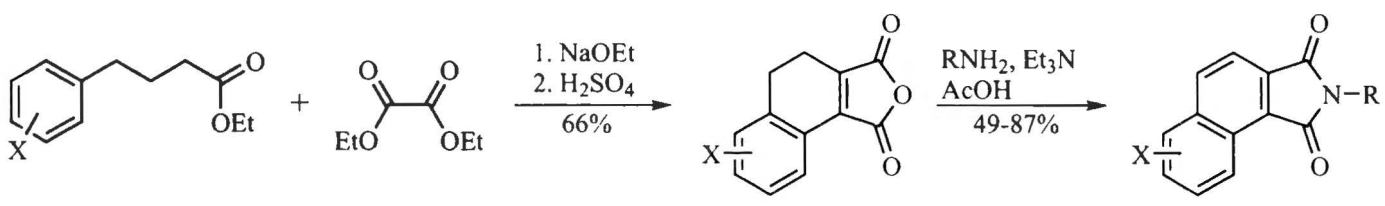
Makarova *et al.*[63] showed recently, that Diels-Alder cycloaddition of α-bromostyrene to maleic anhydride and oxidation of intermediate can undergo in one step (Scheme 2.28). Although the yield is lower than in original method,[58] the product contains no sulfur compounds, which are frequently tedious to remove.

Naphthalene backbone can easily accommodate two imide groups forming exceptionally popular group of compounds called naphthalenediimides (NDI). Usually this name imply 1,8:4,5 isomer since syntheses of other isomers are scarcely known.

Although simple naphthalenediimides are colorless compounds it is possible to alter their optical properties by introducing substituents into naphthalene core.



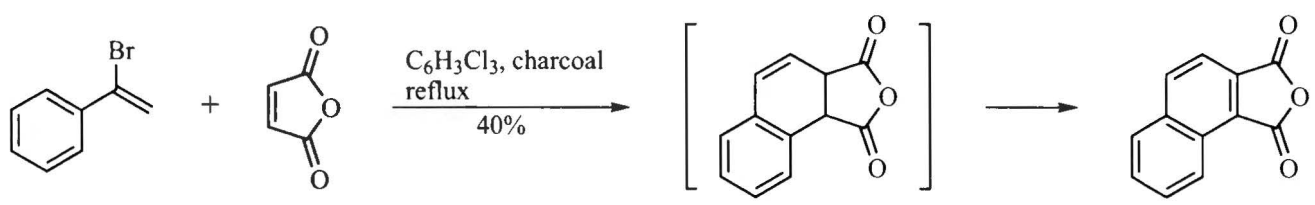
Scheme 2.26



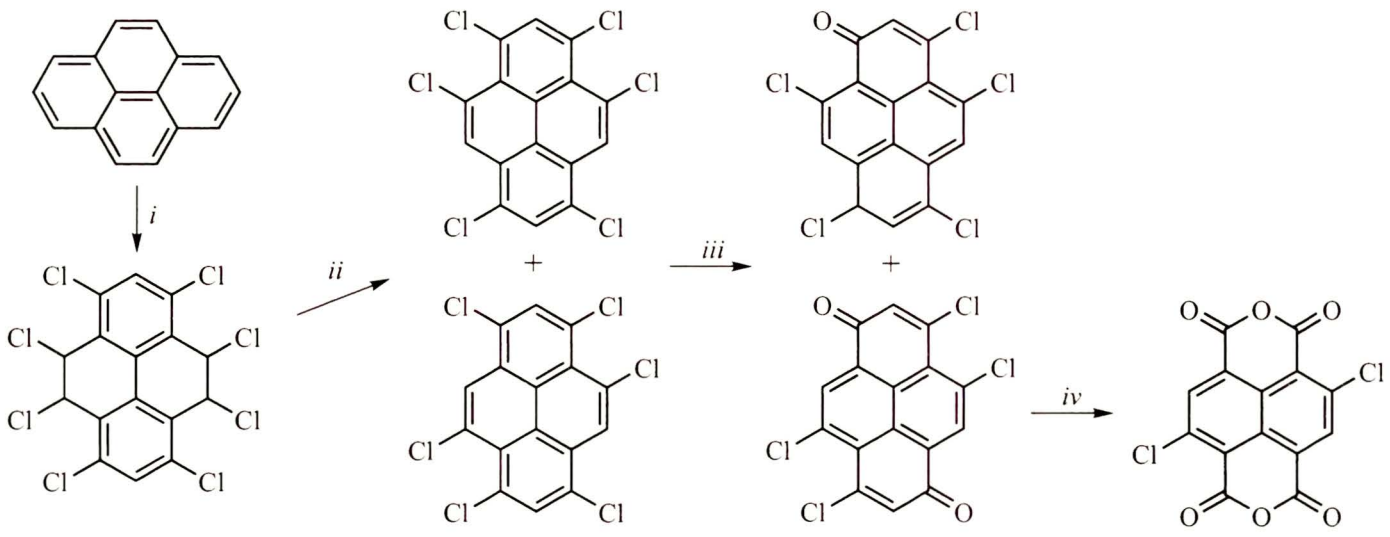
X = H, Br, OMe; R = Me, Bn, Ph

Scheme 2.27

The traditional approach towards core-substituted NDIs starts with the perchlorination and two steps oxidation of commercially available hydrocarbon pyrene. [64] Later works on this topic revealed problems with reproducing of original procedure and in 2006 Thalacker and co-workers [65] published refined protocol (Scheme 2.29). This synthesis involves the excessive use of chlorine gas, that can be a safety risk in an academic environment without dedicated equipment. That is why the alternative approach towards core-substituted NDIs was of interest.



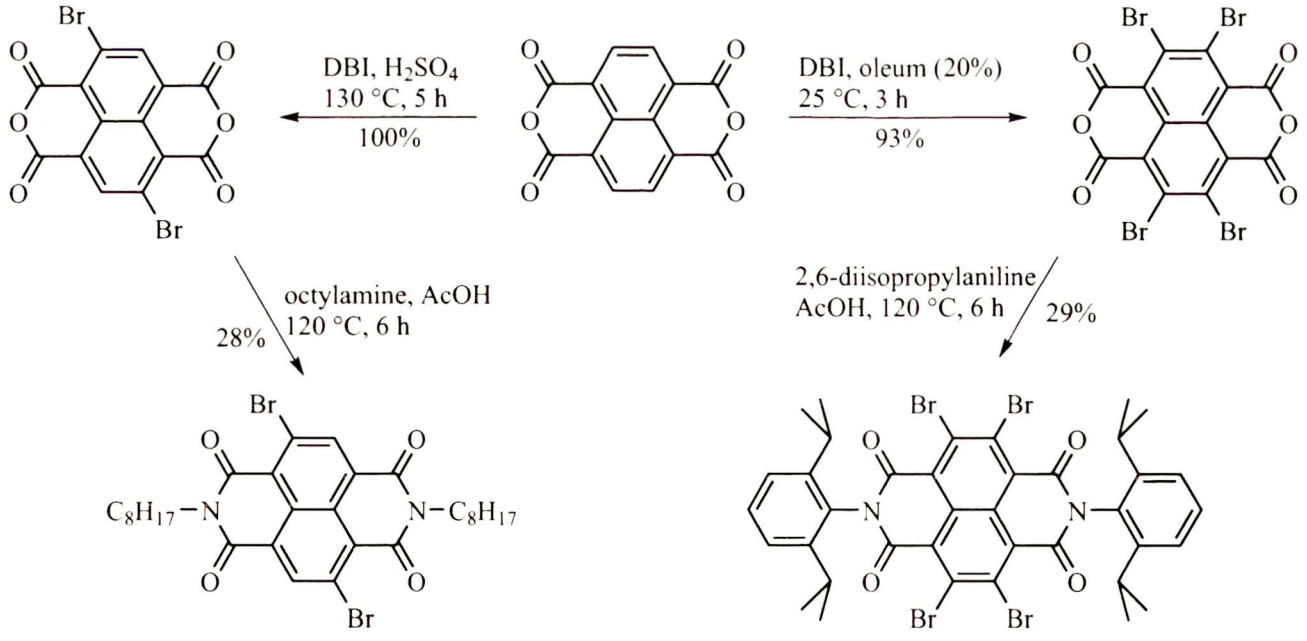
Scheme 2.28



i. Cl_2 (g), I_2 (cat.), 1,2,4-trichlorobenzene, 25-110 °C, 6 h, 36-38%; *ii*. KOH, ethanol, 80 °C, 5 h, 96-97% (mixture); *iii*. fuming HNO_3, 0-5 °C, 15 min, 32-45% (*trans* isomer); *iv*. fuming HNO_3, concd H_2SO_4, 100 °C, 5 min, 45-49%

Scheme 2.29

The results of successful direct bromination of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride with dibromoisocyanuric acid (DBI) appeared in 2007, furnishing corresponding dibrominated[66] and tetrabrominated[67] anhydrides (Scheme 2.30).



Scheme 2.30

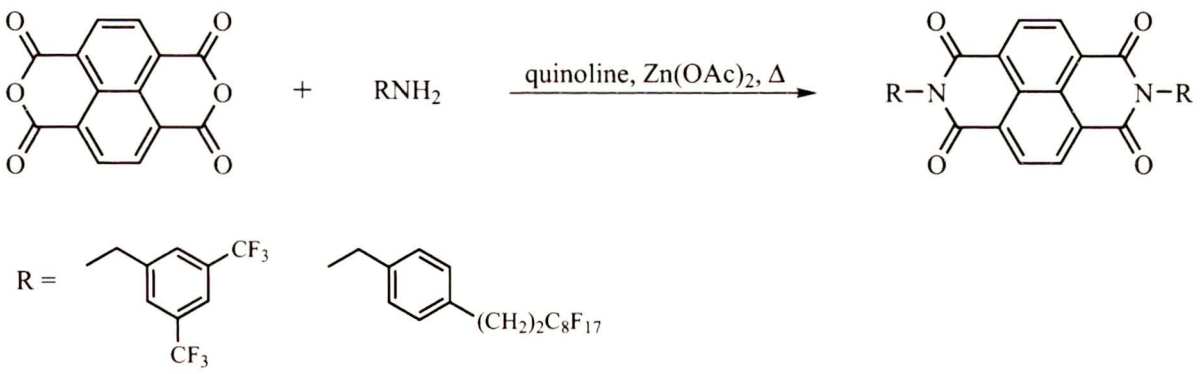
Based on above strategy, an approach to core substituted NDIs becomes facile, robust and general, opening access to wide set of core-substituted NDIs *via* halogen atoms substitution by O-, N-, S- or Se-nucleophiles and palladium catalyzed couplings (Suzuki, Sonogashira, Stille reactions). With electron donors, attached

to the core, NDIs become colorful push–pull systems, whereas electron acceptors produce exceptionally π-acidic aromatic systems.[10]

Comparing to PDIs, the planarity of NDIs is not distorted by introducing substituents in a naphthalene core. This feature is important when ordered π-stacks with high conductivity are of interest. Moreover, core-substituted NDIs are more compact and their color can be tuned precisely over the whole visible spectrum, whereas unsubstituted PDIs absorb already at around 530 nm.[68] The detailed report on core-substituted NDIs is published recently in review article by Sakai and co-workers.[10] There are, however, several new synthetic advances not included therein.

Along with aromatic core expansion, the solubility decreases significantly. At this point substituents at nitrogen atoms become important. They essentially have no effect on electronic structure of NDI core and the relationship between substituent type and solubility was studied in comprehensive manner by Demmig and Langhals.[69]

Another function of these substituent was demonstrated by See *et al.*[70] By a simple one step reaction they have prepared NDIs with two perfluoroalkyl-benzyl N,N′-substituents (Scheme 2.31). This had enormous impact on the air stability of OSC-devices based on them, putting these NDIs among the leading n-channel OFET semiconductors explored to date.

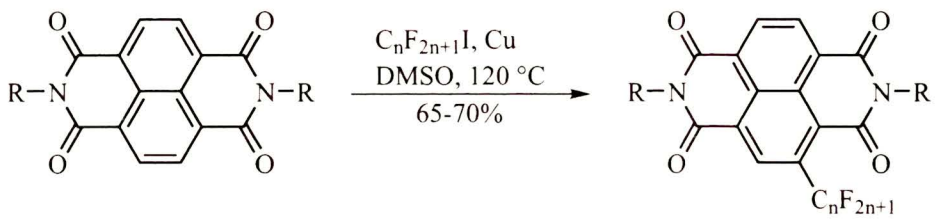


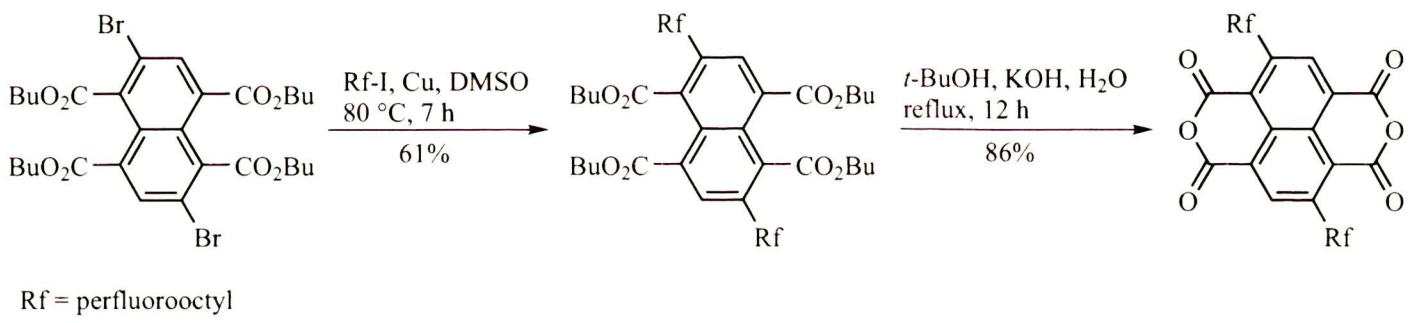
Scheme 2.31

Li and co-workers[71] reported recently an efficient and versatile method to introduce perfluoroalkyl chains directly into the core of various aromatic hydrocarbons (Scheme 2.32). Reaction proceeds via copper-mediated radical perfluoroalkylation and in the case of naphthalene diimides yields monosubstituted products in

good yields.

At the same time, Yuan *et al.*[72] independently reported the synthesis of bis-perfluoroalkylated NDIs from their dibrominated analogues under similar reaction conditions. It is noteworthy, that Li reported that there was no reaction when monobromosubstituted NDI was used as a substrate and Yuan was able to overcome this problem by introducing perfluoroalkyl substituents on the stage of naphthalene-1,4,5,8-tetracarboxylic acid ester, making corresponding dianhydride – the key intermediate in NDI syntheses – ready available.

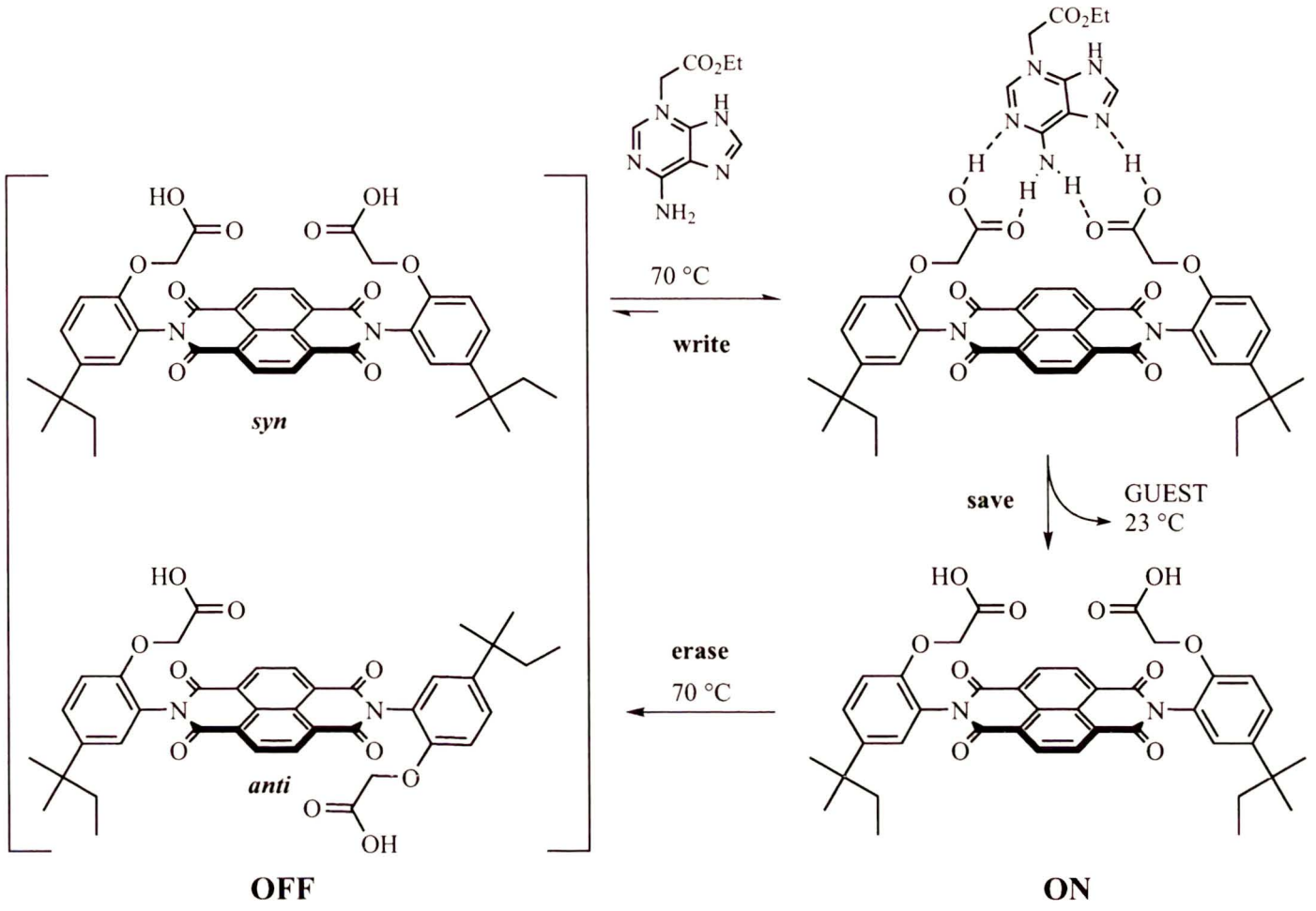




Scheme 2.32

Lavin and Shimizu demonstrated yet another utility of N,N′-substituents.[73] Synthesized by authors NDI-based dicarboxylic acid showed interesting properties as a molecular switch (Scheme 2.33).

They found that diacid is formed as a mixture of atropoisomers which do not undergo interconversion at ambient temperature due to the restricted rotation. However, the sample can be converted to *syn*-form by heating it in the presence of hydrogen bonding guest. After cooling to room temperature and guest removal, the measured *syn*/*anti* ratio was 93:7. When it was heated again – the starting mixture was formed. While in solution, isomerically pure *syn*-diacid have half-life *ca.* 11 days (at 23 °C), in the solid state the sample maintains a stable isomeric ratio for months.

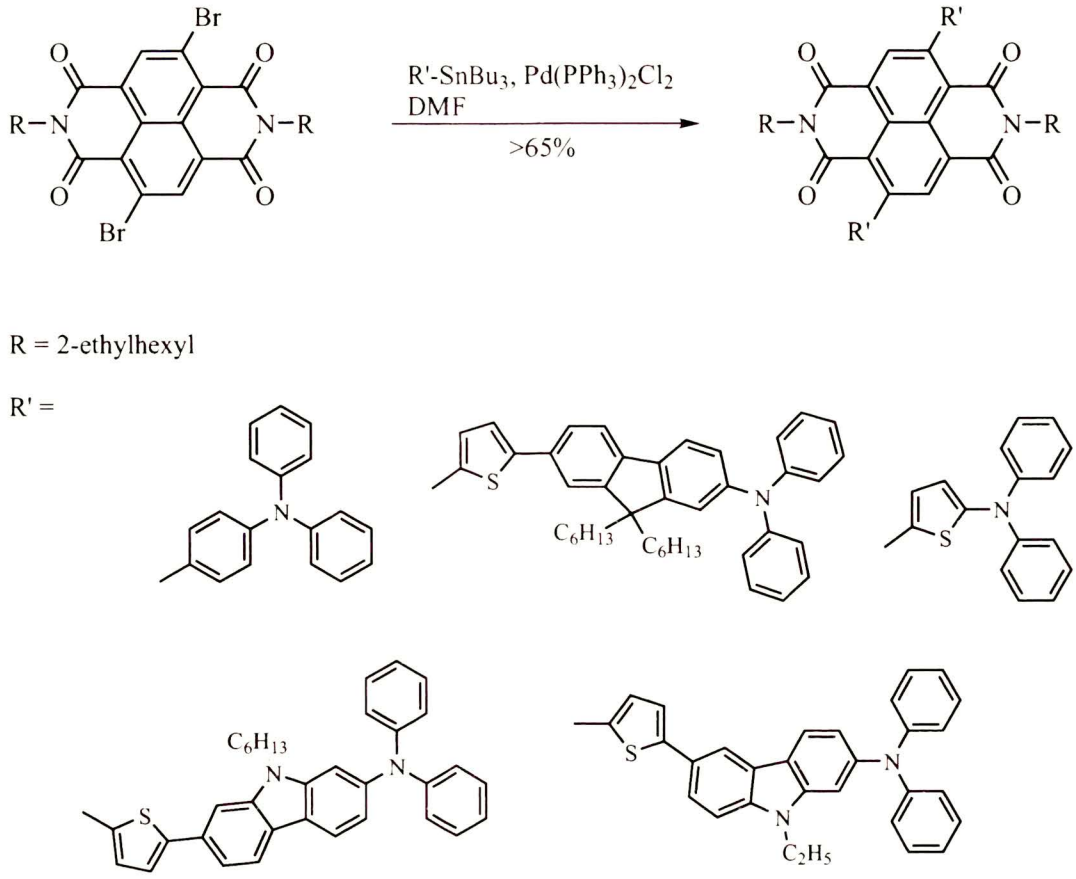


Scheme 2.33

Lin with co-workers demonstrated recently,[74] that NDI can be a viable platform for compounds with two-photon absorption properties (Scheme 2.34). Their observations based on spectroscopic data revealed that in the case when donating arms are connected to NDI core through phenylene linker, there is essentially no coupling between units, but when the linker is substituted by 2,5-thienylene – significant red-shift was observed. Compounds with more expanded side-arms showed promising TPA cross-section values.

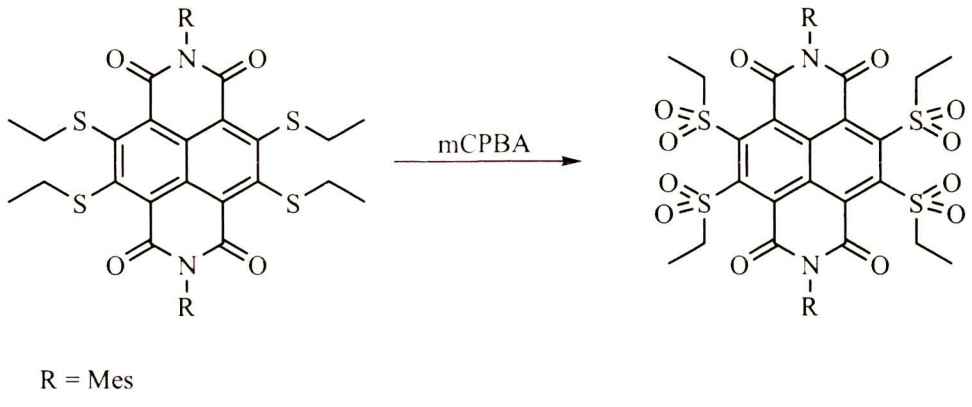
Míšek *at al.*[75] was able to achieve "super π-acidity" by a simple synthesis of NDI-tetrasulfide and subsequent oxidation to tetrasulfone (Scheme 2.35). Such compounds can be of interest in materials science (for example, air-stable n-semiconductors with high charge mobility) and in organocatalysis, as anion-π stabilizing agent.

The same group, after have succeeded in redox chemistry making "super π-acid", decided to break records at the other extreme as well, that is with electron-rich NDIs. Inspired by natural objects (green and red fluorescent proteins from

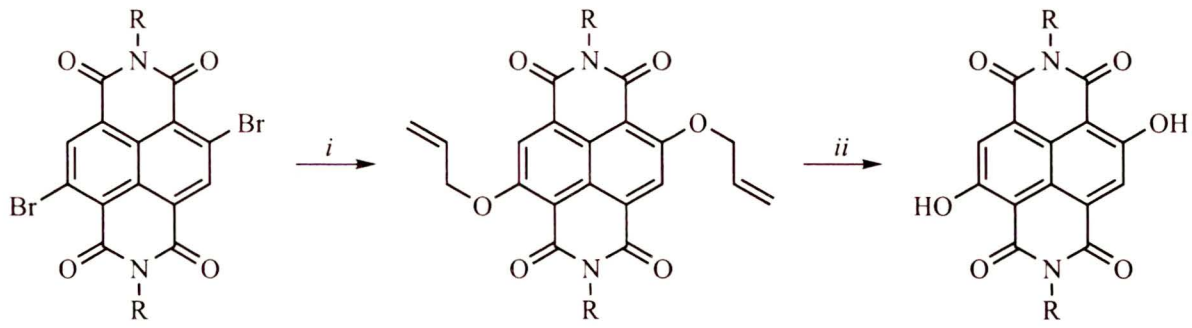


Scheme 2.34

jellyfish and corals) they decided to reach NIR region of absorption, utilizing the phenolate anions as an ultimate π-donors.[76] The synthesis of corresponding hydroxysubstituted NDIs was simple and elegant (Scheme 2.36). Products were studied by deprotonation, observing sharp changes in optical properties. However, the authors were not able to access absorption maxima beyond the 642 nm of tetraamino NDI. Nevertheless the synthetic advances made by authors, by employing new reactions (involving boronic acid esters formation, oxidative amination,



Scheme 2.35

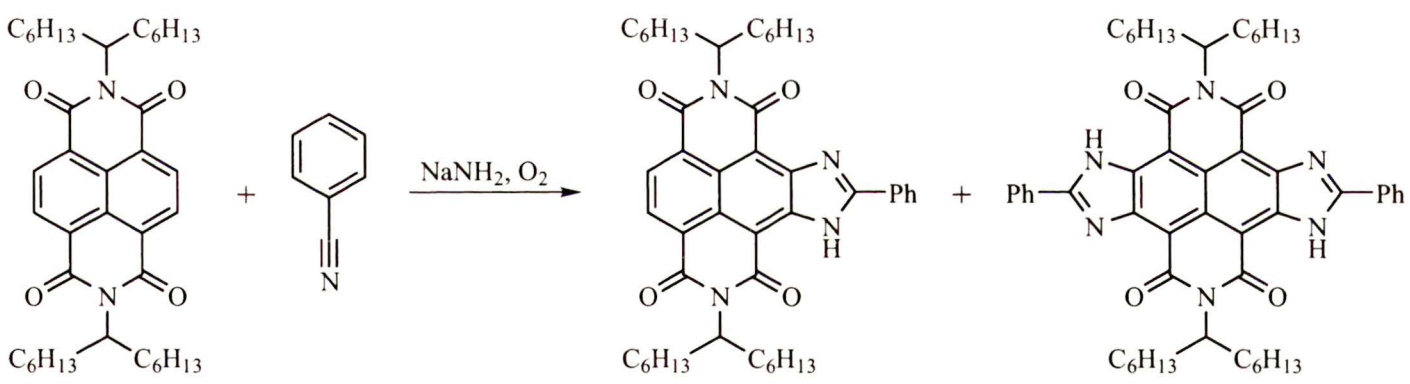


R = Mes
i. allyl alcohol, NaH, DCM, 4Å ms, rt, 4 h, 86%; *ii*. $Pd(PPh_3)_4$, phenylsilane, DCM, 4Å ms, rt, 10 h, 80%

Scheme 2.36

colorful acid/base equilibria) enriched in this way panchromatic collection of NDIs.

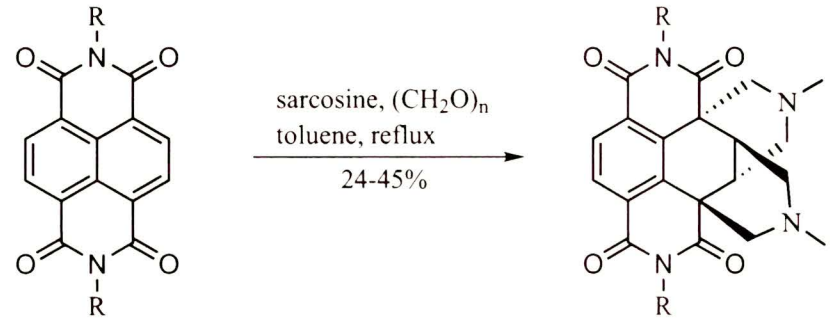
While the introducing of different substituents into NDI core is studied well, there were no reports where lateral extension of NDI by means of a heterocyclic annelation would be described until recently. Langhals and Kinzel demonstrated[77] the reaction of NDI with benzonitrile and sodium amide (Scheme 2.37). Introducing of each imidazole ring caused absorption red-shift for 60–70 nm and



Scheme 2.37

increase in fluorescence quantum yield up to 79%. Reaction with substituted benzonitriles allowed to obtain products absorbing virtually a whole range of visible light.

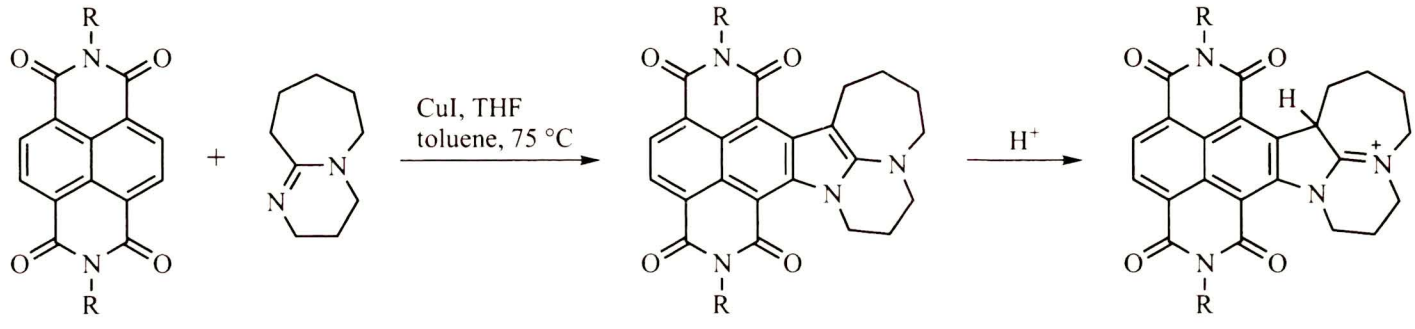
Gryko and co-workers[78] recently reported interesting example of unusual reactivity of NDIs. They appeared to be active towards *in situ* generated azomethine ylides (Scheme 2.38). The reaction proceeds on one benzene ring, while another one remains untouched. The proposed mechanism involves two sequential 1,3-cycloadditions, followed by unconventional, concerted rearrangement of 5-membered to 6-membered rings.



R = Me, *n*-octyl, *n*-decyl

Scheme 2.38

Zhou *et al.*[79] during their research on the "click" reaction, unexpectedly discovered the reaction of NDI with DBU (Scheme 2.39). They found the product to



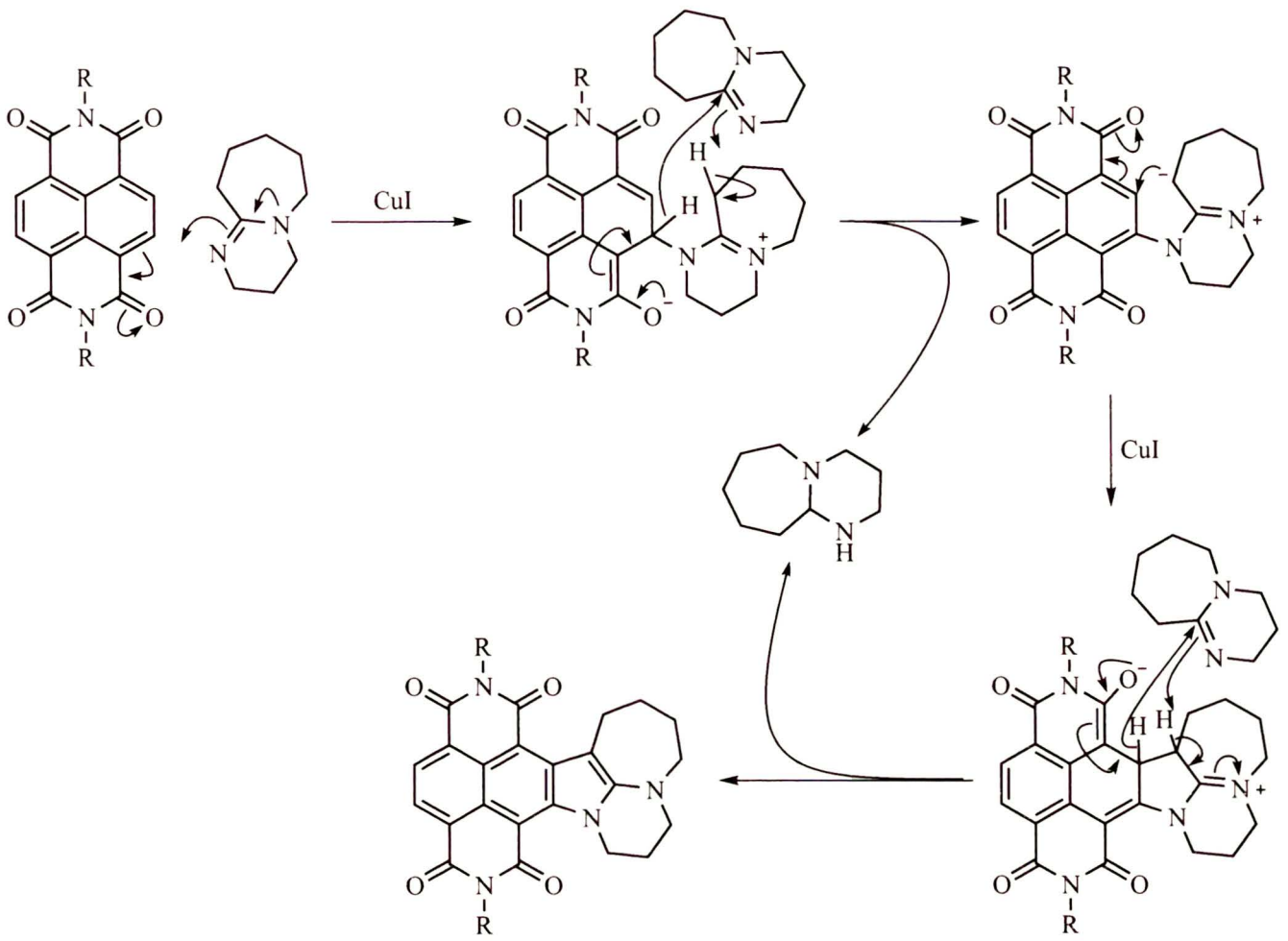
R = *n*-Bu

Scheme 2.39

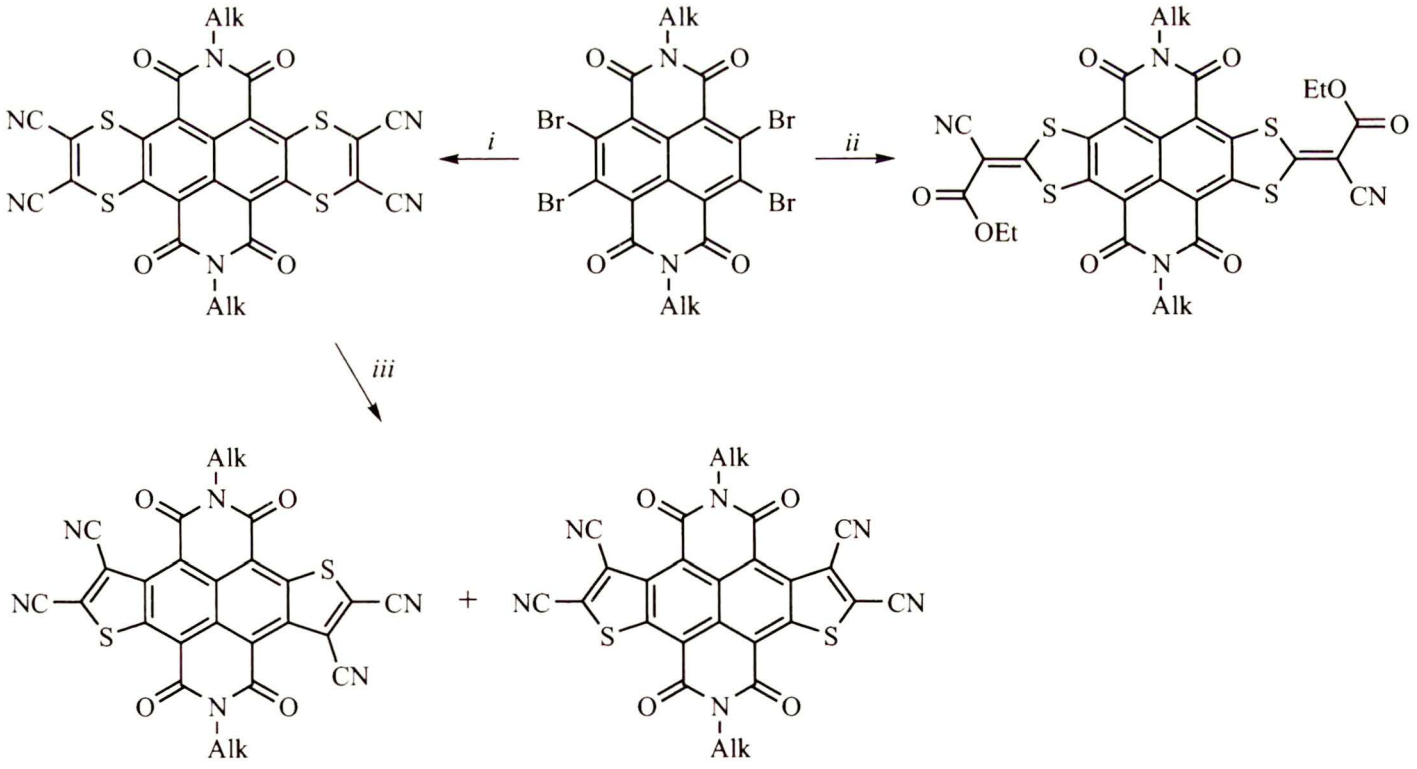
be pH-sensitive and under titration with acid, simultaneous disappearing of broad CT band at *ca.* 650 nm together with fluorescence enhancement was observed.

The authors, based on related literature, proposed the mechanism of their reaction, where copper iodide promotes two sequential Michael 1,4-additions of DBU to NDI core, where DBU plays a role of reactant and oxidant (Scheme 2.40).

Hu *et al.*,[80] continuing their work on NDIs fused with sulfur heterocycles, presented recently new series of laterally expanded NDIs (scheme 2.41). Interestingly, all compounds in the series have very similar optical and electrochemical properties (absorption of NDI core below 400 nm and intense CT band with maximum at 550–600 nm imputed to sulfur heterocycles-CN interactions). On the other hand, OTFT devices based on presented compounds showed good electron mobility characteristics and excellent operating and air stability.



Scheme 2.40

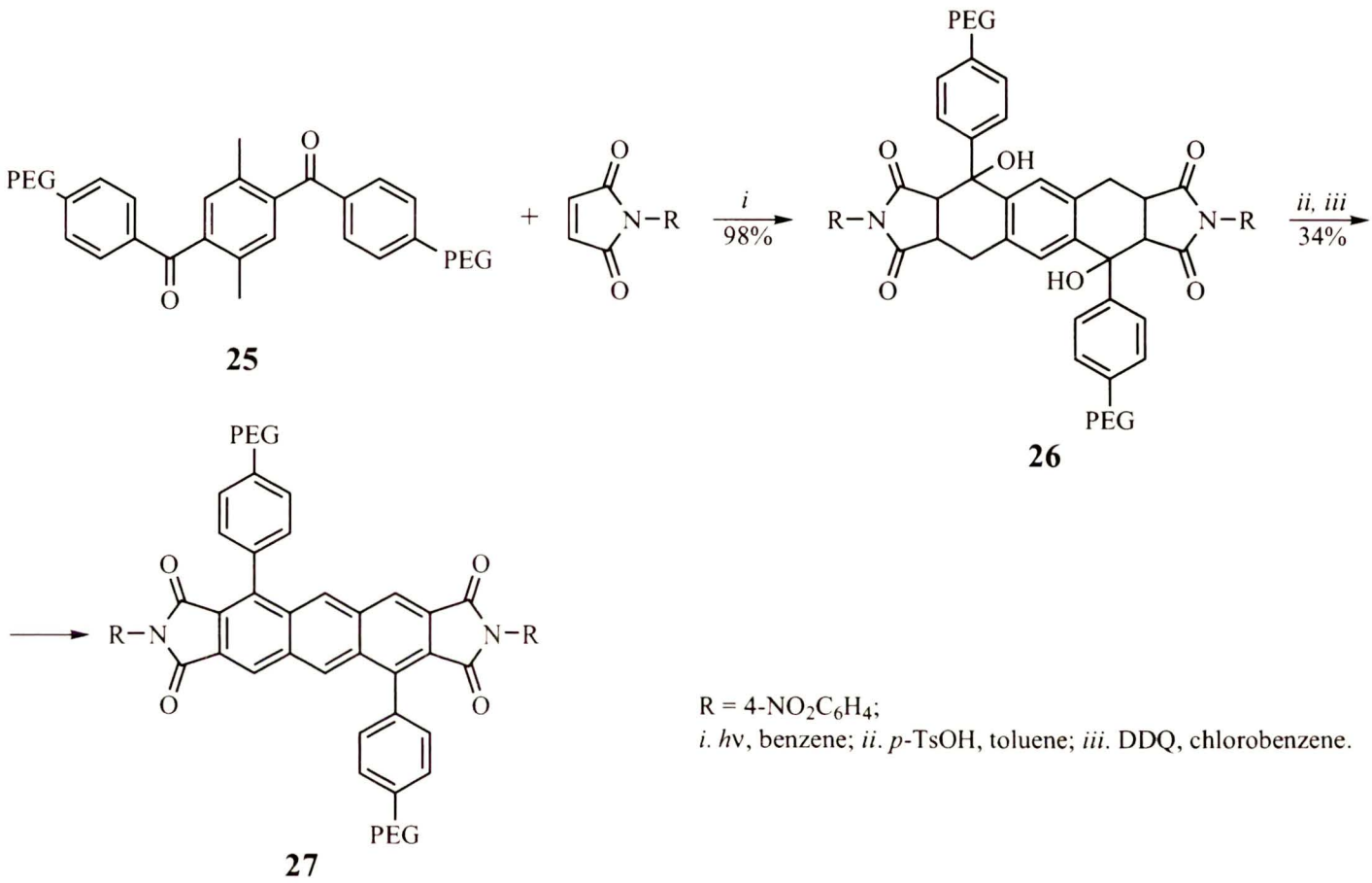


i. sodium 1,2-dicyanoethene-1,2-dithiolate, THF, 30 °C; *ii*. NaH, ethyl 2-cyanoacetate, THF, 0-5 °C; *iii*. H_2O_2 (30%), C_2H_5COOH, 130 °C.

Scheme 2.41

2.4 Imides based on three and more benzene rings

Needless to say, synthetic difficulties in imide chemistry increase with number of fused aromatic rings. One of the first reports on this subject appeared in 2004 – Ilhan *et al.*,[81] based on their previous work on anthracenediimides, demonstrated the synthesis of chemosensor of nerve gases based on anthracene 2,3:6,7-tetracarboxdiimide (Scheme 2.42).

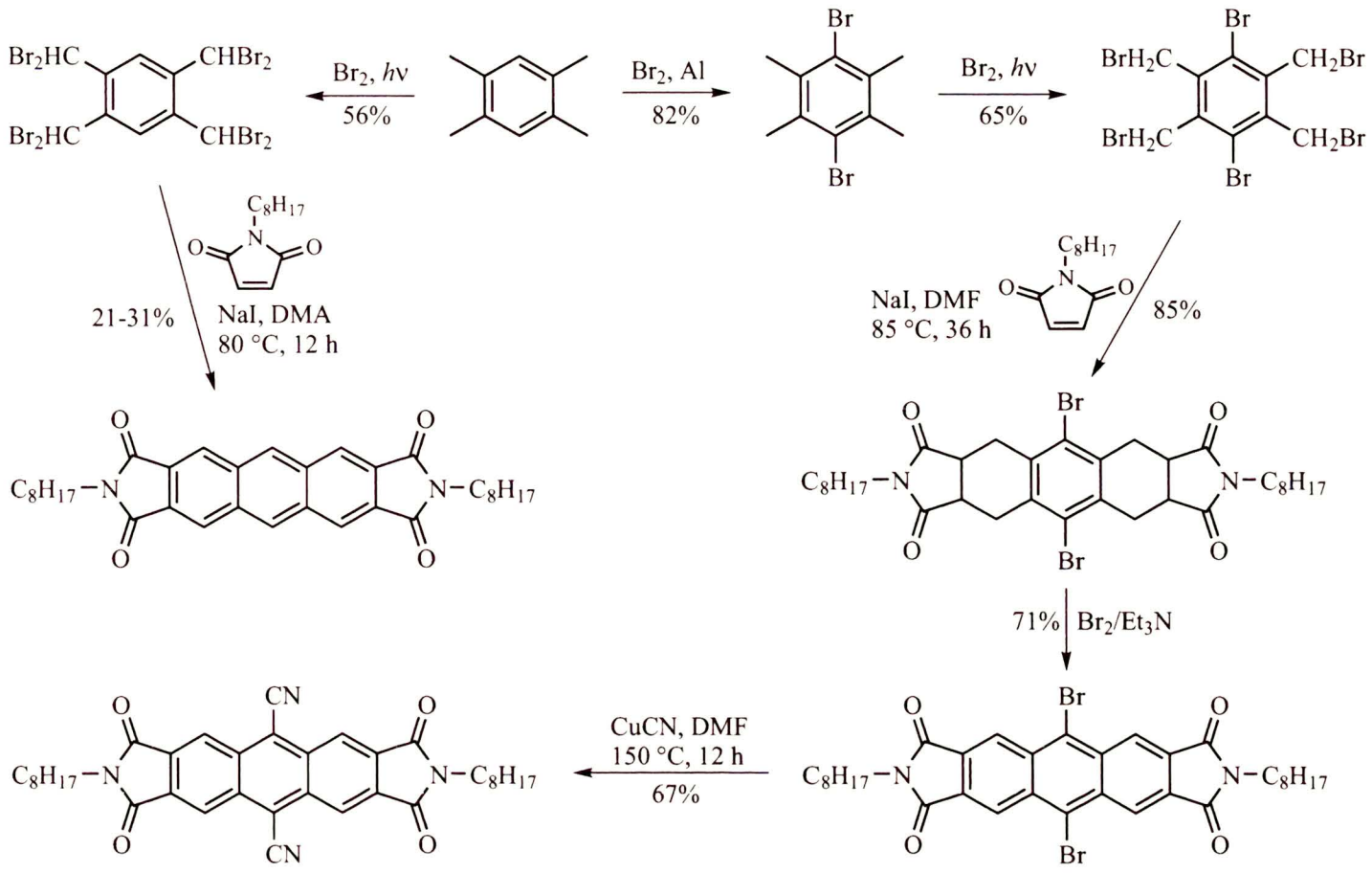


Scheme 2.42

The synthesis is based on the photoenolization of substituted 2,5-dibenzoyl-*p*-xylene **25**, trapping the resulting photoenol with reactive dienophile to produce bisadduct **26**. Dehydration of this compound and subsequent aromatization yields highly substituted anthracene derivative **27**.

After the reduction of peripheral nitro groups at N,N′-substituents, amino groups were quenching fluorescence completely, and after binding with $COCl_2$ visible signal appeared, indicating the presence of analyte.

Alternative route towards similar architecture was proposed by Wang *et al.*[82] (Scheme 2.43).

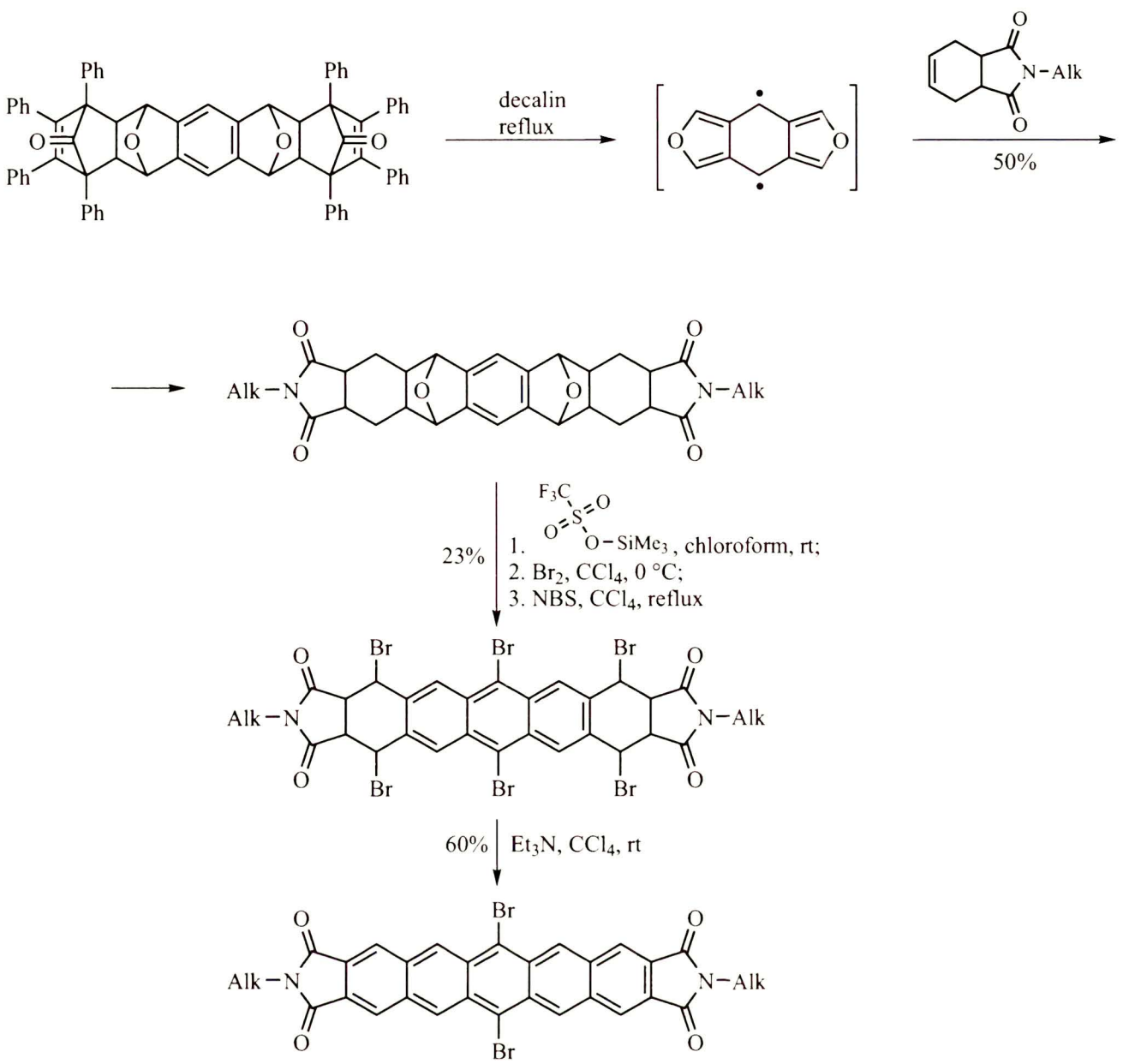


Scheme 2.43

The synthesis involves two simple steps: 1,2,4,5-tetramethylbenzene bromination followed by Diels-Alder cycloaddition/aromatization of 1,2,4,5-tetrakis(dibromomethyl)benzene with the requisite N-alkylmaleimide. Along with unsubstituted diimide, its 9,10-core-cyanated analogue was prepared by slightly modified synthetic sequence. Optical properties of synthesized compounds were not measured while electrochemical characteristics in both cases were rather moderate for using in OSC.

Structurally similar yet core expanded analogue was synthesized by Qu and coworkers[83] (Scheme 2.44). The key step in the synthesis of 6,13-dibromopentacene [2,3:9,10]-bis(dicarboximide) was Diels-Alder reaction of *in situ* generated benzo[1,2-c:4,5-c′]difuran with 1,2,3,6-tetrahydrophthalimide. Subsequent stepwise aromatization steps and the introduction of bromine atoms furnished stable dibromopentacenediimide. Subsequent substitution of bromines with strong electron donor (*p*-dimethylaminophenylacetylene) caused significant bathochromic shift of absorption up to 750 nm.

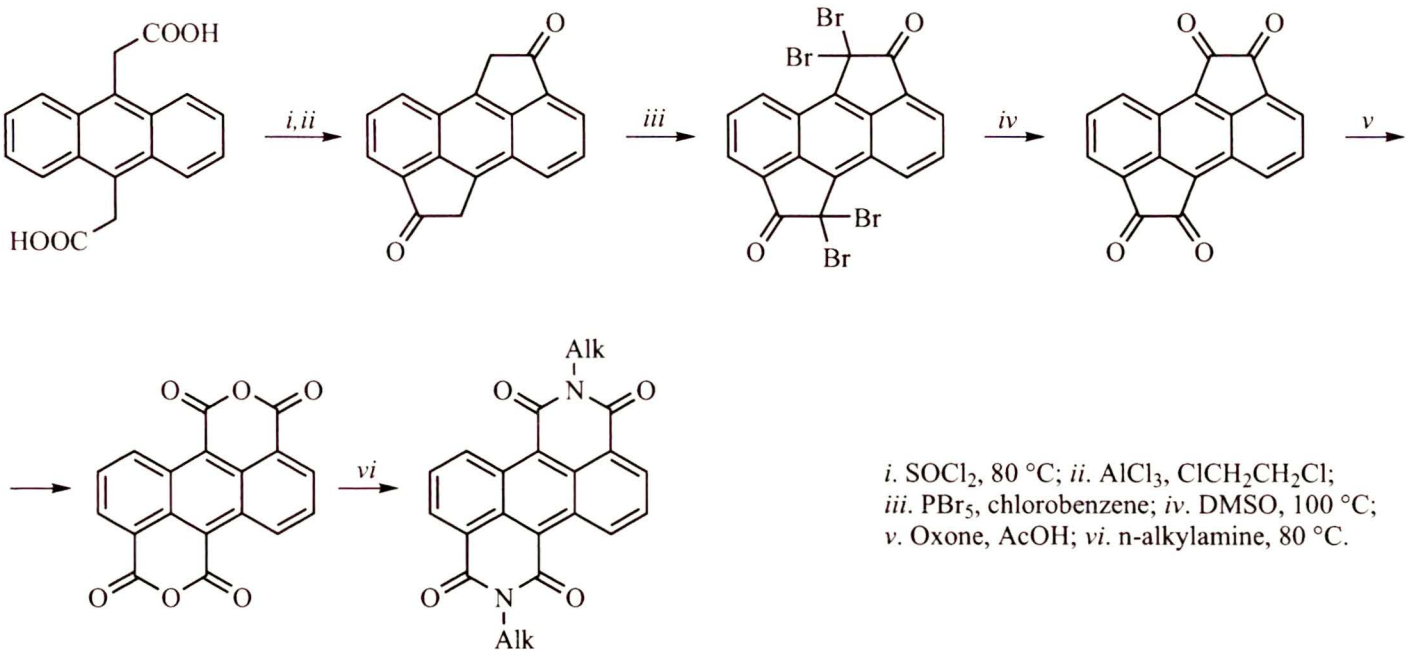
Mohebbi *et al.*[84] were first to synthesize an another type of anthracenediimides



Scheme 2.44

(Scheme 2.45). Smart choice of starting diacid allowed to perform Friedel-Crafts cyclization on opposite benzene rings. Subsequent relatively simple transformations led to highly-fluorescent dianhydride. Imides prepared by condensation reaction showed intense absorption at 480 nm and *ca.* 50 nm Stokes shifts. Their electrochemical data suggest successful applications as air-stable n-channel semiconductors.

Langhals *et al.*[85] reported recently the synthesis of anthracene-1,9-dicarboximides and their dimers (Scheme 2.46). The synthetic route towards anthracene-1,9-dicarboximides was thoroughly updated. In addition, they appeared to be versatile starting materials for developing compounds for pharmaceutical appli-



Scheme 2.45

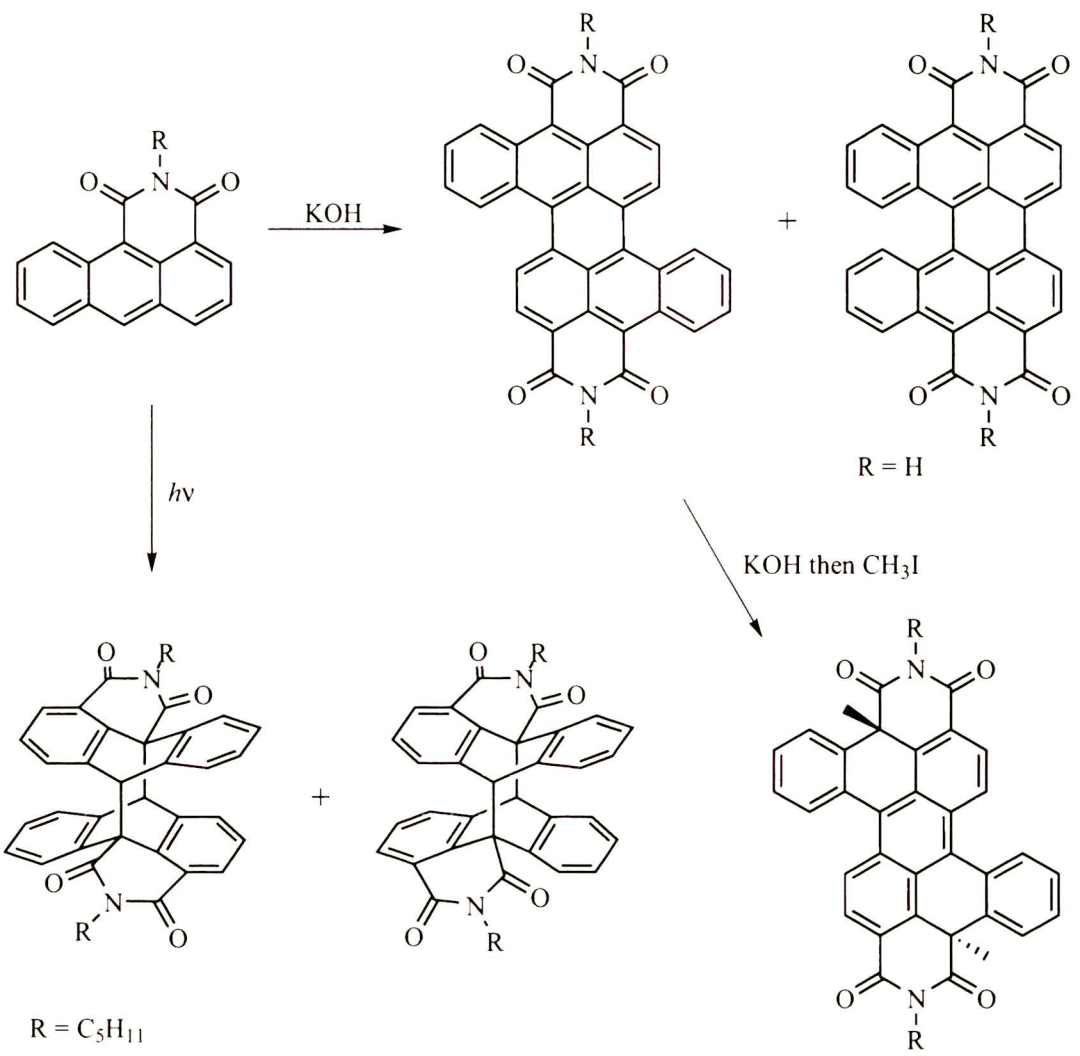
cations as well as switchable, NIR fluorescent dyes. That is, examples of its alkali-promoted dimerization, photochemical dimerization as well as unusual core-methylation of dimer are presented.

Yao with co-workers one year later have published [86] significant improvements of Langhals' approach toward Aceanthrene Green dyes (Scheme 2.47). Their synthetic route started from 10-bromoanthracene-1,9-dicarboximide **28** which was prepared from 9-bromoanthracene following the steps, similar to those mentioned above. Later, however, they utilize $Ni(cod)_2$-mediated Yamamoto homocoupling, followed by mild cyclization to afford *cis*-bisanthracene bis(dicarboxylic imide) **29** in 58% yield.* Most important, they were able to prepare most desired structure, hitherto unknown, fully cyclized bisanthene bis(dicarboxylic imide) **31**, absorbing at ca. 830 nm† by cyclization of alternatively coupled substrate **30**.

Yin et al., [87] after unsuccessful attempt to apply chemistry, used for the synthesis of anthracene dicarboxylic imides, to tetracene, decided to start synthetic sequence from its tetrahydrogenated analogue (Scheme 2.48).

Straightforward transformations brought them to the mixture of anhydrides which in imidation reaction afforded corresponding imides with surprisingly low yields. The authors was not able to explain this failure but, based on the reported

*previously referred as side-product in trans-isomer synthesis [85]
†which is comparable with absorption of pentarylene diimides



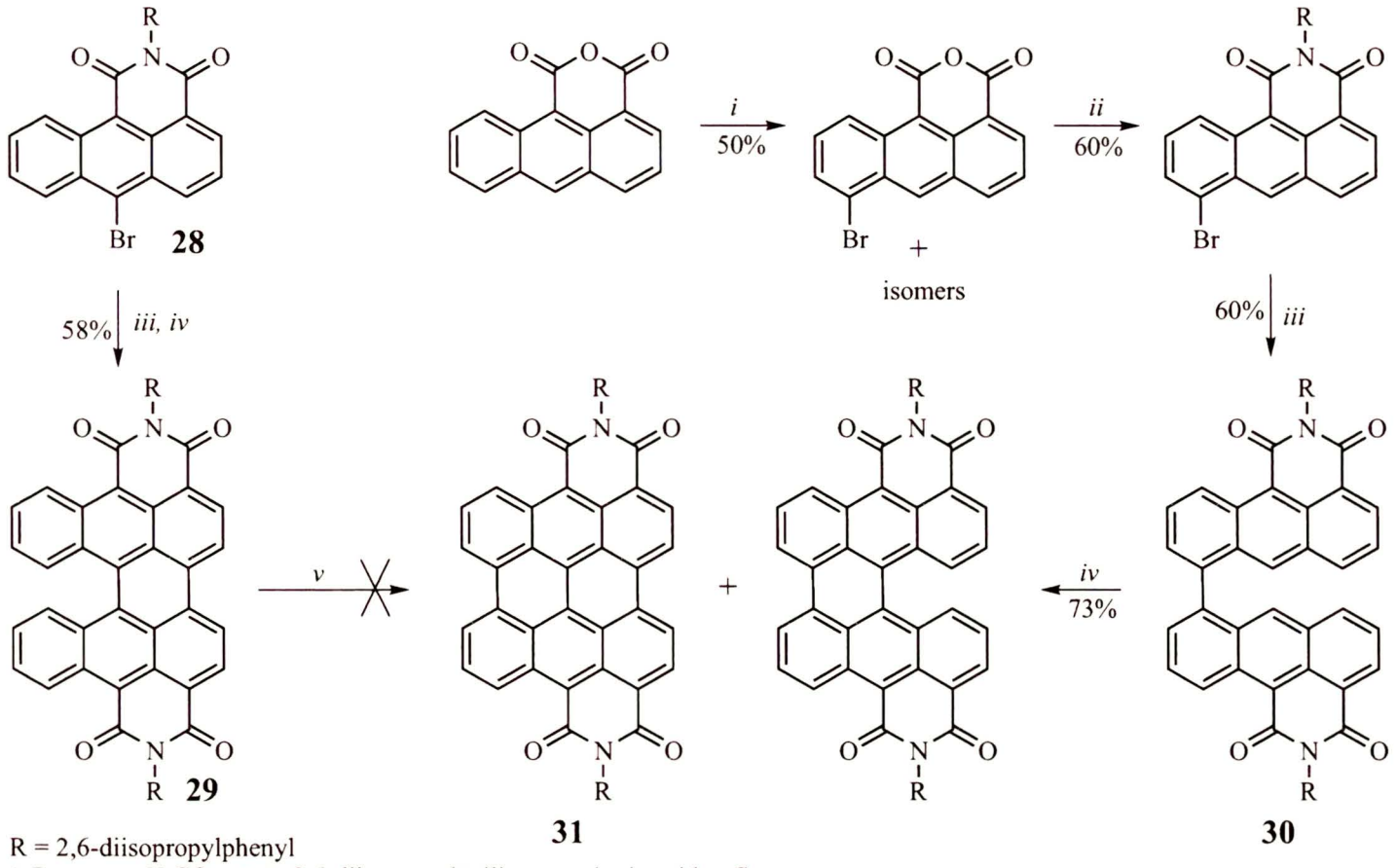
Scheme 2.46

reaction conditions (4 day reflux in toluene or ethanol), I can assume tentatively that bromine atom can be easily substituted by aliphatic amine. Subsequent oxidation with DDQ afforded desired tetracenedicarboximides.

Continuing previous work on Diels-Alder trapping of *o*-xylylenols,[81] Ilhan and co-workers expanded the utility of this approach toward angle and Z-shaped diimides[88] (Scheme 2.49). Angle-shaped diimides show absorption maxima at 380 and 410 mn and are fluorescent. The molecules are highly sterically congested (especially benzo[*e*]pyrene diimide) and relationship between structure distortion and Stokes shifts is analyzed.

Yin et al.[89] recently reported the synthesis of triphenylene and trinaphthylene carboximides – π-expanded analogues of mellitic triimides (Scheme 2.50).

Absorption maxima were detected at 282 and 338 nm (emission: 418 and 455 nm) for **32** and **33** respectively. Reduction potentials showed possibility for



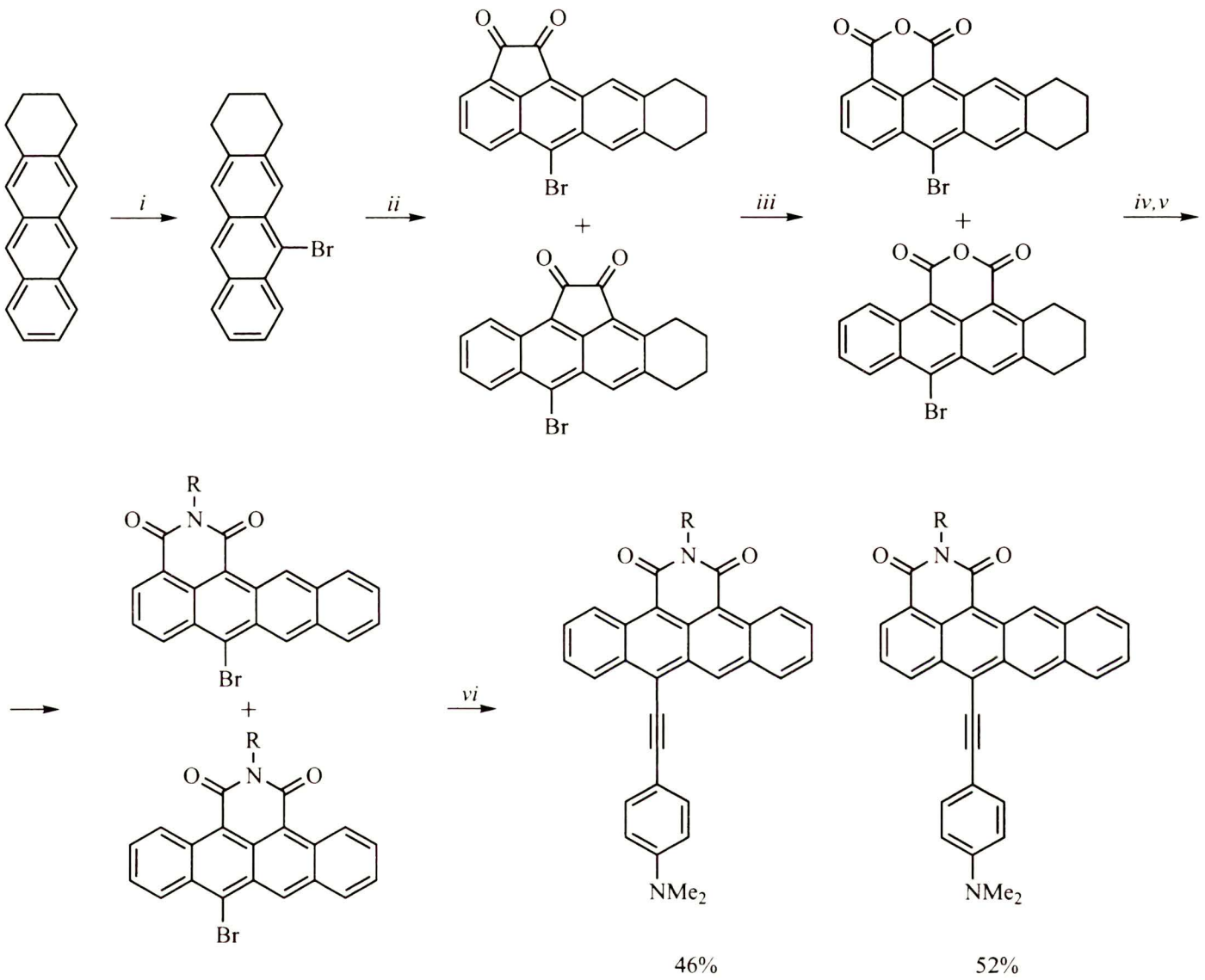
R = 2,6-diisopropylphenyl
i. Br_2, conc. H_2SO_4, rt; *ii*. 2,6-diisopropylaniline, propionic acid, reflux;
iii. Ni-cat, DMF, toluene, 80 °C; *iv*. *t*BuOK, DBN, diglyme, 130 °C; *v*. $FeCl_3$, CH_3NO_2, DCM

Scheme 2.47

the application of prepared materials as n-channel OSC.

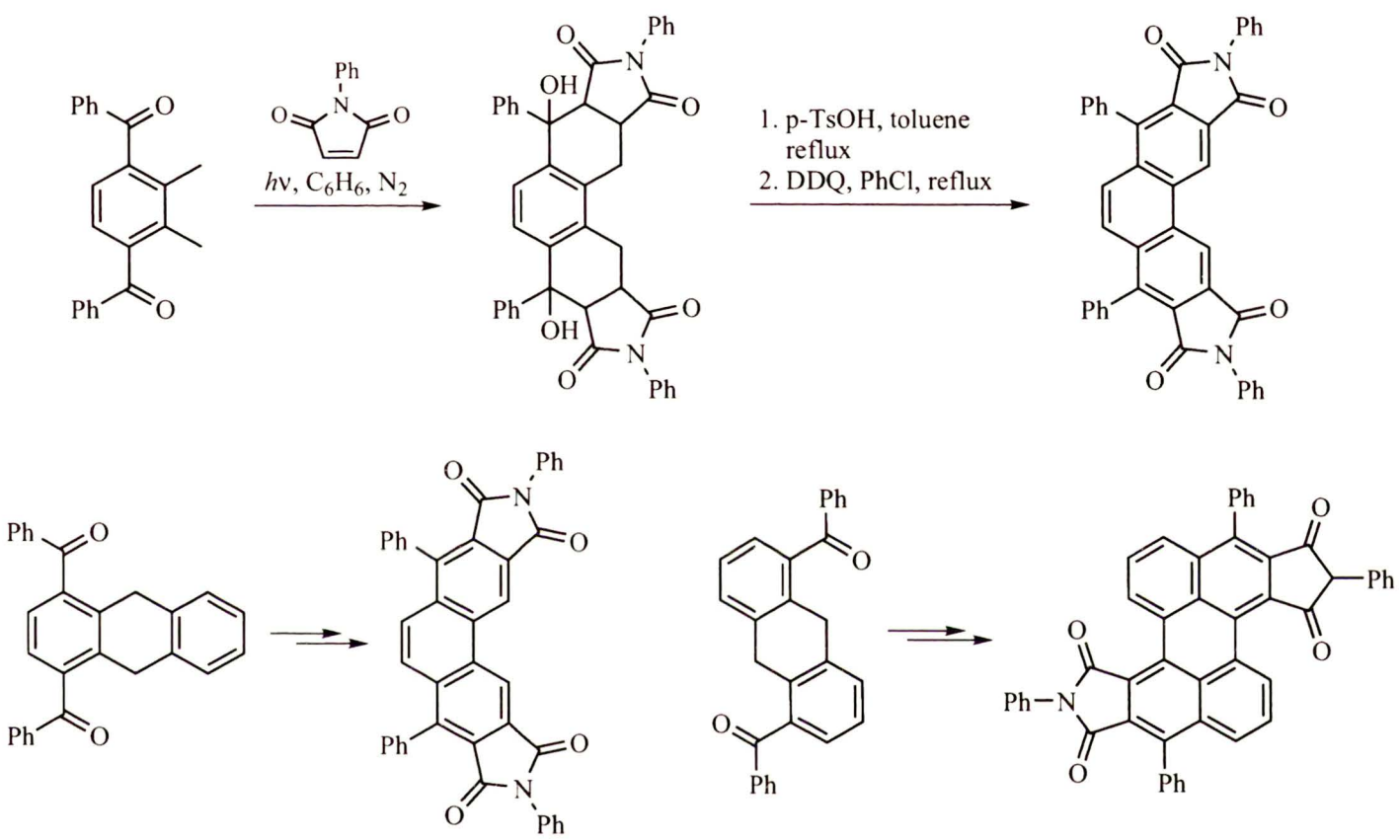
Among somewhat exotic examples of dicarboxylic imides, derivative of corannulene can be mentioned.[90] Bowl-shaped corannulene core represents the bonds network similar with buckminsterfullerene.

As a result of multistep yet simple transformations (Scheme 2.51), using a "wet chemistry" protocols and cheap nickel catalyst, authors were able to obtain dimethyl 1,2-corannulene dicarboxylate in ca. 50% yield. The methoxycarbonyl group exhibit normal chemical behavior and can be converted to diacid and related derivatives. This compound has a potential as a blue emitter (OLED) and can form intermolecular CT complexes.

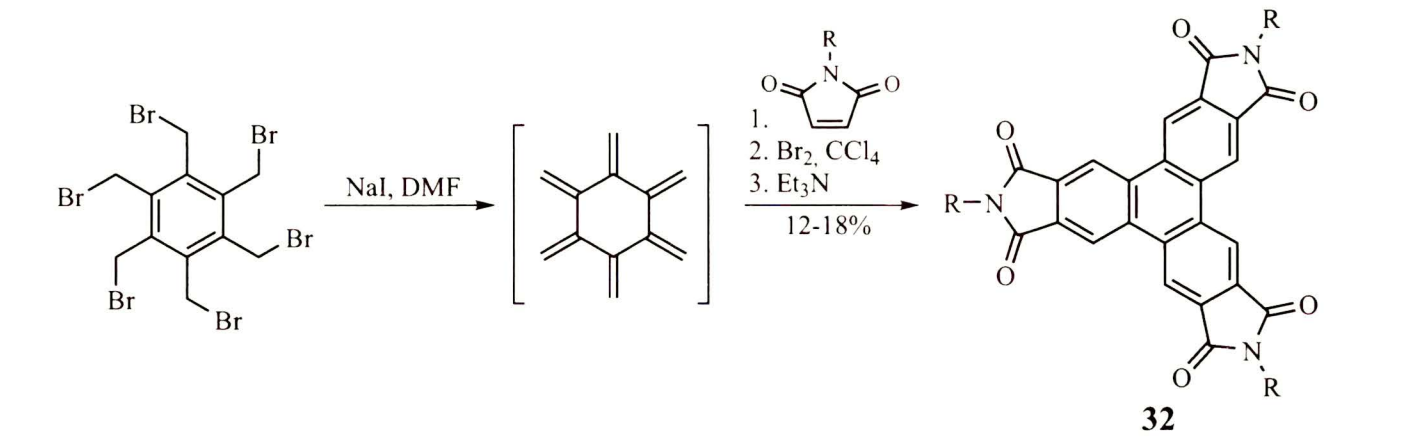


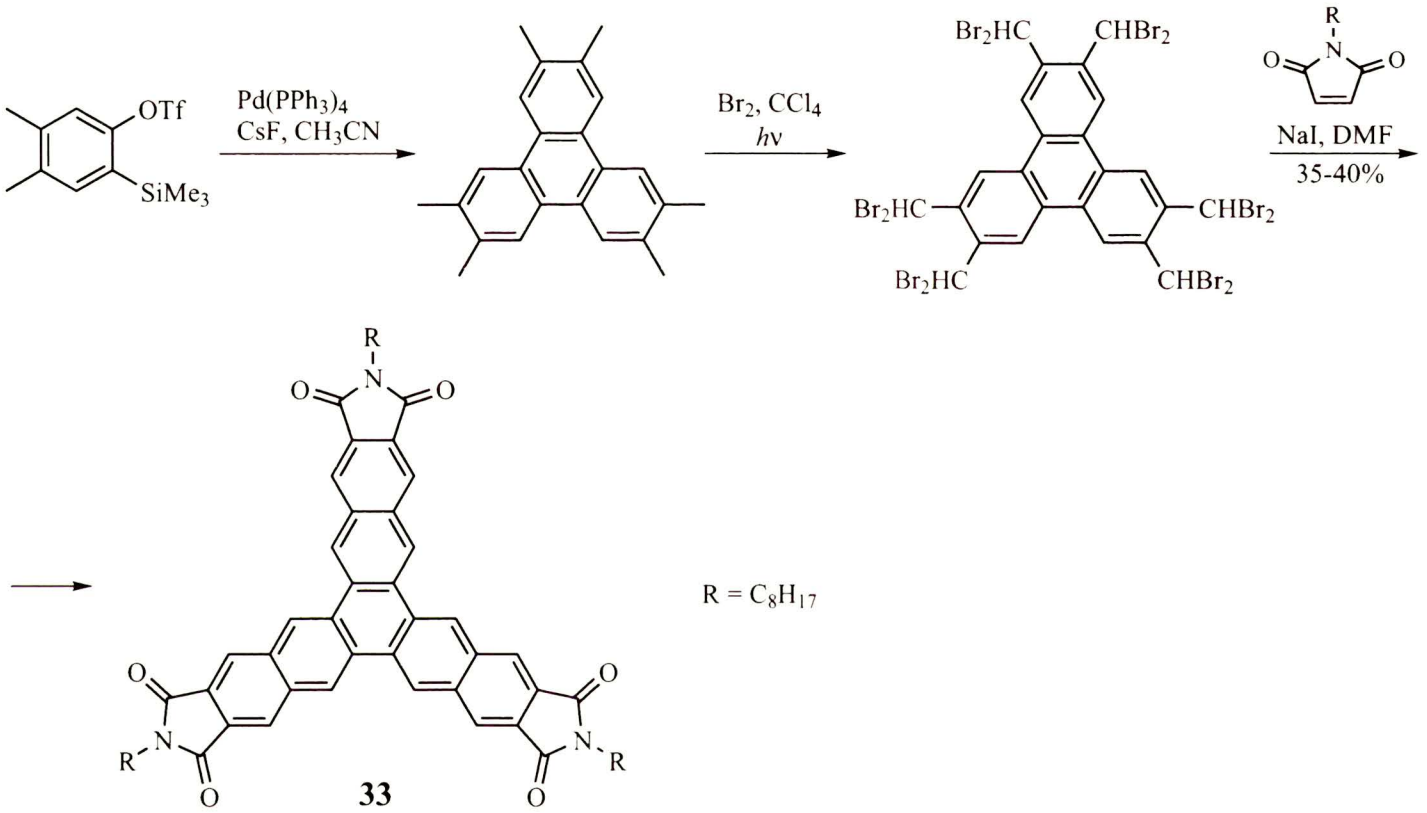
R = $C_{24}H_{49}$
i. $CuBr_2$, CCl_4, 86%; *ii*. oxalyl chloride, $AlCl_3$, CS_2, 76%; *iii*. H_2O_2, dioxane, 90%;
iv. RNH_2, toluene/EtOH, reflux, 4 d, 7-8%; *v*. DDQ, toluene, reflux, 8 d, 37-40%;
vi. 4-dimethylaminophenylacetylene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N, THF.

Scheme 2.48

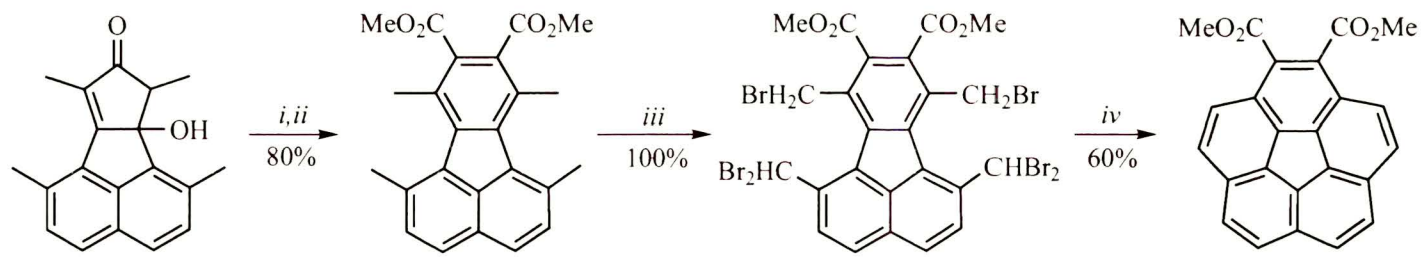


Scheme 2.49





Scheme 2.50



i. Ac_2O, 1 drop of H_2SO_4, rt, 1h; *ii*. dimethyl acetylene dicarboxylate, reflux, 2 h;
iii. NBS, benzoyl peroxide, CCl_4, *h*ν, reflux, 2 h; *iv*. DMF, nickel powder, 70-80 °C, overnight

Scheme 2.51

2.5 Summary

The clearly observed renaissance in the chemistry of aromatic imides is driven by the search of new functional dyes and materials for electronic applications. An exceptional stability and almost unlimited possibilities of structural modifications played the important role for choosing this this particular family of aromatic compounds as a fundamental scaffold for counterpart in corrole-based dyads and triads. Chemists who have chosen this topic also benefit from often unpredictable reactivity of this molecules.[77–79]

3 Results and discussion

3.1 Introduction

Many approaches to artificial photosynthesis are being pursued. Although artificial antenna arrays based on self-assembly are under study, the majority employ covalent bonds to link chromophores and ensure the necessary spatial proximity. In principle there are few points worth consideration while planning the synthesis of complex compounds containing corrole fragment. At least two general strategies exist from the viewpoint of synthetic efficiency. The first one starts with the synthesis of corrole, followed by modifications of peripheral substituents. The second strategy starts with the preparation of an elaborated aldehyde which would then be used in the corrole forming reaction. Given the moderate stability of corroles, it is highly desirable to refrain from the corrole manipulations. On the other hand, it was proved experimentally, that certain limitations in a complex corrole synthesis can be reached: when both aldehyde and dipyrrane have large molecular mass and/or are hydrophobic and poorly soluble, they can not be directly reacted to form *trans*-A_2B-corrole.[6]

3.2 Corrole-imide dyads

In spite of recent progress in the construction of myriads of new aromatic imides (Chapter 2) only a few standard ones were utilized in the construction of dyads and triads for electron- and energy-transfer studies. The choice of imide units was based on various parameters. This short list embraces pyromellitic bisimides, naphthalene bisimides and naphthalene-1,8-imides as well as the most popular perylene diimides. Very recently, also bay-substituted perylene bisimides were utilized in

this regard. I wondered if replacement of these intensively explored imides with new derivatives can change the optical and photophysical properties of dyads. The design was governed by a few principles: prospective optical properties, novelty, the presence of electron-withdrawing groups (crucial for good electron-acceptors) and synthetic accessibility. For previously unknown systems it was rather impossible to predict electrochemical and spectroelectrochemical parameters. For these reasons the study was oriented rather towards preparation of the small library of dyads rather than focusing on one specific example.

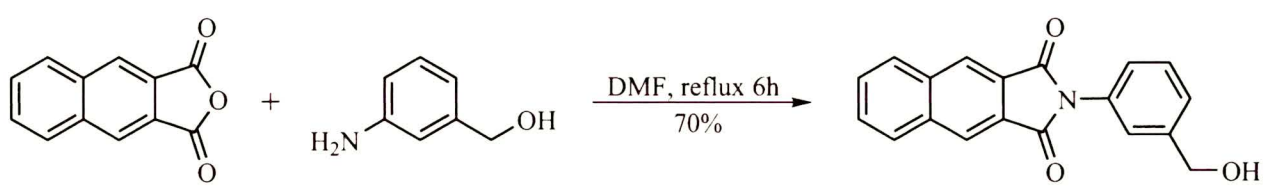
I designed a few relatively novel aromatic imides, derivatives of benzene and naphthalene, possessing additional functional groups and/or expanded chromophores. I was interested in the study of relationship between structure of dyads containing corrole and these imides, and their electrochemical and optical properties.

Having said above, my general strategy was as follows: the synthesis of imide-derived aldehyde followed by final condensation with dipyrrane. In all cases 5-(pentafluorophenyl)dipyrrane was chosen, since previous studies showed that electron-withdrawing substituents are necessary to secure reasonable stability of final corrole.[7,91]

The shortest strategy would be to use aminoaldehydes and perform their direct condensation with corresponding anhydrides. Such compounds, however, are generally unstable and even traces of acids provoke their polymerization.[92] Therefore some kind of protection of an aldehyde functionality has to be used. The decision was made to investigate two approaches: protection of aldehyde in the form of acetal and the use of aminobenzyl alcohols as one oxidation level lower precursors for corresponding aldehydes. The latter option is justified by the fact that such alcohols are readily oxidized to corresponding aldehydes by variety of methods.[93]

Taking into consideration the above comment about the synthesis of imide-derived aldehydes, I decided to start with 3-aminobenzyl alcohol because of its availability and straightforward transformation to the corresponding aldehyde. As an anhydride component in the imide formation reaction 1,8- and 2,3-naphthalenedicarboxylic acid anhydrides were chosen as simple yet promising members of aromatic anhydrides family. While 1,8-naphthalenedicarboxylic imides have been

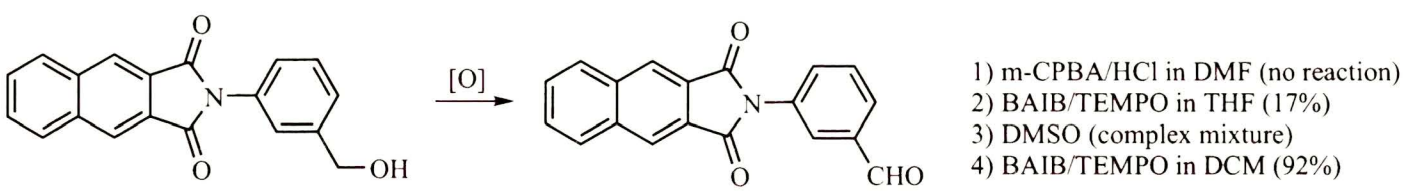
extensively studied, it is not the case for 2,3-substituted analogs. As a first example, 2,3-naphthalenedicarboxylic acid anhydride was reacted with 3-aminobenzyl alcohol in a boiling DMF and, after aqueous workup and flash chromatography purification, desired alcohol **36** was obtained in 70% yield as a readily crystallizing solid (Scheme 3.1).



34 **35** **36**

Scheme 3.1

The solubility of the prepared alcohol **36** in common organic solvents was rather low, presumably due to intermolecular hydrogen bond formation, and this fact can complicate the search for appropriate conditions for oxidation reaction. The brief survey of oxidizing systems was made and in most cases either conversion was incomplete or complex mixtures arose. Performing the oxidation in DMF by *m*-peroxybenzoic acid in the presence of hydrochloric acid [94] did not gave desired product. In the case of THF as a solvent for BAIB/TEMPO oxidizing system, [95] the yield was only 17%, and heating in a DMSO in the presence of air [96] produced side products with unpleasant smell and purification of the main product was troublesome. Surprisingly, oxidation of alcohol **36** with BAIB/TEMPO system in dichloromethane (which is definitely not the best solvent for solubilization of this imide) gave target aldehyde **37** in a yield of 92%, though substrate was never dissolved and the reaction was performed in solid-to-solid regime (Scheme 3.2).

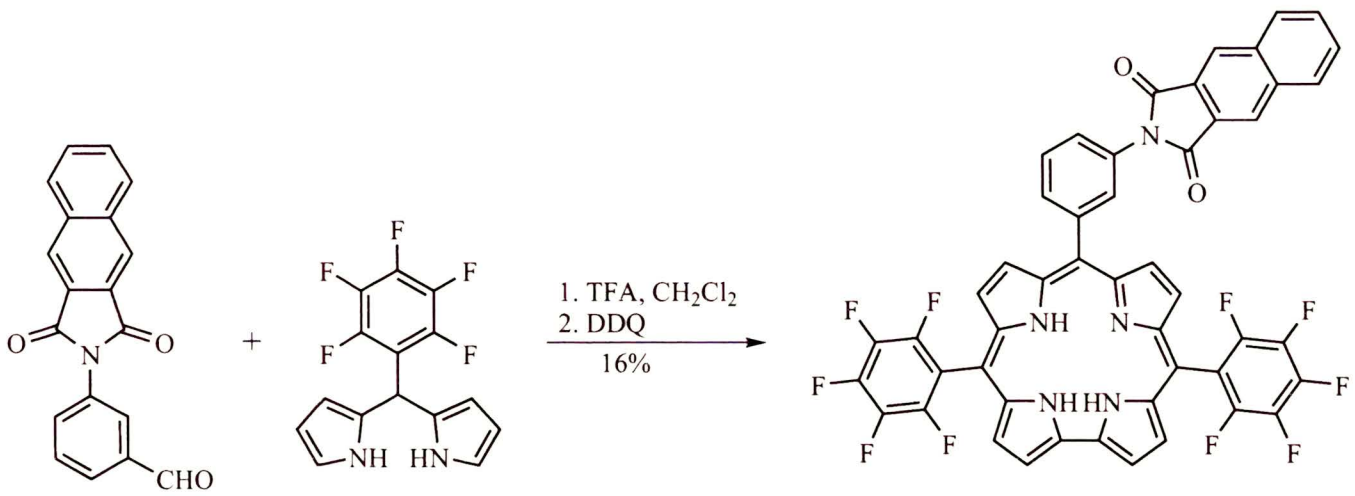


36 **37**

Scheme 3.2

As soon as the identity of aldehyde **37** was confirmed, the corrole synthesis with 5-(pentafluorophenyl)dipyrrane (**38**) in the presence of TFA was performed

(Scheme 3.3). I have chosen the reaction conditions optimized for corroles bearing



37 **38** **39**

Scheme 3.3

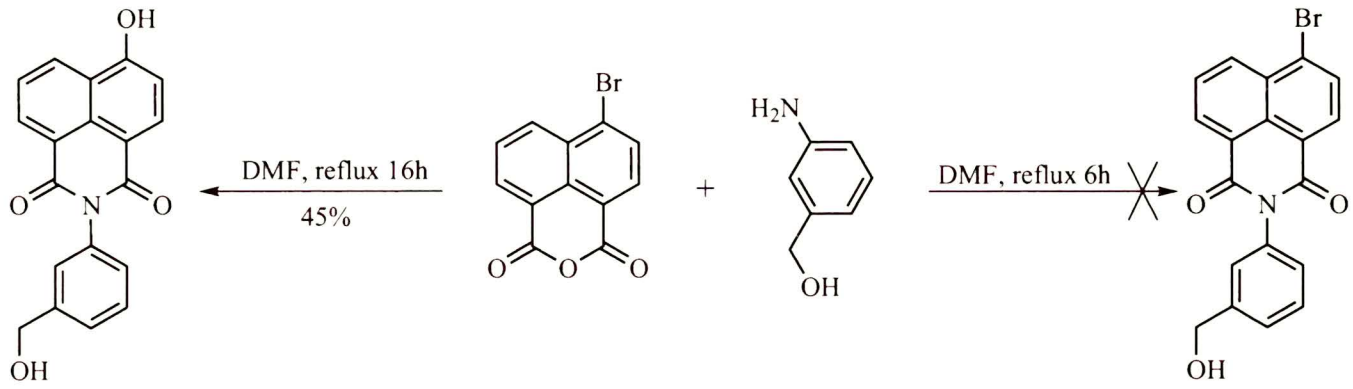
electron-withdrawing substituents,[91] which were elaborated in our group. The reaction was performed in dichloromethane as a solvent with TFA concentration of *ca.* 13 mM. After bilane* formation the oxidation step was performed with DDQ. Usually DDQ and *p*-chloranil are used as oxidants and are almost interchangeable. Bilanes bearing two pentafluorophenyl groups can however be oxidized to the corresponding corroles only with DDQ.[97] Following this procedure[91] one can prepare corroles with the yield up to *ca.* 20%, and in my case corrole **39** was obtained with 16% yield.

In order to investigate utilization of 1,8-naphthalenedicarboximide-based aldehydes in a corrole synthesis I made the plan to synthesize corresponding derivatives from commercially available anhydrides using similar protocol as in the case of 2,3-naphthalenedicarboximides.

There are several dyads comprised of corroles and unsubstituted 1,8-naphthalenedicarboximides synthesized and photochemically characterized.[98] My goal was to significantly alter the structure (hence properties) mostly *via* π-expansion of imide's chromophore. To achieve this goal it would be advantageous to have substrates with incorporated derivatization site. Bromo-substituted 1,8-naphthalenedicarboximides can be synthesized from commercially available anhydride **40**. Such

*the linear tetrapyrrolic corrole precursor

compounds are suitable for chromophore expansion by means of Sonogashira reaction. Unfortunately, the reaction of 4-bromo-1,8-naphthalenedicarboxylic anhydride (**40**) with aminoalcohol **35** in refluxing DMF did not gave bromo-substituted product (Scheme 3.4).



42 **40** **35**

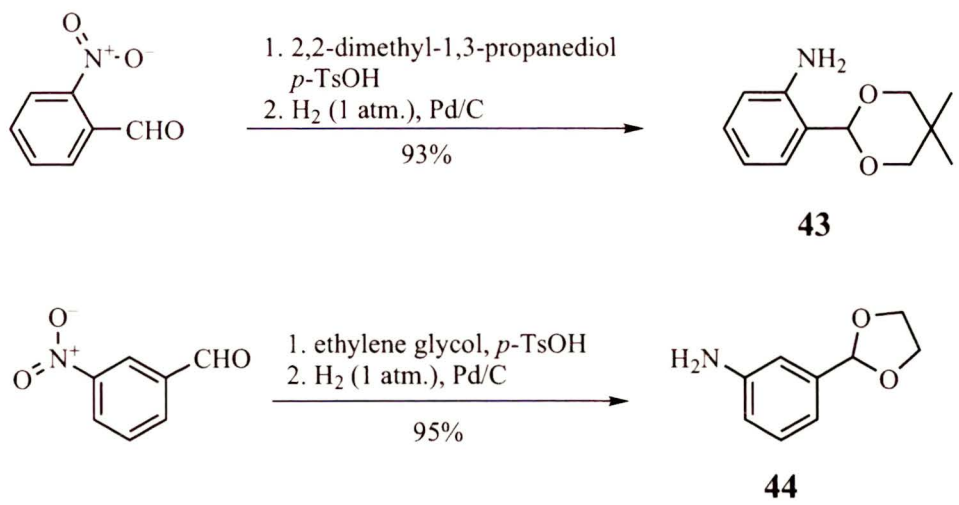
Scheme 3.4

The substrate was not fully consumed during usual reaction time and after prolonged heating with excess of aminoalcohol instead of expected reaction, along with imide formation, nucleophilic aromatic substitution of bromine with hydroxyl group was observed. The hydroxy-substituted imide **42** was isolated with 45% yield as a crystalline solid. Imide **42** turned out to be very poorly soluble in typical organic solvents and further experiments using this substance were not conducted.

It was interesting for me, how spatial arrangement (especially strained face-to-face orientation) of dyad counterparts will influence its optical properties. That is why I decided to synthesize suitable formyl-imides starting from 2-nitrobenzaldehyde.

Since the method based on aminoalcohols appeared to be not versatile enough, I decided to study in detail an another approach towards "imidoaldehydes" synthesis. As it was already mentioned on page 57, another option to overcome aminobenzaldehyde selfcondensation is to use acetal-protected analogs. On the scheme 3.5 the synthesis of two protected regioisomers of aminobenzaldehyde (**43** and **44**) using known procedures[99,100] is presented. Commercially available nitrobenzaldehydes were quantitatively transformed into corresponding cyclic acetals (with dioxane and oxolane rings) under acidic catalysis and water removing

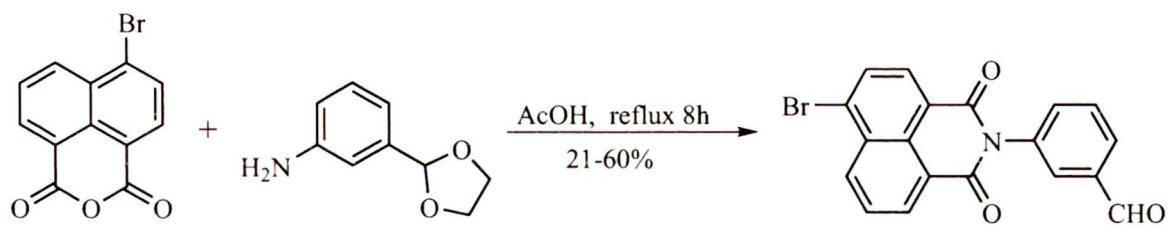
conditions, while subsequent nitro group reduction by hydrogen in presence of palladium on activated carbon furnished acetals **43** and **44** with excellent yield.



43 **44**

Scheme 3.5

In order to synthesize imide **45**, anhydride **40** was reacted with acetal **44** in boiling acetic acid giving expected product. Acetic acid has been chosen as a solvent since in non-acidic solvent nucleophilic aromatic substitution can take place (Br $\longrightarrow$ NH$-$R) leading to the formation of side products.[101] However, this procedure was not reproducible and gave moderate yields ranging from 21 to 60% (Scheme 3.6).

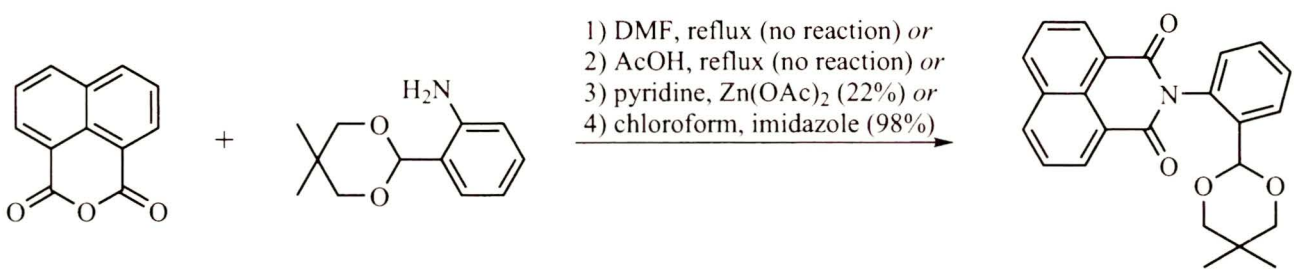


40 **44** **45**

Scheme 3.6

It can be easily noticed, that along with condensation reaction aldehyde deprotection took place. It is rather difficult to judge if deprotection occurs before or after imide formation but, given capricious yields, there is a serious probability of starting acetal cleavage which can interfere with normal reaction course. Leastwise, prepared aldehyde **45** could be used in further transformations without separate deprotection step.

Reaction of unsubstituted 1,8-naphthalenedicarboxylic anhydride (**46**) with sterically hindered acetal **43** failed both in refluxing DMF and glacial acetic acid and gave only 22% of expected product when pyridine was used as a solvent and zinc acetate as a catalyst (Scheme 3.7).

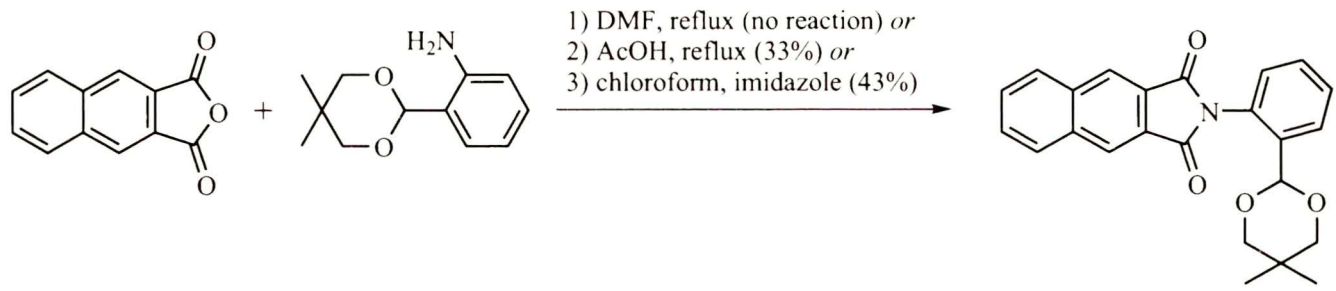


46 **43** **47**

Scheme 3.7

After quite a few attempts with different reaction conditions, fortunately, it was found, that boiling substrates in chloroform with an excess of imidazole [102] allows to obtain desired imide **47** with the yield as high as 98%. Moreover, a sample of satisfactory purity could be obtained without chromatography.

In the case of 2,3-naphthalenedicarboxylic anhydride I was not able to obtain corresponding imide in boiling DMF, however, the reactions in acetic acid and chloroform/imidazole were successful and in both cases gave expected imide **48** with comparable yields (Scheme 3.8).



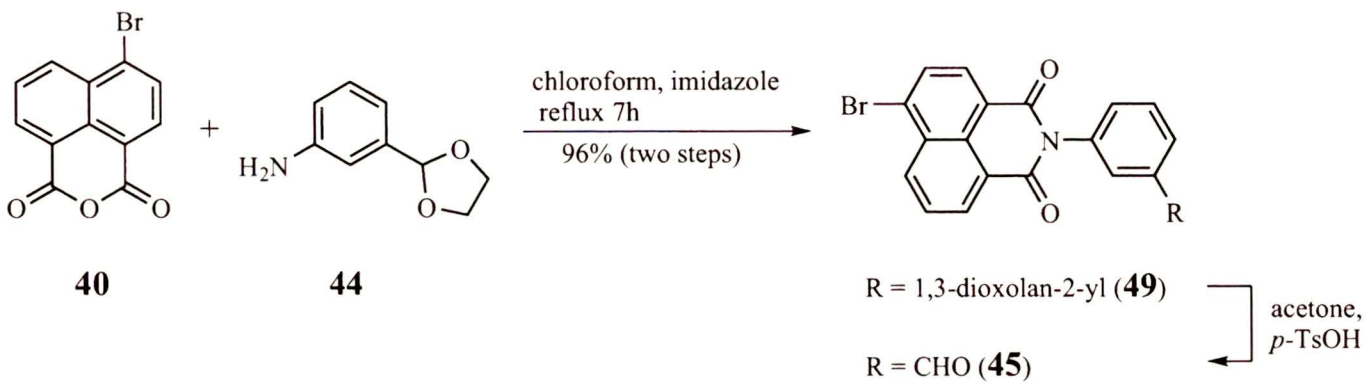
34 **43** **48**

Scheme 3.8

In analogy to reaction shown on scheme 3.6, bromo-substituted anhydride **40** was reacted with acetal **44** in chloroform in the presence of imidazole giving a mixture of products which arose from partial acetal cleavage.* Pure sample

*amount of aldehyde can be estimated as 30–40% from NMR spectrum

of aldehyde **45** was obtained while stirring the mixture with acetone by acetal exchange, catalyzed by *p*-toluenesulfonic acid (Scheme 3.9).

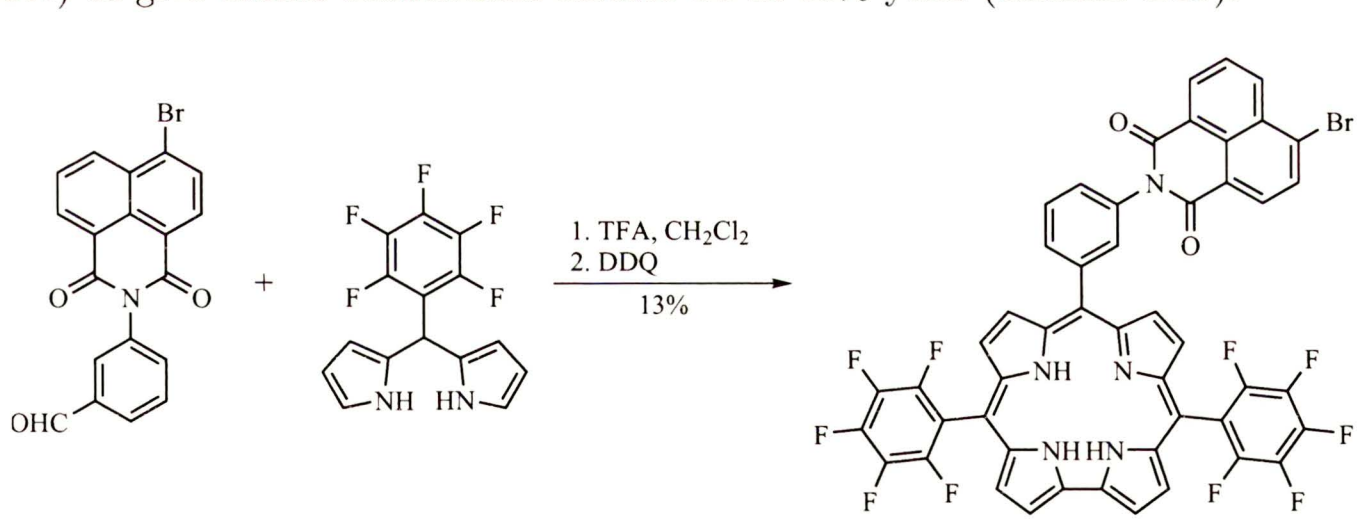


40 **44**

Scheme 3.9

Passing resulting mixture through silica pad was enough to wash out 2,2-dimethyl-1,3-dioxolane and collect product **45** as a crystalline solid.

Bromo-substituted imide **45** possessing free aldehyde group was subjected to corrole-forming reaction under established conditions. Thus, aldehyde **45** was reacted with two equivalents of dipyrrane **38** in the presence of acidic catalyst (TFA) to give bromo-substituted corrole **50** in 13% yield (Scheme 3.10).



45 **38** **50**

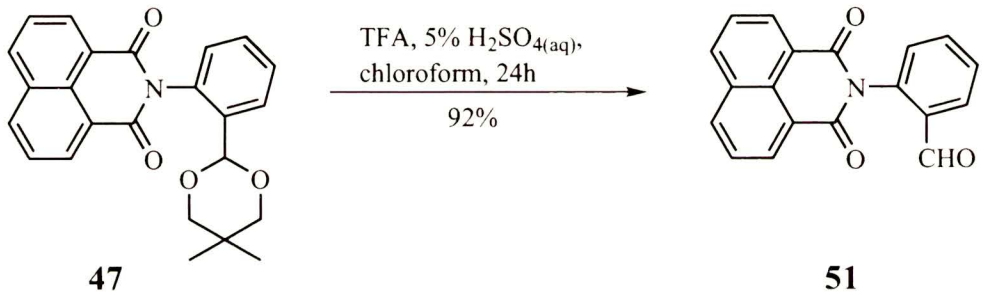
Scheme 3.10

Surprisingly, corrole **50** showed characteristic red fluorescence under UV light (long-wave ultraviolet) despite of heavy atom presence. Usually, introduction of atoms with high atomic number into the molecule of aromatic hydrocarbon creates a dramatic increase in the rates of "spin forbidden" transitions. Consequently, one should expect strong fluorescence quenching. The fact that corrole fluorescence is

retained can be explained by considering corrole and imide parts as separate chromophores without significant electronic coupling between them: corrole's excited state remains unaffected, though imide part experiences non-radiation relaxation.

In contrast to the situation depicted on scheme 3.9 on the previous page, dioxane acetals **47** and **48** were stable enough to survive reaction conditions and were isolated as a sole products. This is because of higher steric hindrance and overall greater durability of six-membered cyclic acetals. Consequently, additional deprotection step was inevitable.

Usually, *p*-toluenesulfonic acid is not strong enough for cleavage of 5,5-dimethyl-1,3-dioxane and stronger acid should be used. Taking this fact into consideration, dioxane acetals were cleaved to corresponding aldehydes **51** and **52** by stirring in TFA/$H_2SO_{4(aq)}$/chloroform mixture[103] (Scheme 3.11).



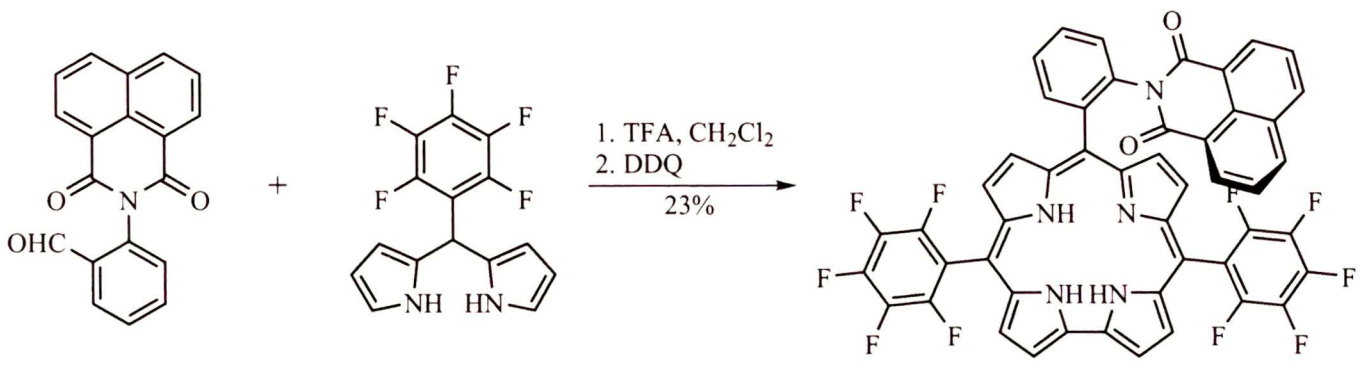
47 **51**

48 **52**

Scheme 3.11

Moving now to corrole synthesis, one should consider eventual methodological challenge concerning steric hindrance of used aldehydes. There are no reports in the literature, describing so bulky substituent (which is to be connected with corrole core through *o*-phenylene linker) incorporated in the molecule directly from corresponding aldehyde by the corrole forming reaction.

I have chosen previously described conditions (see page 59) as a point to start with and, thereby, aldehyde **51** was subjected to reaction with 5-(pentafluorophenyl)dipyrrane (**38**) according to scheme 3.12.



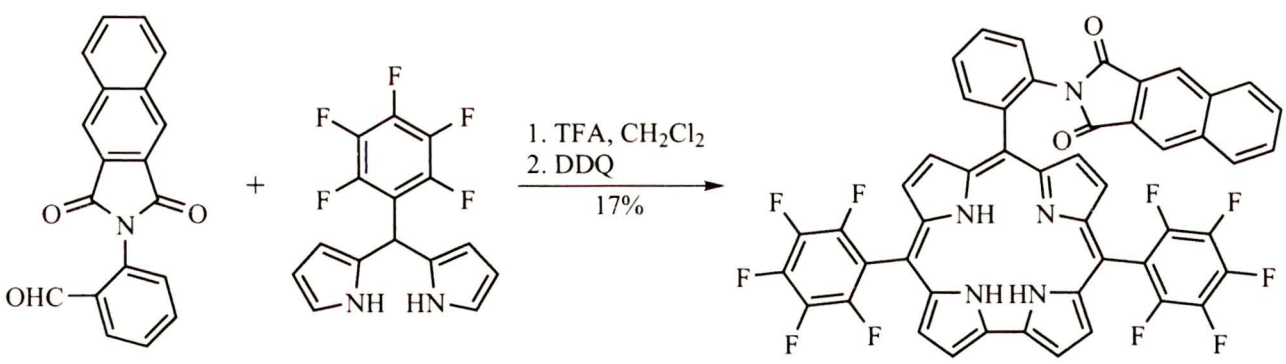
51 **38** **53**

Scheme 3.12

I was pleased to find out that after 20 min of reaction starting aldehyde was consumed almost entirely and after oxidizing step and purification, expected corrole **53** was obtained in 23% yield, which is more than average value for corroles of such type.

In a similar manner, aldehyde **52** derived from 2,3-naphthalenedicarboximide was reacted with dipyrrane **38** affording corrole **54** with somewhat lower yield (Scheme 3.13).

Both corroles with *o*-phenylene linker showed excellent solubility thanks to the spatial orientation of the imide substituent relative the plane of corrole which suppresses π-stacking.



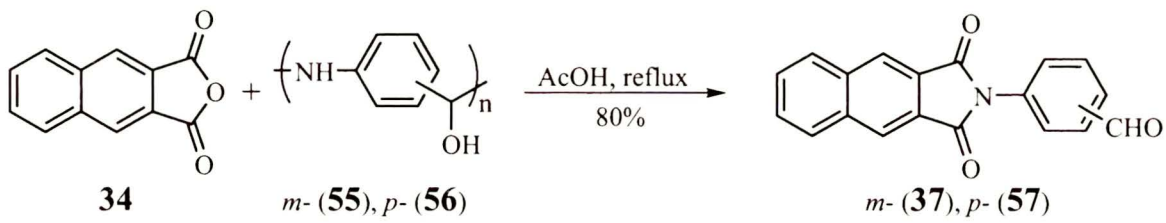
52 **38** **54**

Scheme 3.13

Although, acetal-protected aminoaldehyde approach was shown to be successful, it still involves two more steps (protection and deprotection of aldehyde functionality). As a result of previous study in our group,[7] it was shown that polymer of 3-aminobenzaldehyde, formation of which all the time was so carefully avoided,

under certain conditions can act as a source of monomeric aminobenzaldehyde. Since polymers of both 4- and 3-aminobenzaldehyde were commercially available, I decided to study briefly the scope of this method.

It was shown by Tasior et al.[98] that 4-aminobenzaldehyde polymer is inactive towards anhydride of 1,8-naphthalenedicarboxylic acid, but its *meta-* analog reacts readily, forming desired imidoaldehyde in one step. In my case, anhydride of 2,3-naphthalenedicarboxylic acid appeared to be more reactive inasmuch as with both polymers (**55**, **56**) affording desired aldehydes **37** and **57** with good yields (Scheme 3.14).



34 *m-* (**55**), *p-* (**56**) *m-* (**37**), *p-* (**57**)

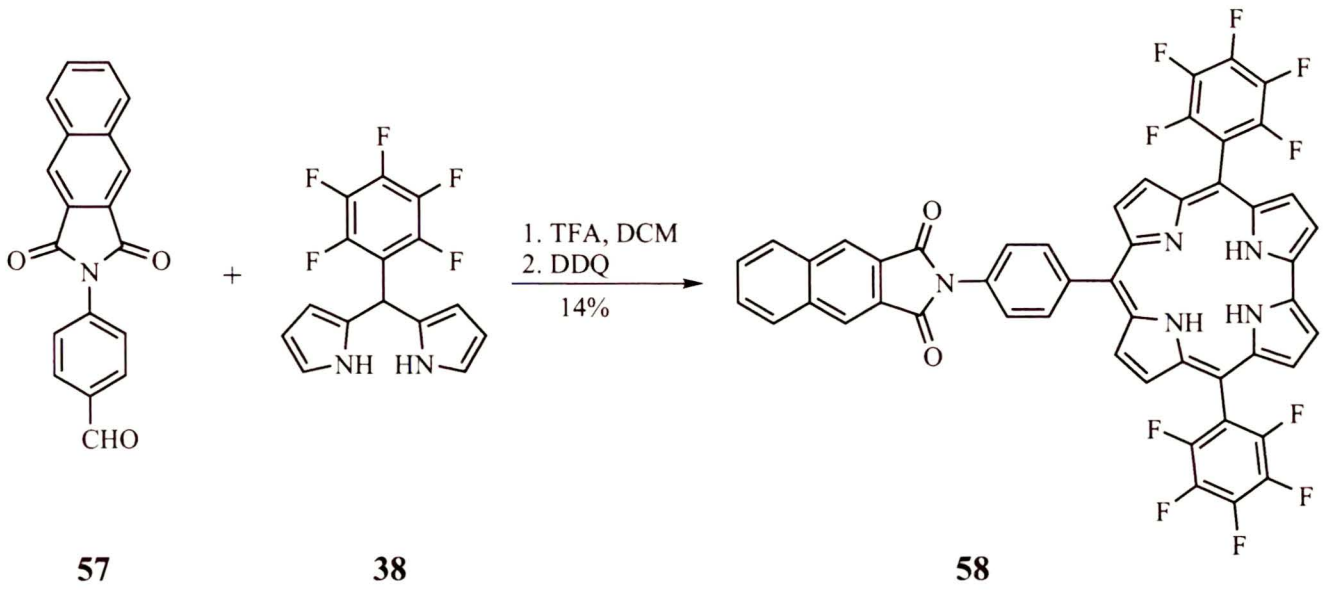
Scheme 3.14

This success can be explained "post-factum" based on the reactivity of carboxylic anhydrides **34** and **46**. The presence of two carbonyl groups attached to one benzene ring makes anhydride **34** more reactive (toward addition to carbonyl group) than anhydride **46**.

The reaction is carried out in boiling acetic acid (appropriate medium for slow hydrolysis of aminobenzaldehyde polymer) and reactive species – free aminobenzaldehyde – are dosed into reaction mixture maintaining more or less constant, and at the same time, low concentration. This can be beneficial in the case of substrates, where competitive reactions of nucleophilic aromatic substitution can take place.

Though the synthesis of aldehyde **57** appeared in the literature in 2011,[104] the transformation involves three steps and overall reported yield is 10% lower than in my case.

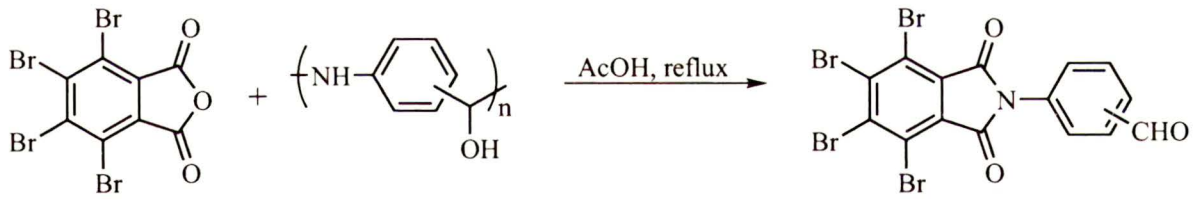
When aldehyde **57** was reacted with dipyrrane **38** under standard conditions corrole **58** was formed in moderate yield (Scheme 3.15). Slightly decreased yield, comparing to other regioisomers, can probably be caused by lower solubility and bigger losses of corrole during purification.



57 **38** **58**

Scheme 3.15

To investigate further the scope of polymer-based method, "imidoaldehydes" starting from tetrabromophthalic anhydride (**59**) were synthesized (Scheme 3.16). It is actually the case, when low nucleophilicity of amine becomes important. Such amides can be interesting substrates for further transformations by means of, for example, Sonogashira reaction, which in turn would allow to expand π-conjugation of imides, changing their electronical properties significantly. Though, tetrabromo-

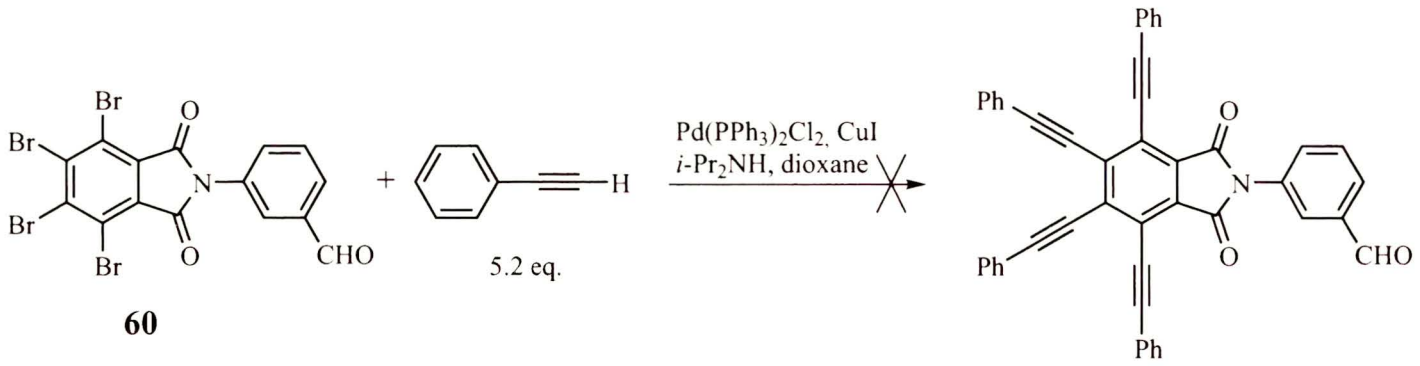


59 *m*- (**55**), *p*- (**56**) *m*- (**60**), 94%
p- (**61**), 56%

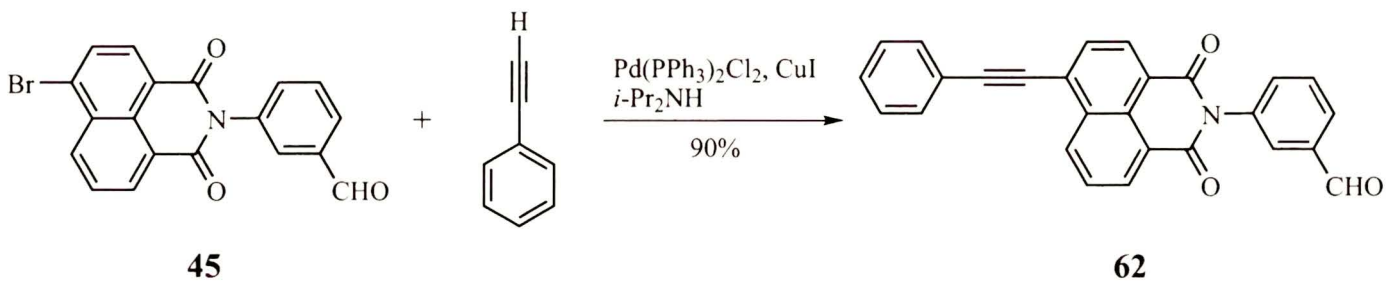
Scheme 3.16

substituted aldehyde **60** was submitted to modern Sonogashira reaction conditions[105] with phenylacetylene (Scheme 3.17), substrate remained unchanged even after stirring reaction overnight at elevated temperature.

During further investigation, I decided to couple bromo-substituted aldehyde **45** with phenylacetylene under the same conditions (Scheme 3.18) and indeed, after stirring overnight at 25 °C, desired aldehyde was formed with excellent yield.

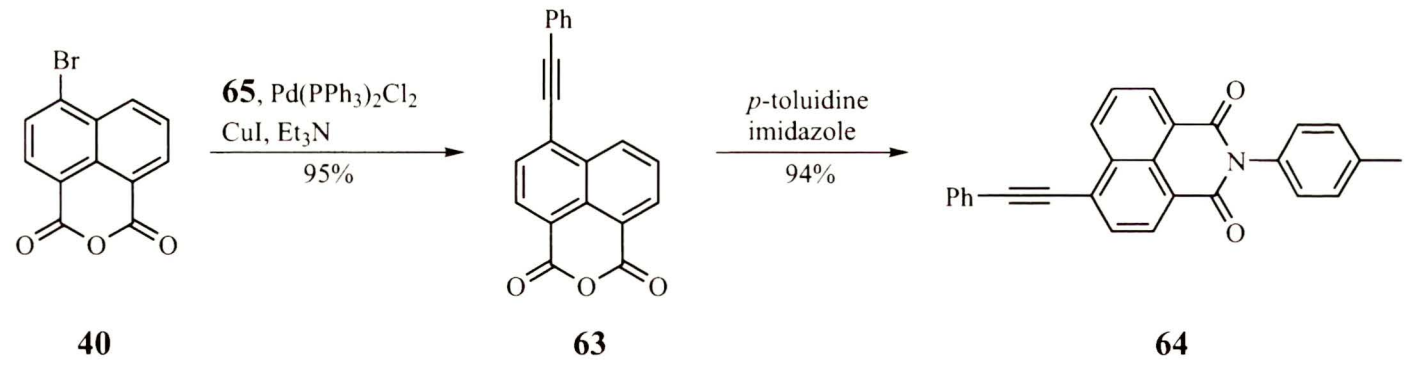


Scheme 3.17



Scheme 3.18

Aldehyde **62**, however, appeared to be photosensitive, and it underwent decomposition both on silica and on alumina. To understand such behavior, model compound **64**, was synthesized in two steps starting from 4-bromo-1,8-naphthalenedicarboxylic anhydride (**40**) (Scheme 3.19).



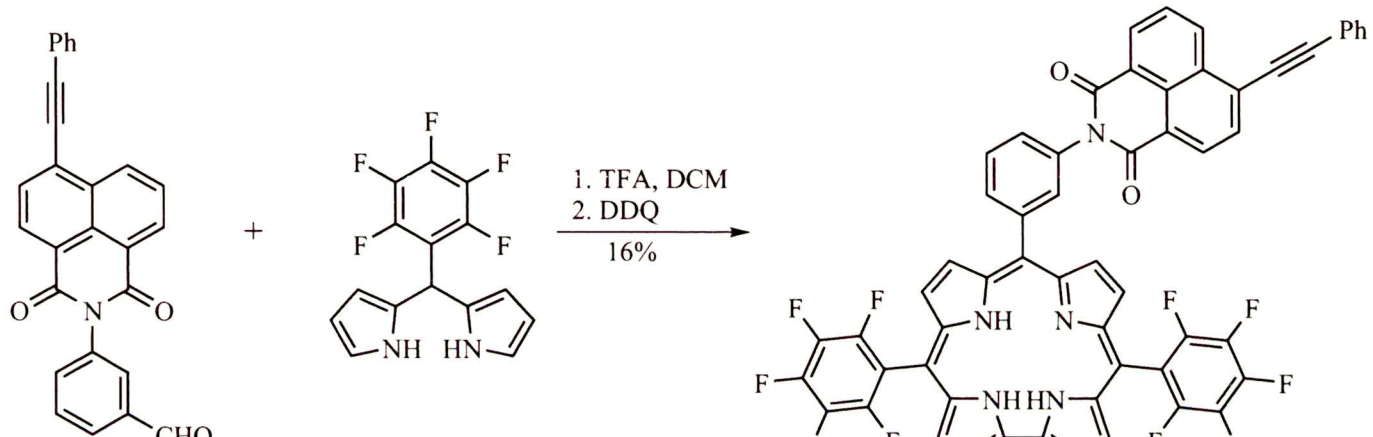
Scheme 3.19

Imide **64** lacking formyl group showed much higher stability. This hard to understand difference can only be explained by favoring triplet excited state formation by the presence of CHO group.

Careful reader will notice, that model compound **64** (Scheme 3.19) was synthesized using slightly different strategy, *i.e.* bromo-anhydride was modified first,

and then imide formation step followed. Such order of steps turned out to be more convenient since for both steps the chromatography was unnecessary.

After numerous attempts to purify aldehyde **62**, I was able to obtain the pure* sample, appropriate for corrole synthesis. It was questionable whether the corrole, synthesized from this modified imide, will be stable enough for isolation and characterization. After condensation of aldehyde **62** with dipyrrane **38** in the presence of TFA, oxidizing with DDQ and simple purification, desired corrole was obtained in 16% yield as a crystalline solid (Scheme 3.20). The stability of corrole **66** does not differ much from that of the corroles synthesized earlier, which serves as further confirmation of special role of CHO group in starting aldehyde.



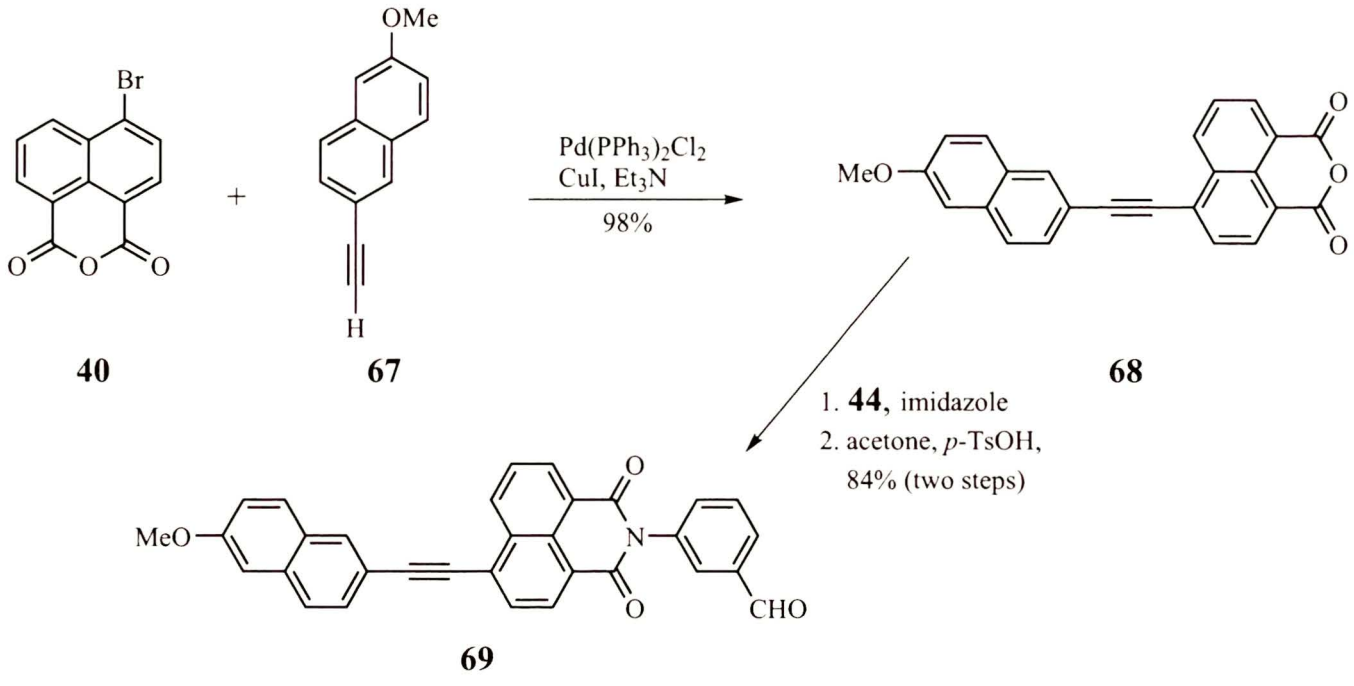
62 **38** **66**

Scheme 3.20

Inasmuch as π-expanded aldehyde showed satisfactory reactivity in corrole-forming reaction, I decided to perform another sequence of transformations in order to obtain aldehyde, bearing two naphthalene units connected by ethynylene linker. Such combination can provide new chromophore with interesting properties.

In the first step 4-bromo-1,8-naphthalenedicarboxylic anhydride (**40**) was coupled with commercially available naphthalene based arylacetylene **67** under Sonogashira reaction conditions[106] (Scheme 3.21). New anhydride **68** readily precipitate from reaction mixture and without further purification it was reacted with 3-aminobenzaldehyde ethylene acetal (**44**) in imidazole/chloroform mixture. The deprotection step was required (acetone/*p*-TsOH) since acetal cleavage under reaction conditions was only partial (*ca.* 40%).

*according to NMR; one signal from CHO group



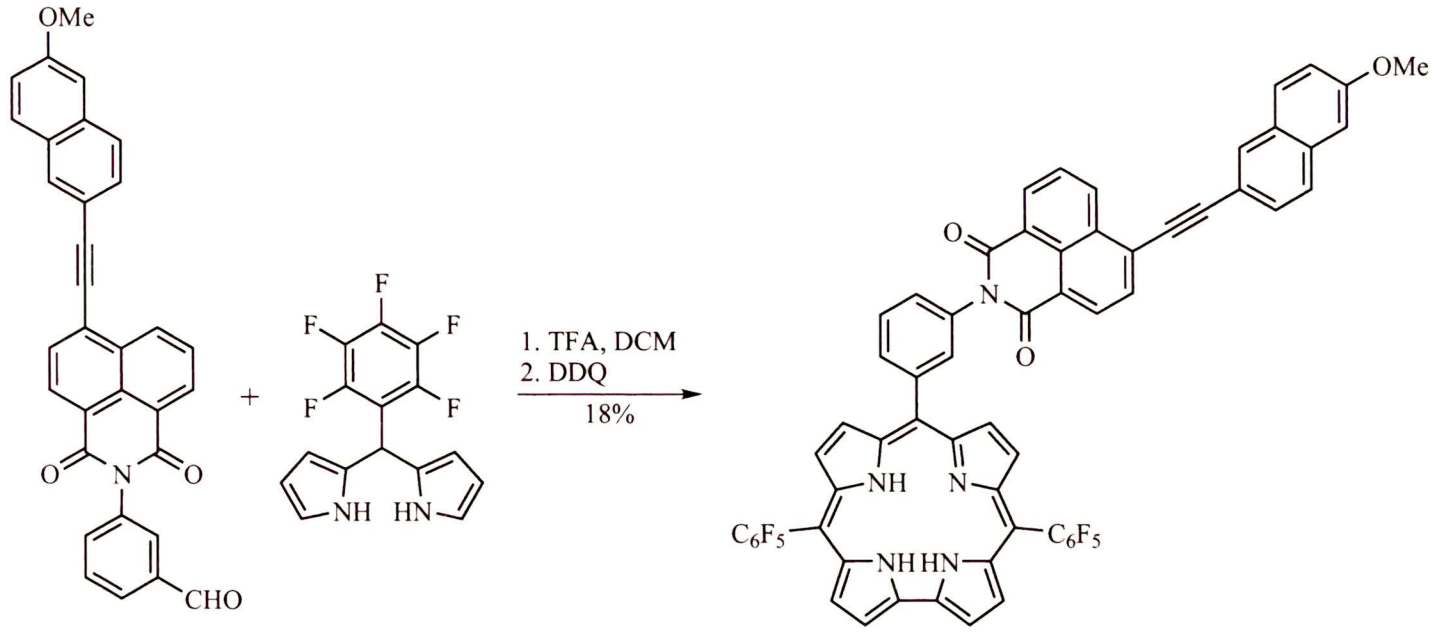
Scheme 3.21

Again, the choice of the order of reactions allowed to prepare aldehyde **69** in satisfactory purity avoiding chromatography.

Similarly to the aldehyde posessing phenylethynyl group **62**, its analog with methoxynaphthalene unit was also photosensitive and it decomposed slowly on silica. Along with photostability issue of aldehyde **69**, problems with its solubility arose during corrole synthesis. I found that under typical conditions (*i.e.* $C_{Ald.} \approx 67\,mM$ and $C_{TFA} \approx 13\,mM$) there were no signs of reaction even after one hour – aldehyde remained unchanged in the form of suspension. Surprisingly, when the flask was left overnight, I found that reaction mixture became clear and aldehyde was entirely consumed. After oxidation step I was able to isolate desired corrole **71** in 18% yield, though purification was troublesome (Scheme 3.22). This result can be explained considering the fact, that sometimes, in the case of aldehydes with low solubility, the bilane synthesis gains characteristics of solubility-driven reaction and slightly elongated reaction times are required.

Reduced solubility of aldehyde **69** can probably be explained by its flat structure and, in addition, head-to-tail orientation of molecules in a crystal due to the attraction of electron rich methoxynaphthalene unit and electron poor imide part. All this characteristics favor the π-stacking and hence decrease solubility.

An alternative approach towards corroles of this type is convergent synthesis



69 **70** **71**

Scheme 3.22

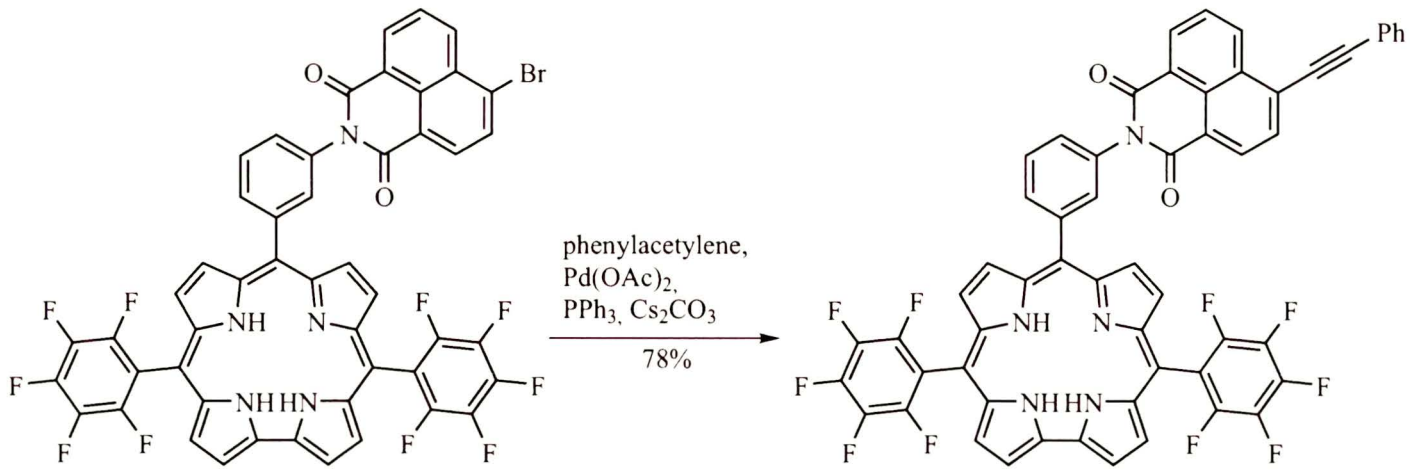
from arylacetylene and bromo-substituted corrole **50** (synthesis on page 63).

Sonogashira reaction is known as well established synthetic tool with great number of variations, but usually, along with palladium catalyst, certain amount of copper salt is involved in a catalytic cycle. Corroles, on the other hand, are known to form strong complexes with copper and drastic conditions are required for free-base corrole recovering.[107] Fortunately, there are copper-less variants of Sonogashira coupling and one of them, proposed by Shirakawa *et al.*,[108] was used to synthesize corrole **66*** with good yield (Scheme 3.23).

In the case of aldehydes **37**, **45**, **51**, **52**, **57**, **62** and **69** usual output of macrocyclization reaction varies from 15 to 20%. In such situation over 80% of starting material is wasted. Considering two routes towards corrole **66**, one can notice that overall yield† in both cases is comparable. But, when expensive or commercially unavailable arylacetylenes are used, it becomes more important to bypass inefficient step of corrole formation. Hereby, overall material loss (calculated for arylacetylene) can be expressed as 85 *vs.* 20% for convergent approach. Moreover, when certain degree of substrates complexity is reached, there is no method to synthesize corroles directly due to the solubility issue. The latter strategy, thereby,

*its synthesis directly from aldehyde is described on page 69

†Two steps, starting from *N*-(3-formylphenyl)-4-bromo-1,8-naphthalenedicarboximide (**45**)

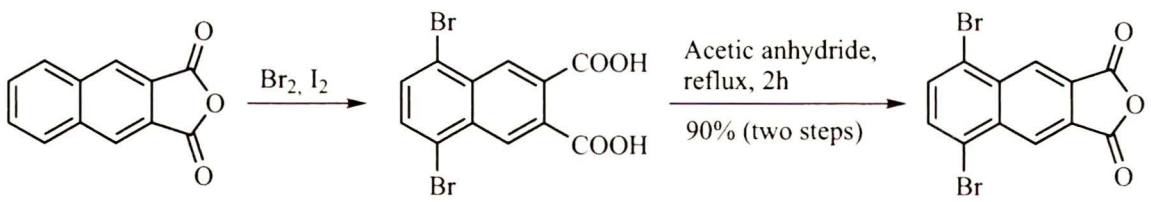


50 **66**

Scheme 3.23

becomes the only way to synthesize elaborated multi-chromophoric corrole-based systems.

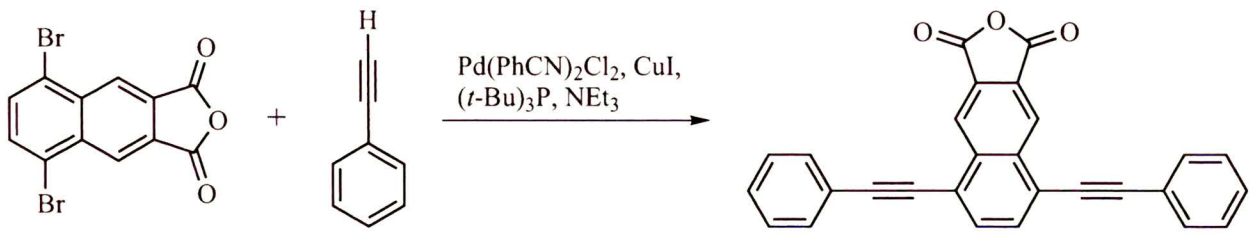
Continuing the motif of halogen-substituted imides, anhydride **73** was synthesized (Scheme 3.24). Naphthalene-2,3-dicarboxylic anhydride (**34**) was brominated in water with iodine addition and as a product 5,8-dibromonaphthalene-2,3-dicarboxylic acid (**72**) was obtained.[109] Afterwards, dibromoanhydride **73** was recovered by refluxing diacid in acetic anhydride. The attempt was made to bromi-



34 **72** **73**

Scheme 3.24

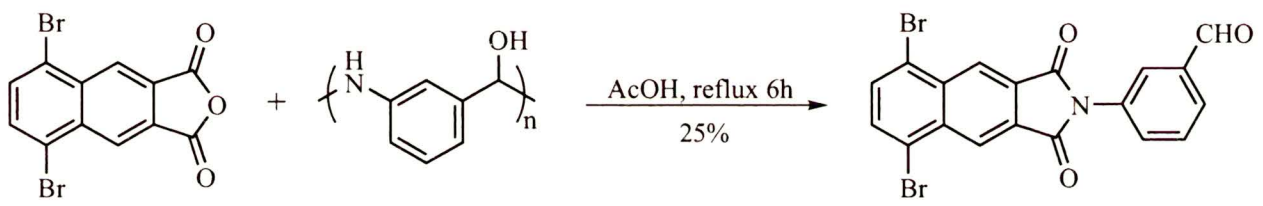
Anhydride **73** has two bromine atoms which give the handle to its diverse derivatization. Consequently, Sonogashira coupling was performed with phenylacetylene (Scheme 3.25). Unfortunately, complex mixture arose and purification was tedious. Therefore, I decided to synthesize imide first and then perform coupling on bromine atoms.



73 **65** **74** (minor product)

Scheme 3.25

The shortest pathway to the desired "imidoaldehyde" was to react dibromoanhydride **73** with polymeric 3-aminobenzaldehyde (**55**) in acetic acid (Scheme 3.26) and indeed, aldehyde **75** was formed, but unfortunately in rather low yield. The reaction was not clean and purification of target compound was complicated by surprisingly low solubility.



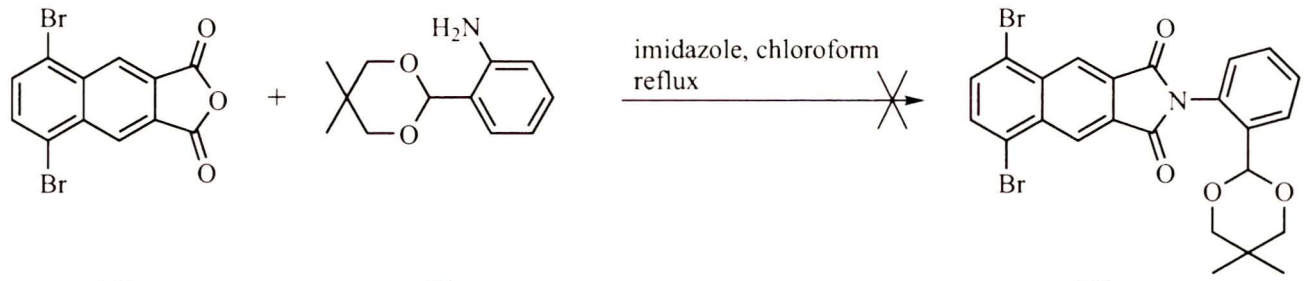
73 **55** **75**

Scheme 3.26

In order to optimize the imide formation reaction, anhydride **73** was allowed to react with protected 2-aminobenzaldehyde **43** in chloroform in the presence of the excess of imidazole (Scheme 3.27). This procedure gave best results for some early mentioned imides and was the only way to prepare imides in some other cases. Unfortunately, it failed for dibromoanhydride **73** and instead of imide **76** the main product, isolated from the reaction mixture, had no bromine atoms at all (determined by MS).

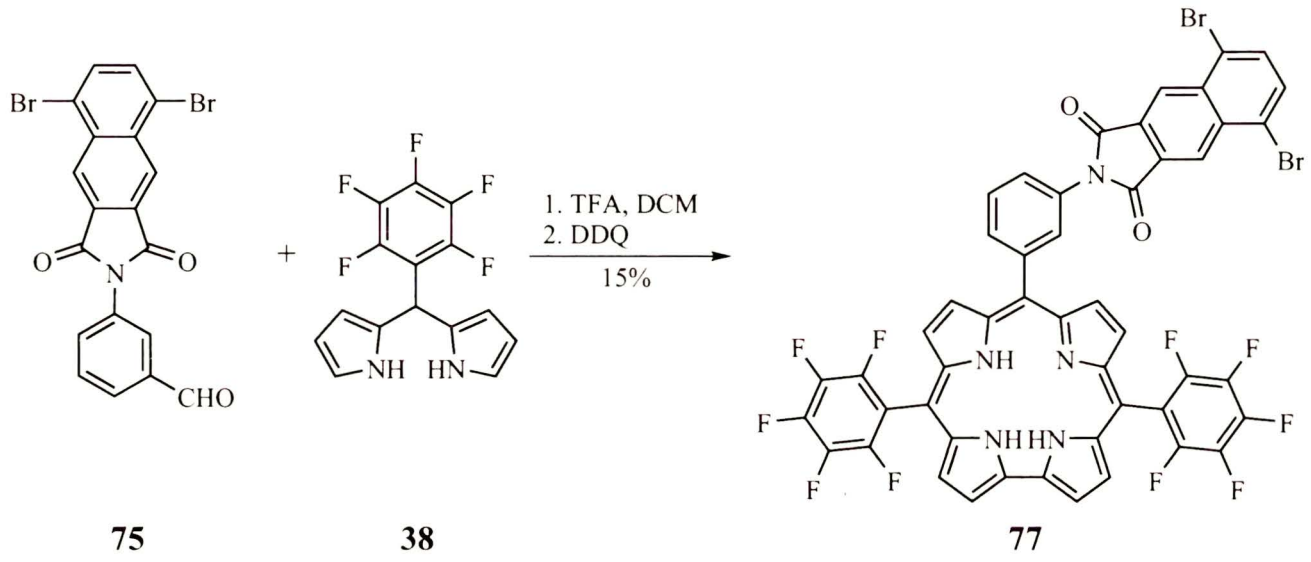
Despite the fact, that only small amount of dibromoaldehyde **75** was obtained from aminobenzaldehyde polymer, it was enough to perform condensation with 5-(pentafluorophenyl)dipyrrane (**38**) under standard conditions, which furnished expected corrole **77** in 15% yield (Scheme 3.28). Its purification was straightforward, but rapid decay of red fluorescence on TLC indicates its low stability.

Corrole **77** (similarly to corrole **50**), can be further functionalized using bromine atoms as synthetic handles. Previously tested conditions for copper-less Sono-



73 **43** **76**

Scheme 3.27



75 **38** **77**

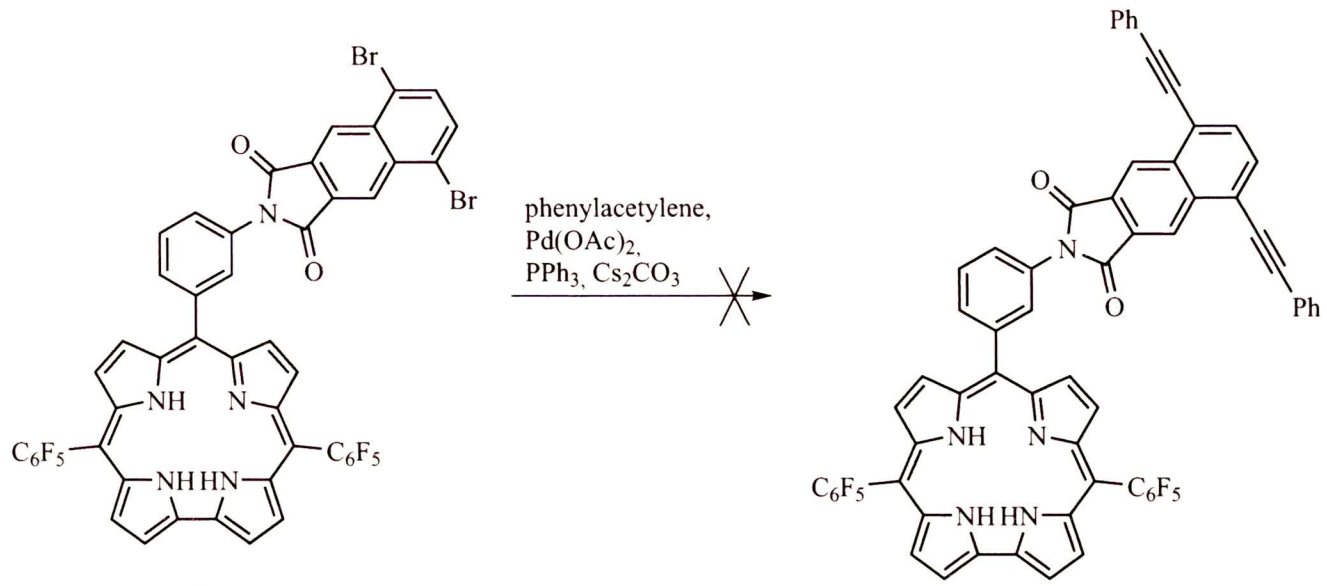
Scheme 3.28

gashira coupling were used to react corrole **77** with phenylacetylene (Scheme 3.29).

Unfortunately, corrole **77** failed to react with phenylacetylene and only numerous products of decomposition were visible on TLC.

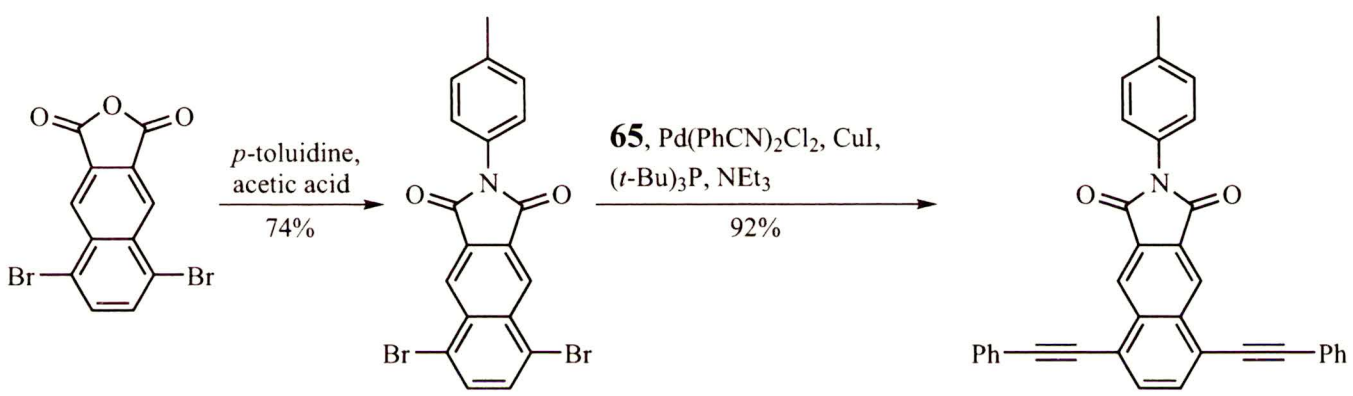
Although the synthesis of corrole failed, I was still determined to prepare at least previously unknown model imide in order to study its optical and electrochemical properties. In order to synthesize model compound which is relatively chemically inert, anhydride **73** was reacted with *p*-toluidine in boiling acetic acid to give imide **78** with good yield (Scheme 3.30) which then was coupled[110] with phenylacetylene (**65**) to give imide **79** in 92% yield.

In principle, one cannot expect that simple, substituted phthalimides will display suitable optical properties from the point of view of eT. In most cases they absorb only UV-light and have high reduction potential. Still, when the substituents are placed in very special arrangement, the resulting substance can



77

Scheme 3.29



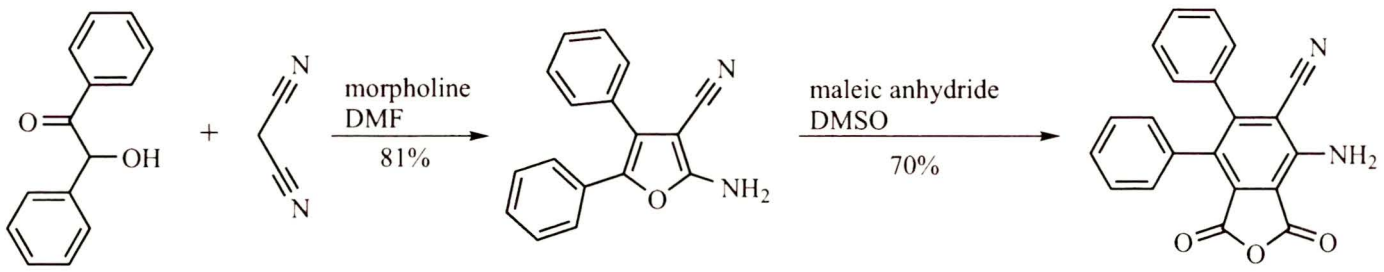
73 **78** **79**

Scheme 3.30

absorb visible light.

Continuing the search toward new chromophores with interesting optical properties, derivatives of 3-amino-4-cyano-5,6-diphenylphthalimide were synthesized. Corresponding anhydride **83** (Scheme 3.31) was synthesized according to published procedure.[111] Even though it is known compound, its synthesis is not trivial and is worth to be described in detail. Benzoin (**80**) was used as a starting material and was allowed to react with malononitrile (**81**) under Gewald conditions affording furan derivative **82**, which can be considered as an active diene component in Diels-Alder reaction and indeed, it readily reacts with maleic anhydride giving, after acidic hydrolysis, desired derivative of phthalic anhydride **83**.

Simple derivatives of this anhydride (phthaloyl hydrazide and *N*-hydroxy ph-



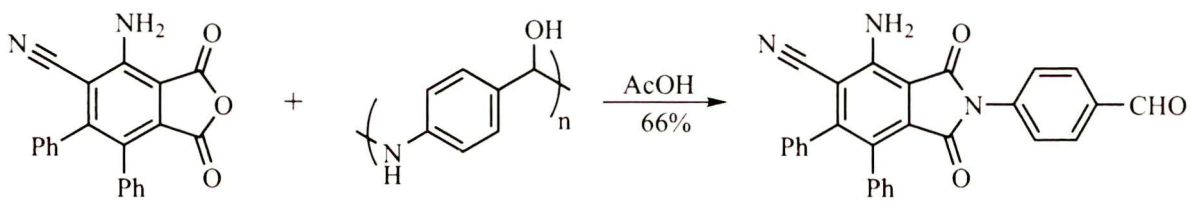
80 **81** **82** **83**

Scheme 3.31

thalimide) were described in the literature exclusively from the point of view of their biological activity (antitumor agents). Their spectroscopic properties were never studied and N-aryl substituted amides of such type were unknown before my work.

The combination of electron-withdrawing and electron-donating groups alters the electronic structure of organic chromophore decreasing the difference between HOMO and LUMO. As a result, anhydride **83** strongly absorbs green light.

Assuming that free amino group will not cause complications during imide formation due to the combined effect of steric hindrance and its electron-poor character, anhydride **83** was used in further steps without modifications. In order to synthesize aldehyde – a precursor for corrole synthesis – the mixture of anhydride **83** and *p*-aminobenzaldehyde polymer (**56**) was refluxed in acetic acid (Scheme 3.32). Aldehyde **84** was obtained with good yield and acceptable purity without chromatographic purification.

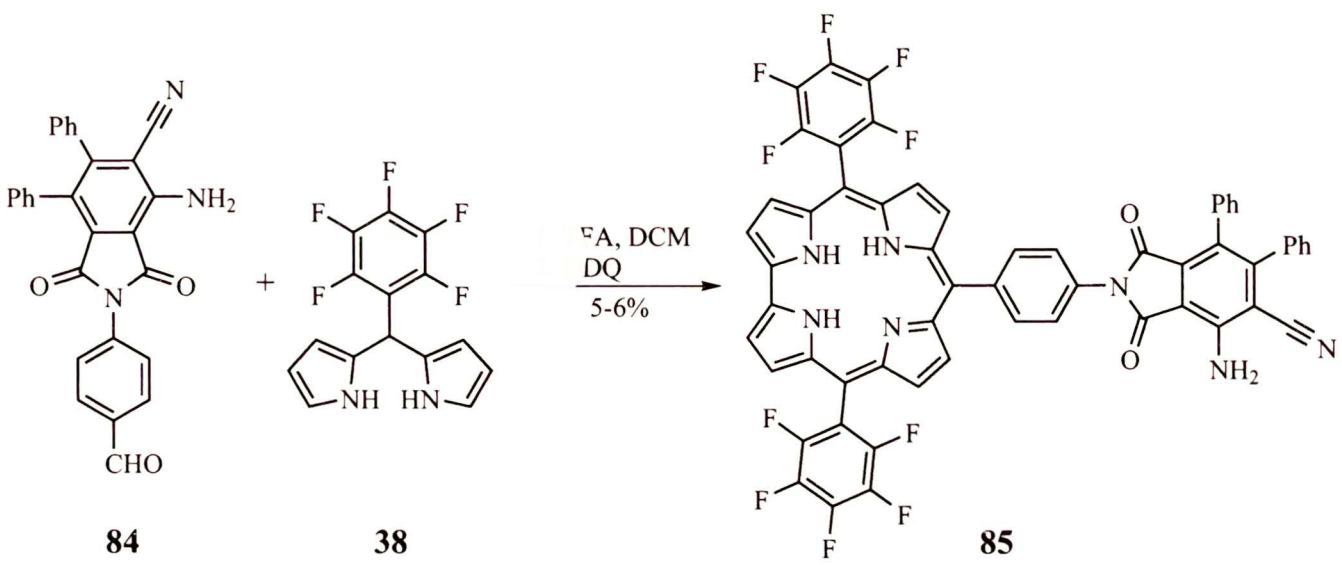


83 **56** **84**

Scheme 3.32

The corrole synthesis was performed by reacting aldehyde **84** with 5-(pentafluorophenyl)dipyrrane (**38**) under acidic catalysis (Scheme 3.33). After oxidation with DDQ followed by typical workup and purification I found that corrole **85** was formed with rather low yield (6%). Among possible unfavorable factors, free

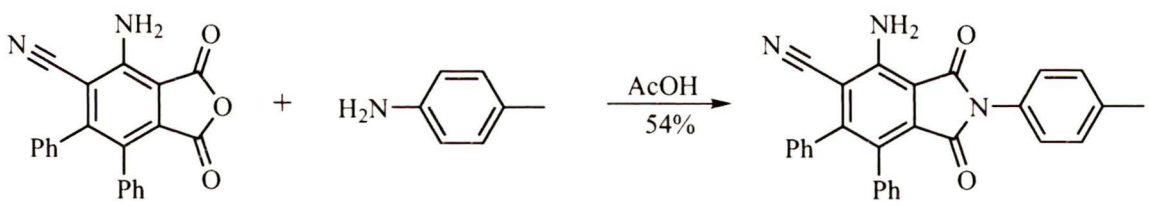
amino group of aldehyde was considered to be a site which is capable to coordinate acidic catalyst and hence reduce its active concentration in the reaction mixture. Having this in mind, reaction was repeated with doubled concentration of TFA (*ca.* 27 mM) but, unfortunately, it did not improved outcome of the experiment.



84 **38** **85**

Scheme 3.33

Chromophore, incorporated in corrole **85** has strong fluorescence and it is of interest to study its spectroscopic properties. The model compound **86** with toluidyl substituent at nitrogen atom was synthesized by refluxing the mixture of anhydride **83** with *p*-toluidine in acetic acid (Scheme 3.34).



83 **86**

Scheme 3.34

3.3 Corrole-coumarin dyads

Coumarin (2*H*-chromen-2-one) and its derivatives are found in many plants and often define their pleasant fragrant. They are widely used as aromatizing agents

but are gradually banned from foods, beverages and tobacco due to their moderate toxicity. Many benzopyranones are characterized by strong biological activity and, accordingly, there are numerous pharmaceuticals with, for example, anti-tumor, analgesic, antiseptic effects based on them.[112] Among technical applications, coumarins are used as a gain medium in dye lasers,[113] as emitter layers in OLED,[114] and as optical brighteners.[115] Furthermore, there is a growing number of publications in the literature, where coumarin-based compounds are used as fluoroionophores and chemosensors.[116–118] Increasing interest in coumarins as components in multichromophoric systems for inter- and intramolecular electron transfer studies[119–122] is stimulated by the ease of their synthesis and beneficial combination of their photophysical properties, namely, intensive absorption band in UV region and high fluorescence quantum yield.

The structure-property relationship of coumarin derivatives has recently been studied in detail.[123] In most of assemblies displaying EnT, only the simplest coumarins were employed. Additionally, there are only few reports published to date on the photophysical properties of coumarin-porphyrinoid conjugates.[124,125]

The idea of combining corroles and coumarins in one molecule is very attractive and my work is aimed at the attachment of coumarin unit in a covalent manner to a corrole. Construction of such systems involves multistep transformations but, on the other hand, produces models for eT studies with well defined chemical structure and geometry.

There are already few examples of corrole-coumarin dyads published.[122] Photochemical investigations revealed that coumarin moiety, when its electronic structure is modulated properly, can efficiently act as an electron acceptor in a corrole-coumarin dyad. While in a previously published dyads coumarin was usually attached to corrole core directly, in a present research the coumarin unit is moved further away by a *p*-tetrafluorophenylene linker to diminish electronic coupling between components in a dyad. Another reason for which *p*-tetrafluorophenylene linker was chosen, is its electron-withdrawing character, which is known to improve stability of corroles.

In order to enhance the fluorescence of coumarin as well as move to the absorption bands from deep UV to around 400-450 nm, facilitating in this way photochemical measurements (observation of fluorescence decay), it is essential to

secure the presence of electron-donating substituent at position 7. That is why only coumarins with hydroxy and dialkylamino substituents were of interest in my research. Hydroxy group compared with dialkylamino has additional benefit as it retains some reactivity and can be used for coumarin-to-corrole bridge formation. In the case of 7-dialkylaminocoumarins, another sequence of reactions was used in order to obtain corresponding aldehyde and in that case, from the synthetic considerations, *p*-phenylene linker was an alternative to tetrafluorinated analog.

Among several different possibilities of attachment coumarin to linker, the nucleophilic substitution, which was developed in our group recently, [126] was used and corresponding 4-aryloxy-2,3,5,6-tetrafluorobenzaldehydes were easily prepared with good yields. In the case of 7-dialkylaminocoumarin, aldol-type condensation was utilized and the presence of methyl group in the position 4 of a coumarin was a substantial requirement.

Similarly to corroles with imide acceptors, 5-(pentafluorophenyl)dipyrrane was used exclusively herein (see page 57 for justification) as a bipyrrolic component in corroles syntheses.

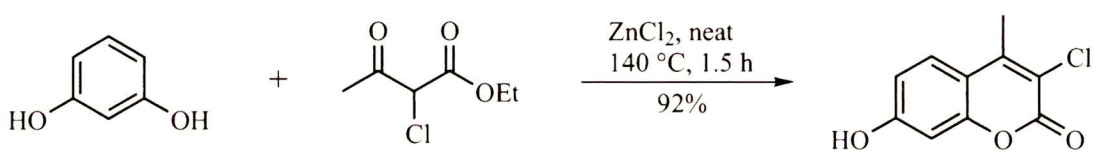
In the light of previous research in our group it is clear, that electronic properties of simple coumarins are often insufficient for utilizing them as good electron acceptor. Their first reduction potential is too high and consequently HOMO-LUMO levels of both counterparts (corrole and coumarin) do not match. The good electron acceptor usually posseses a few electron withdrawing substituents which facilitate electron allocation on it. However, of equal importance is that molecule in question has appropriate core with sufficient "electron capacity" in which electrons can be delocalized efficiently. This can be ensured by, for example, constructing the system of condensed or electronically linked (through double or triple bonds) aromatic carbo- or heterocycles.

From the synthetic point of view, there are two general strategies toward π-expanded coumarins: a) synthesis of relatively simple coumarins followed by their chemical modification; b) preparation of structurally elaborated starting material which is subsequently utilized in coumarin forming reaction. Both approaches will be presented in this section.

Sonogashira reaction is one among many possible tools for coumarin core modification which allows to expand π-conjugation forming a new chromophore, though

retaining its main structural features. It was noticed, that optical properties of umbelliferone* are sensitive to the presence of electron withdrawing substituents at position 3 and bathochromic effect was observed for coumarins of this type. [127] Suchwise, umbelliferone with halogen at C-3 position seemed to be a good candidate for derivatization.

In order to synthesize 3-chloro-4-methyl-7-hydroxychromen-2-one (**89**), the procedure, published by Okuda *at al.* [128] was used after minor modifications, that is, resorcinol (**87**) was reacted with commercially available ethyl 2-chloroacetoacetate (**88**) in the presence of Lewis acid and without a solvent (Scheme 3.35). The chlorocoumarin **89** was isolated in good yield and was used without further purification. It is worth to mention, that the presence of methyl group at position 4 of compound **89** simplifies synthesis as well as substrate choice, and I hoped that it will not interfere in subsequent transformations.



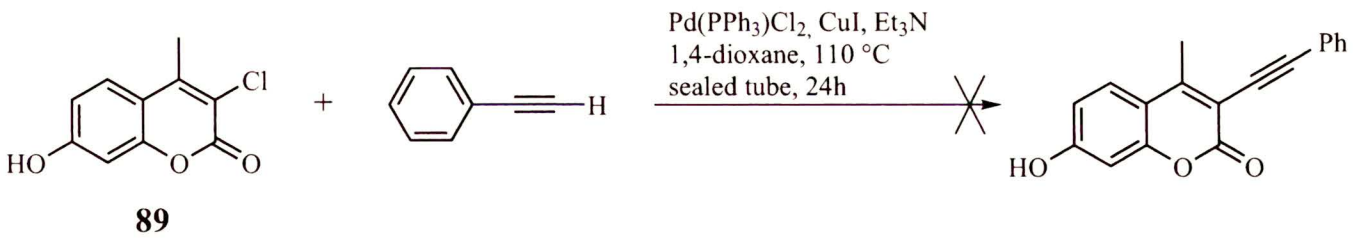
87 **88** **89**

Scheme 3.35

There are only a few reports to date, where sterically hindered aryl chlorides are successfully coupled with arylacetylenes. [129,130] Furthermore, elaborated reaction conditions and/or exotic, commercially non-available ligands were usually employed. Consequently, in order to couple chloro-coumarin **89** with phenylacetylene I decided to use more user-friendly conditions which are reported to work with aryl bromides, [131] but to perform the reaction at higher temperature and prolonged time (Scheme 3.36). Unfortunately, after 24 hours no signs of substrate conversion were noticed (TLC).

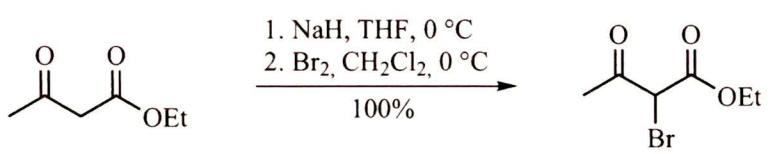
During thorough literature analysis I noticed, that only bromo-substituted coumarins were used as a substrate in a Pd-catalyzed coupling reactions. [123,131,132] In the light of above facts, I decided to prepare bromo-substituted coumarin. In order to synthesize ethyl 2-bromoacetoacetate (precursor of 3-bromocoumarin),

*historical name of 7-hydroxychromen-2-one



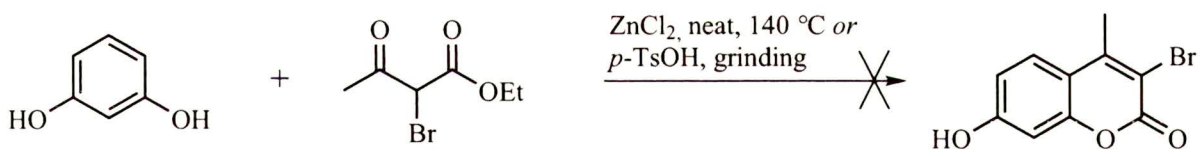
Scheme 3.36

sodium salt, generated from ethyl acetoacetate, was brominated according to published procedure[133] with quantitative yield (Scheme 3.37).



Scheme 3.37

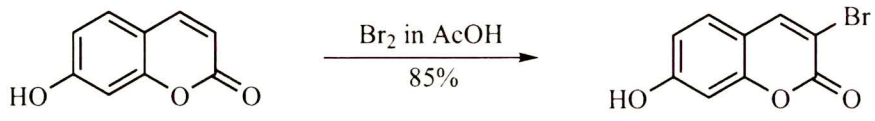
Cyclisation of ethyl 2-bromoacetoacetate with resorcinol was performed under the same conditions as for chlorocoumarin **89** (Scheme 3.38). Reaction was very energetic and as a result, tarry mixture was formed, from which I was not able to separate any individual compound. Bromine atom, compared to chlorine is known to be more labile in substrates of this type and, for this reason, I decided to repeat reaction under milder conditions, with *p*-TsOH as a catalyst.[134] However, the complex mixture with multiple fluorescent spots was formed again.



Scheme 3.38

Luckily, bromine atom can also be introduced at position 3 of the coumarin derivatives by direct bromination. In this case it becomes easy to avoid methyl substituent at position 4. This can have positive effect on Pd-catalyzed coupling reaction due to reduced steric hindrance at C-3 position. In order to synthesize 3-bromo substituted coumarin derivative, I made a few attempts of bromination with NBS using relatively new and simple procedures,[135] however, in spite of reports of their regioselectivity, both in case of umbelliferone as well as 4-methylumbelliferone, mixtures were formed which were difficult to separate using

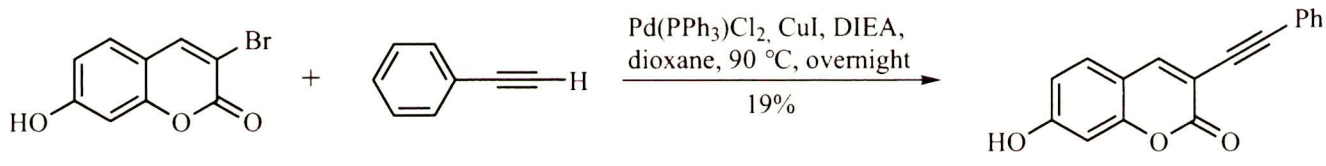
chromatographic methods. Finally, following the procedure published by Reisch and Zappel,[136] after very slow addition* of diluted solution of bromine in acetic acid to a suspension of umbelliferone (**90**), I was able to isolate desired coumarin **91** in 85% yield (Scheme 3.39).



90 **91**

Scheme 3.39

Subsequently, bromocoumarin **91** was submitted to Sonogashira coupling with phenylacetylene under slightly modified reaction conditions published by Schiedel *at al.*[123] (Scheme 3.40).



91 **92**

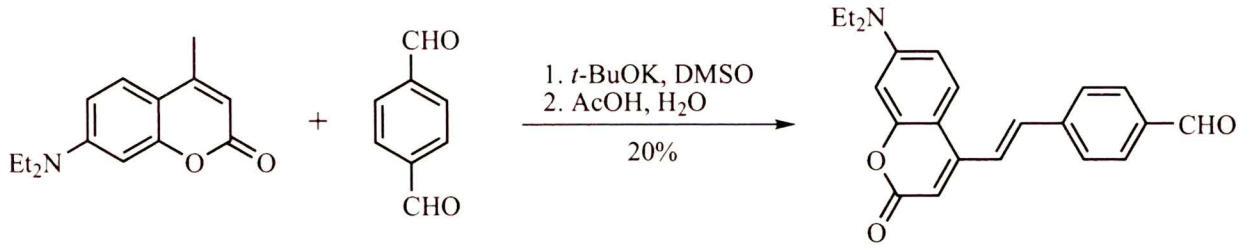
Scheme 3.40

It was mentioned by Schiedel that reaction is sluggish in the case of substrates with free OH group and indeed, coumarin **92** was isolated in low yield. Unfortunately, I was not able to improve the yield by minor changes of reaction conditions. Poor efficiency of this reaction lead to my decision of discontinuation of this approach.

An another concept for π-expansion of coumarin can be based on its conjugation with another aromatic unit *via* the carbon-carbon double bond. Coumarins with a methyl group at position 4 are known to undergo condensations with aromatic aldehydes in the presence of strong base[137] giving coumarins with vinylene group at position 4, and condensation with aminals of unsaturated aldehydes does not even require strong base for activation.[138] Based on these literature precedences, coumarin **93** bearing methyl group at position 4 was used as a starting

*dropwise, over 48 hours

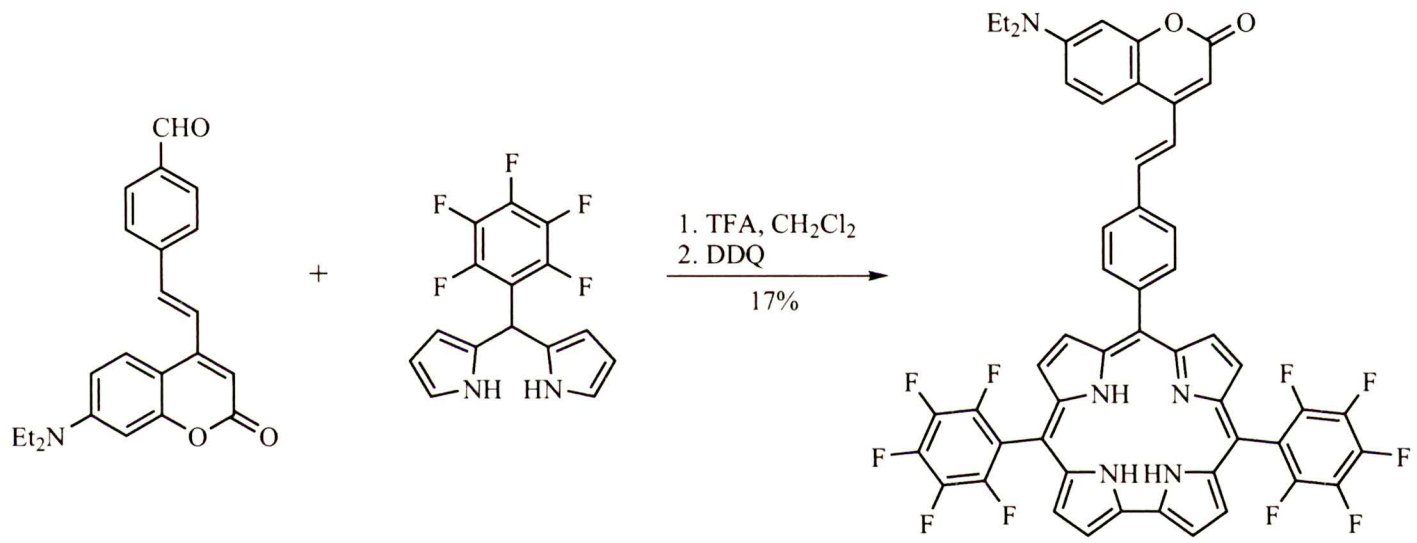
material in the synthesis of formyl-coumarin **95** according to a slightly modified procedure developed by Tkach *et al.*[137] (Scheme 3.41).



93 **94** **95**

Scheme 3.41

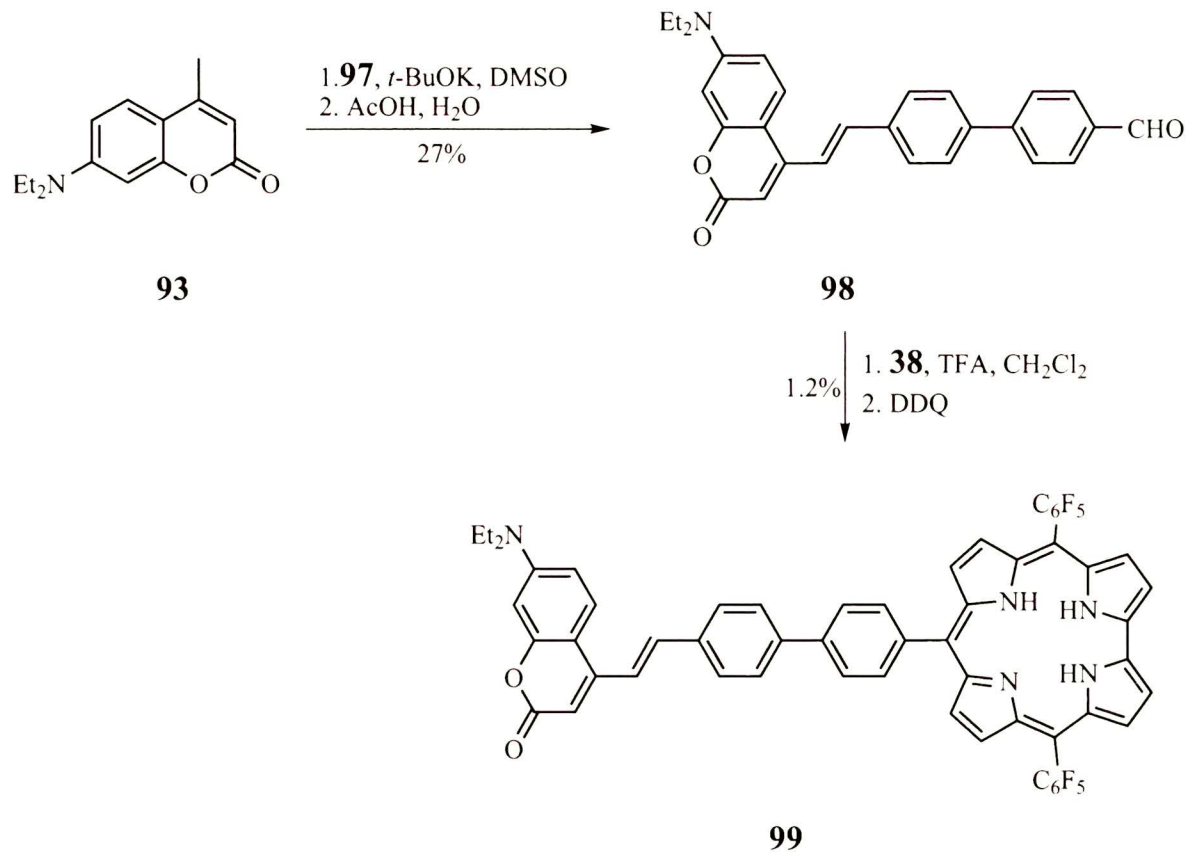
Subsequent condensation of aldehyde **95** with 5-(pentafluorophenyl)dipyrrane afforded corrole **96** (Scheme 3.42) which is stable and easy to purify.



95 **38** **96**

Scheme 3.42

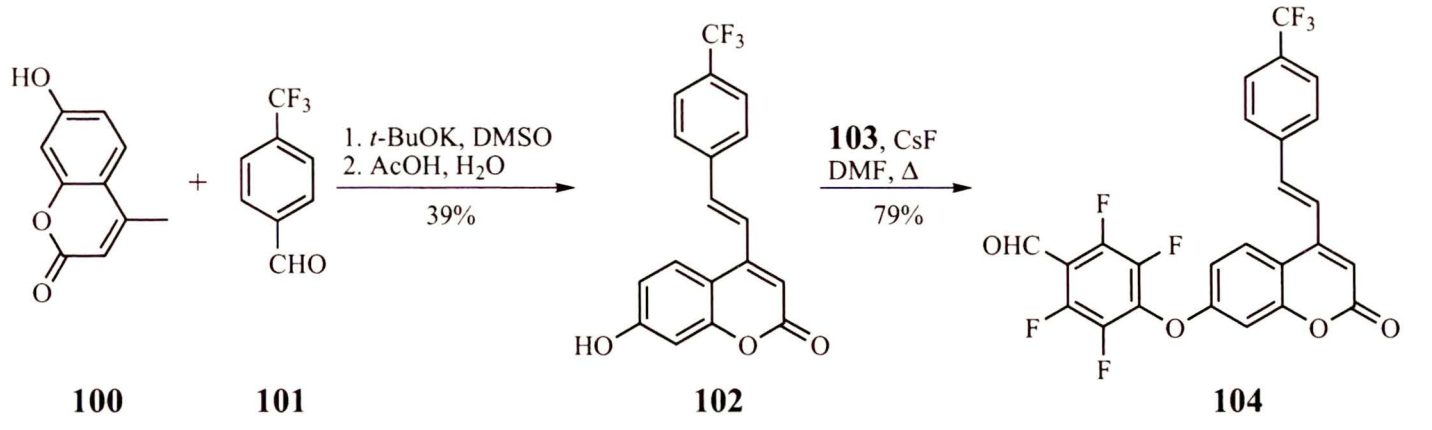
Encouraged by this result, I decided to change the distance between the corrole and coumarin by introducing an additional phenylene linker. While the synthesis of analogue **98** (Scheme 3.43) starting from 7-diethylamino-4-methylcoumarin (**93**) and (1,1′-biphenyl)-4,4′-dicarboxaldehyde (**97**) was quite straightforward, its condensation with 5-(pentafluorophenyl)dipyrrane gave the required corrole **99** in a yield 1.2% only. Moderate yields in condensations leading to formyl-coumarins **95** and **98** along with unexpected difference in yields of corrole cyclisation are main drawbacks of presented approach.



Scheme 3.43

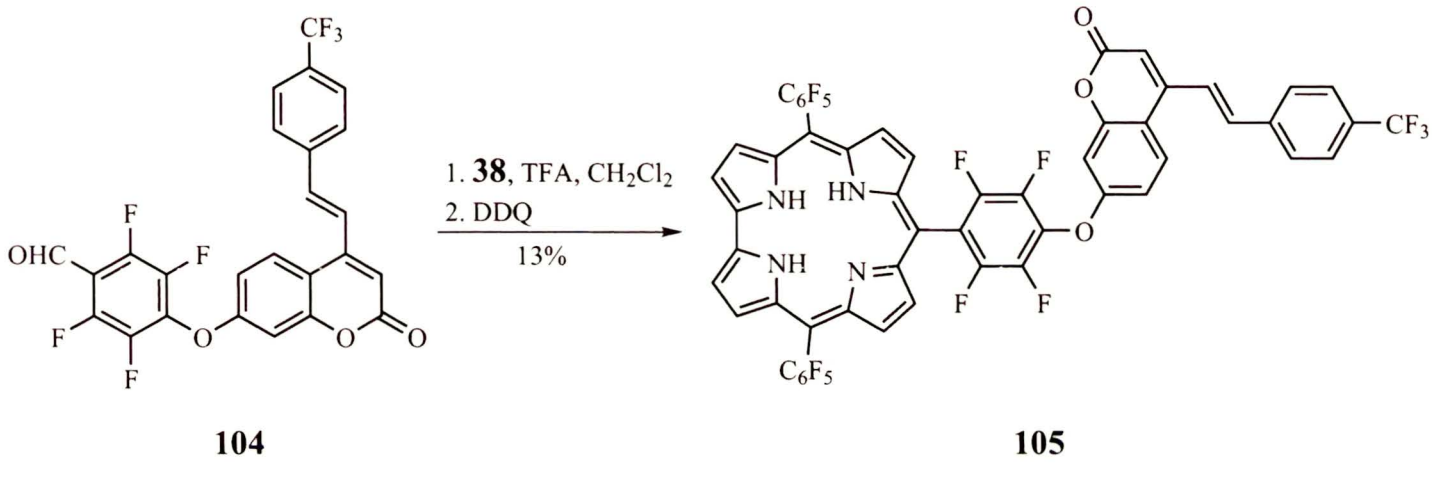
These results forced me to consider an alternative way to link π-expanded coumarins to the corrole core. In order to examine another attachment pattern, π-expanded coumarin bearing a free OH group have to be synthesized. Such coumarin can then be submitted to nucleophilic substitution reaction with pentafluorobenzaldehyde (**103**) in the presence of CsF which was proven to be reliable procedure towards 4-aryloxytetrafluorobenzaldehydes. Indeed, appropriate hydroxycoumarin **100** reacted with *p*-trifluoromethylbenzaldehyde* (**101**) affording corresponding expanded hydroxycoumarin **102** with considerably improved yield which in turn, as depicted on the scheme 3.44, gave desired aldehyde **104** with the yield reaching 79%. One can expect difficulties when hydroxycoumarin is involved in the reaction catalyzed by sodium *tert*-butoxide but, to my delight, reaction proceeded smoothly. Subsequent condensation of aldehyde **104** with 5-(pentafluorophenyl)dipyrrane (**38**) and oxidation with DDQ gave, in 13% yield, corrole-coumarin dyad **105**, possessing completely different architecture compared to compounds **96** and **99** (Scheme 3.45).

*It has been noted by Tkach[137] that only electron-poor aldehydes react with 4-methylcoumarins to give styryl coumarins in good yields.



100 **101** **102** **104**

Scheme 3.44

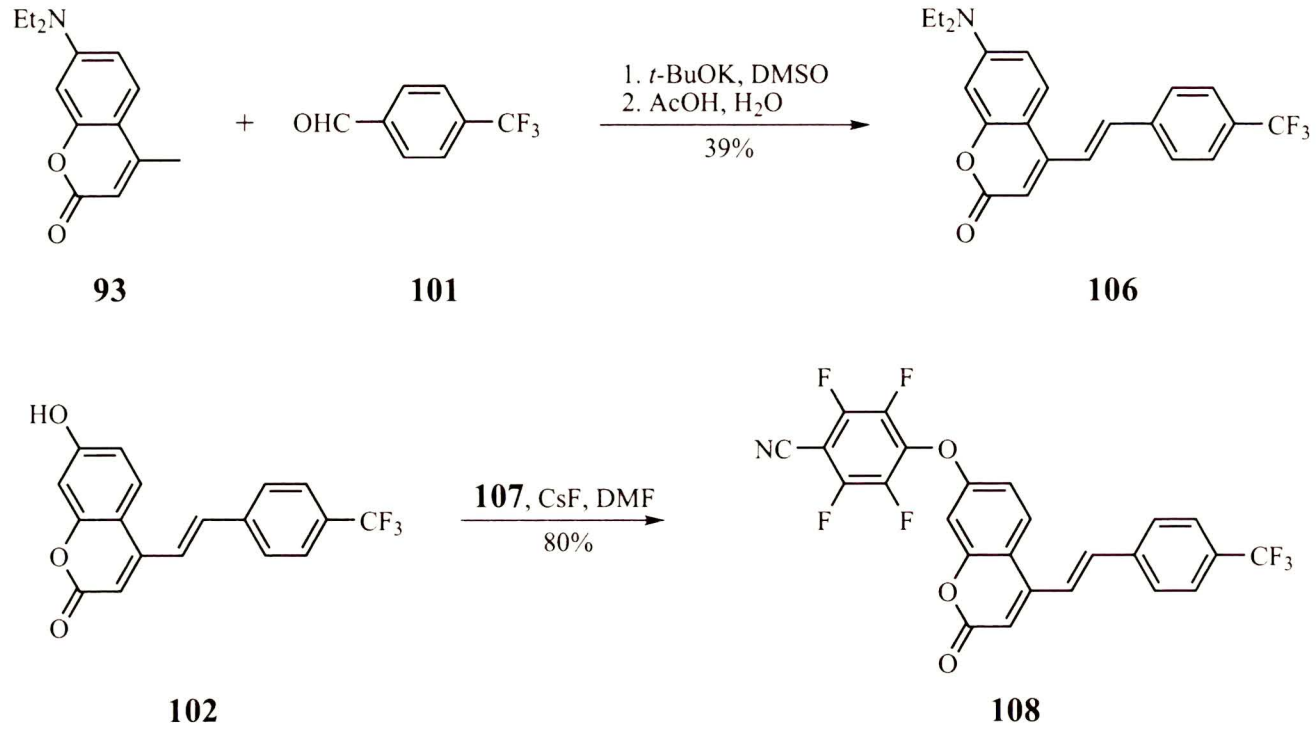


104 **105**

Scheme 3.45

Full evaluation of electrochemical properties and especially final photophysical studies require measurements of not only target dyads but also structurally simpler compounds. Consequently, model compounds **106** and **108** were synthesized utilizing reaction types used above: condensation of coumarin **93** with *p*-trifluoromethylbenzaldehyde (**101**) and nucleophilic aromatic substitution of *p*-fluorine atom of pentafluorobenzonitrile (**107**) respectively (Scheme 3.46).

The mean angle between two benzene rings in biphenyl molecule excludes full overlap of π-orbitals. Still, certain degree of π-conjugation exists in such compounds. Moreover, the conformation often changes to coplanar in the excited state which results in large Stokes-shift. To form such a connection, Pd-catalyzed coupling reactions are generally utilized.[131,132] While this approach is convenient for carbocyclic components (libraries of boronic acid esters are readily accessible), it becomes problematic for more complex heteroaromatic compounds. Therefore, utilizing of appropriate substituents, which can be easily introduced during coumarin



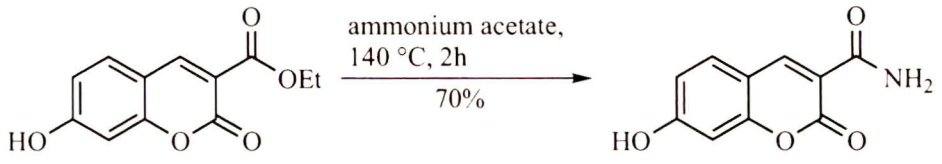
Scheme 3.46

synthesis, for the purpose of later heterocyclizations becomes attractive.

I decided to focus on one of five-membered rings as a heterocyclic component since it induces smaller mean angle (hence greater degree of π-conjugation). 1,3-Oxazole was chosen mainly because of its synthetic flexibility – there are many methods of its construction (some of them have similarity with preparations of other five-membered heterocycles, contributing to overall generality of chosen strategy).

It was shown by Takechi and co-authors,[139] that 7-diethylaminocoumarin scaffold can serve as a starting point on the synthetic pathway to corresponding 3-oxazolylcoumarins. In order to maintain the possibility of later nucleophilic substitution with pentafluorobenzaldehyde, 7-hydroxycoumarin analog was chosen in my case.

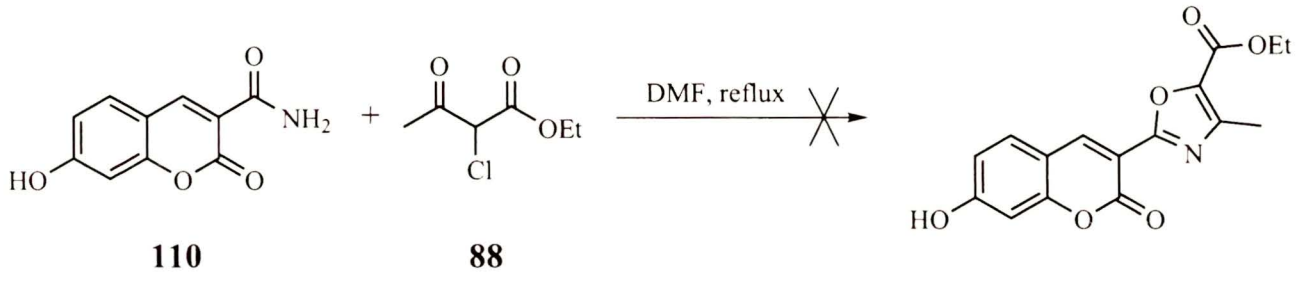
In order to synthesize amide derivative, 3-ethoxycarbonylumbelliferone (**109**), which is readily available from β-resorcylaldehyde and diethyl malonate,[140] was submitted to ammonolysis reaction (Scheme 3.47). Surprisingly, this simple transformation failed with aqueous ammonia in DMF and, after brief search, heating with ammonium acetate above its decomposition temperature[141] appeared to be excellent procedure as it furnished pure product **110** even without crystallization.



109 **110**

Scheme 3.47

Subsequently, aiming to synthesize oxazole derivative, 7-hydroxycoumarin-3-carboxamide (**110**) was reacted with ethyl 2-chloroacetoacetate (**88**) in boiling DMF following the procedure for diethylamino-analogue. [139] Unfortunately, conversion was not full and mixture of few fluorescent products (TLC) was formed (Scheme 3.48).



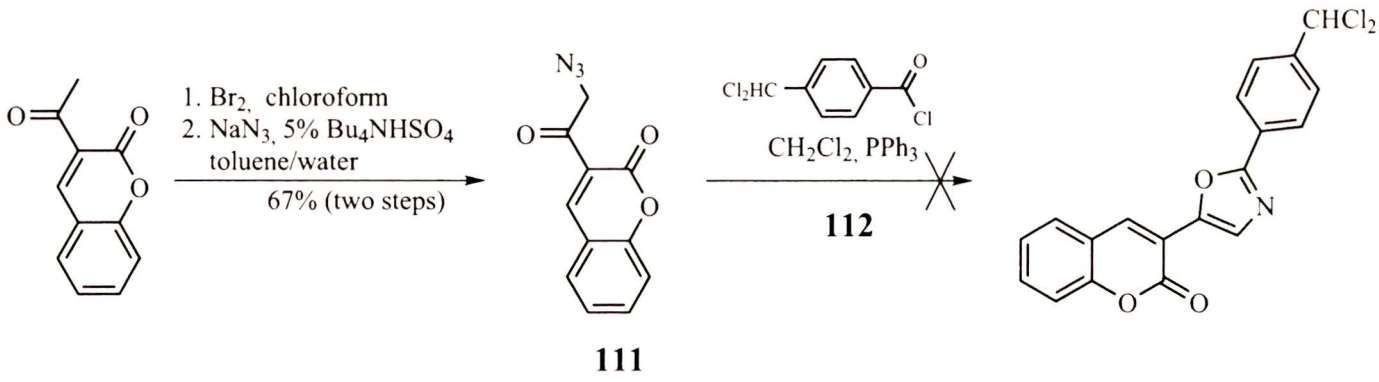
110 **88**

Scheme 3.48

Mass spectrometry analysis of the crude reaction mixture did not showed the presence of expected product. Replacement of DMF with glacial acetic acid or pyridine did not improved reaction outcome. Probably, unprotected hydroxyl group can be responsible for this negative result.

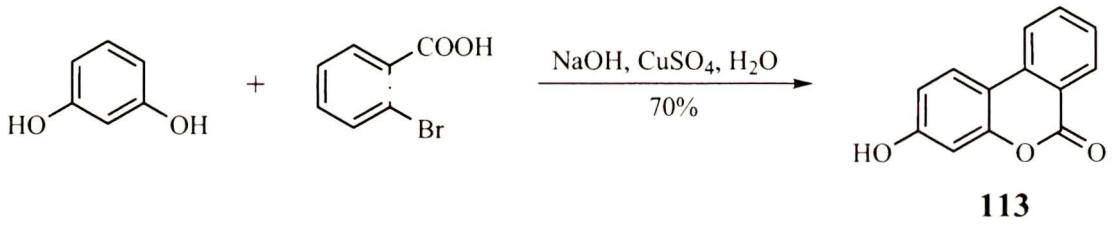
To study the possibility of the formation of oxazolocoumarin *via* another strategy, azide **111**, synthesized by bromination of 3-acetylcoumarin and subsequent substitution with sodium azide*, was transformed to aza-ylide under Staudinger reaction conditions. Intermediate without isolation was then allowed to react with acid chloride **112** in order to form oxazole (Scheme 3.49). The dichloromethyl group of acid chloride was introduced as a hidden aldehyde function. Unfortunately, after workup it occurred that the multiple products were obtained and MS analysis of reaction mixture did not revealed the presence of desired product.

*after several attempts with "classical" protocols which gave poor yields of desired coumarin I choose Mąkosza's PTC method [142] which provided virtually quantitative conversion



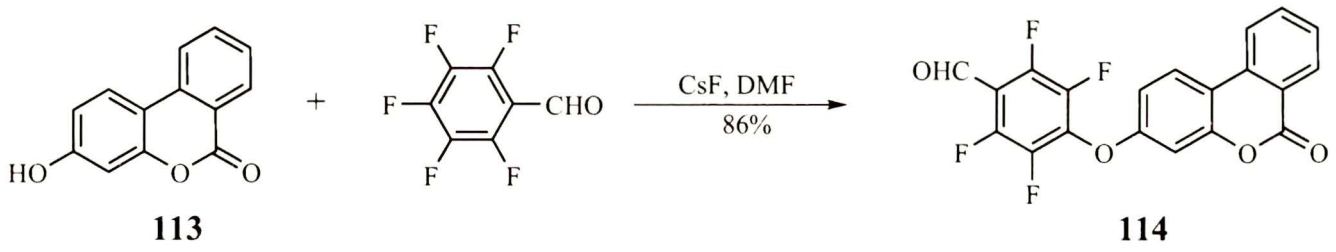
Scheme 3.49

During design of coumarins for my studies I paid particular attention to less utilized ways of π-expansion of the chromophore. In this context benzo[c]coumarin seemed to be promising scaffold. The required building block, namely 3-hydroxy-benzo[c]chromen-6-one (**113**), was synthesized using Hurtley's procedure[143] from *o*-bromobenzoic acid and resorcinol (Scheme 3.50).



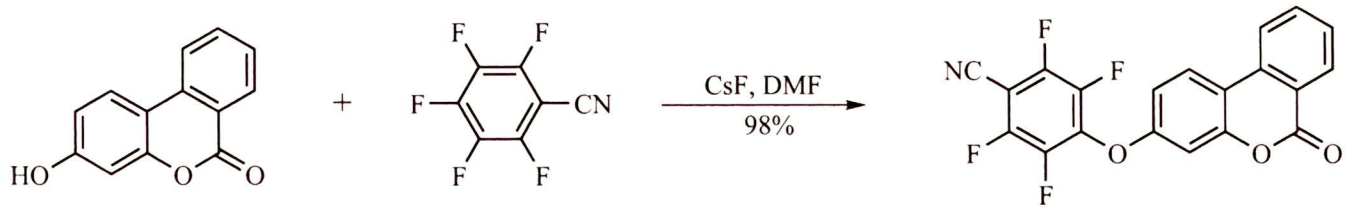
Scheme 3.50

To transform coumarin **113** into aldehyde, it was allowed to react with pentafluorobenzaldehyde to give formylcoumarin **114** in 86% yield after crystallization (Scheme 3.51).



Scheme 3.51

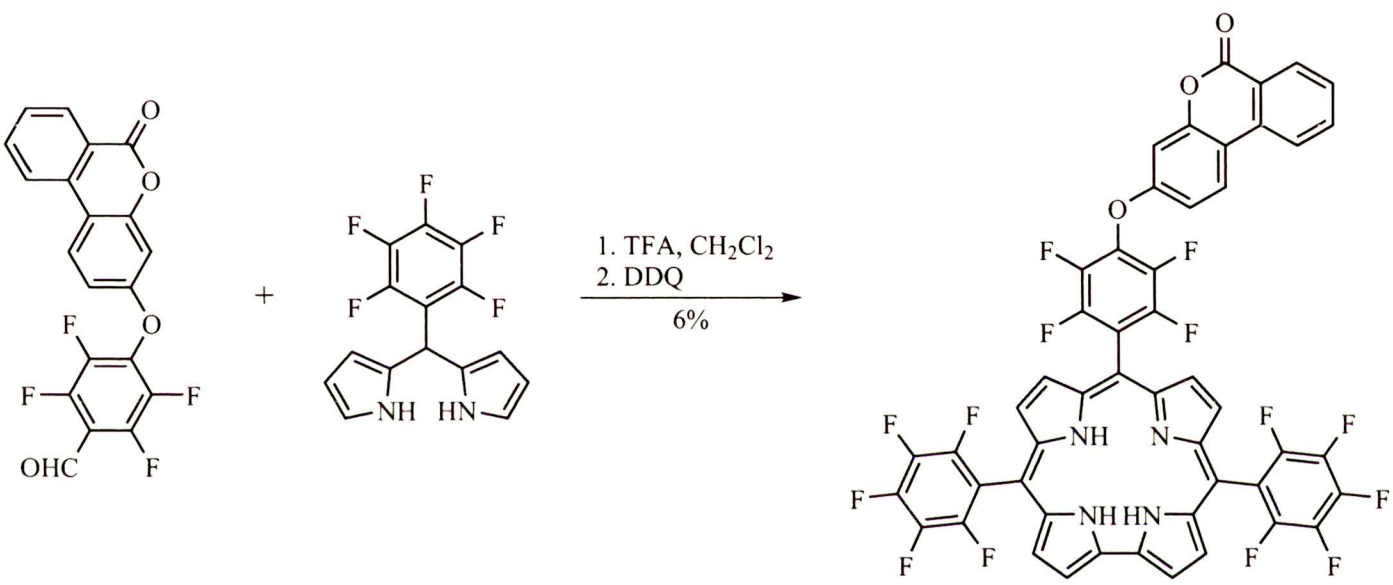
I was not able to find electrochemical properties of benzocoumarin **113** or any other related molecules in the literature, consequently, model compound **115** for such investigation was synthesized by nucleophilic substitution on pentafluorobenzonitrile in the presence of cesium fluoride (Scheme 3.52).



113 **115**

Scheme 3.52

In order to synthesize corrole, formylcoumarin **114** was condensed with 5-(pentafluorophenyl)dipyrrane (**38**) under standard conditions but, after typical reaction time (20 min) aldehyde was only partially consumed (TLC) and additional 25 min was needed for reaction completion (Scheme 3.53).



114 **38** **116**

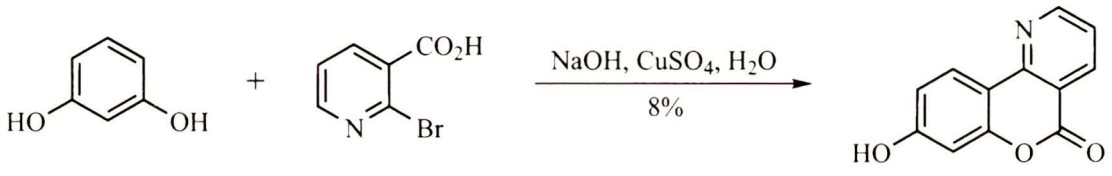
Scheme 3.53

This fact was, probably, caused by moderate solubility of aldehyde **114** in methylene chloride. It is well known, that condensation reaction of dipyrranes and aldehydes in 2:1 ratio does not stop after bilane formation and proceeds further to form a whole range of oligocondensates, from which, after oxidation step, some other porphyrinoids can be formed. Prolonged reaction times usually favor these side reactions. And indeed, in the case of the preparation of corrole **116** additional two red-fluorescent spots were formed. Fortunately, it was possible to separate desired corrole using column chromatography while increasing eluent polarity slowly.

In many previous cases, the low yields in the syntheses of corroles from

coumarin-derived aldehydes was explained arguing about Michael reaction of α,β-unsaturated double bond to pyrrole unit. Obviously, in present case this explanation can not be valid since benzene ring replaced C=C bond.

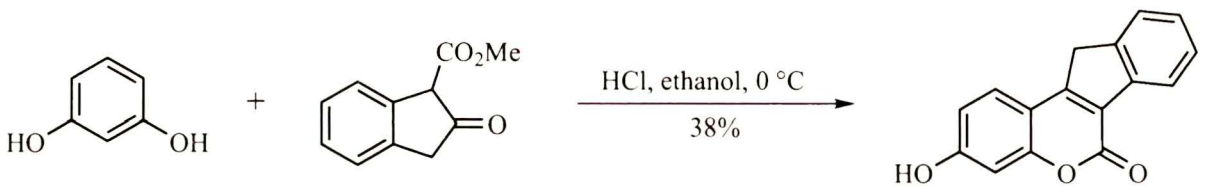
Nevertheless, the synthetic route showed above was considered to be promising and decision was made to study the synthesis of similar annulated coumarin starting from 2-bromonicotinic acid (**117**). In this case, target coumarin is expected to have interesting properties not only due to π-expansion of parent coumarin scaffold but also by electron withdrawing character of annulated pyridine ring. The synthesis of coumarin **118** was performed according to the procedure proposed by Hurtley for coumarin **113** and is shown on the scheme 3.54. Unfortunately, desired coumarin derivative **118** was formed with the yield of only 8% and some minor changes to a reaction conditions did not caused substantial improvement.



117 **118**

Scheme 3.54

While developing the project of annulated coumarins I decided to synthesize electronic analogue of simple 3-phenyl-7-hydroxycoumarin, possessing, however, methylene bridge connecting *ortho*-position of phenyl substituent and position 4 of coumarin scaffold (Scheme 3.55). This would make final chromophore more rigid and angle between two planes of aromaticity would be similar to that of fluorene (*i.e.* 0°).

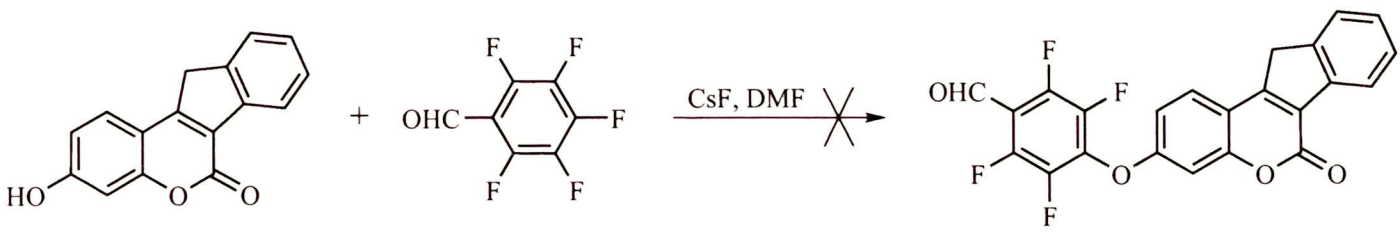


119 **120**

Scheme 3.55

Coumarin derivative **120** was synthesized with moderate yield by condensation of resorcinol with 1-methoxycarbonylindan-2-one (**119**), catalyzed by hydro-

gen chloride.[144] The yield of this reaction can be reduced by side reactions caused by the presence of at least two highly reactive sites – activated keto- and methylene groups. Furthermore, active methylene function retains in the product and subsequent reaction with pentafluorobenzaldehyde failed to give desired formylcoumarin **121** (Scheme 3.56).

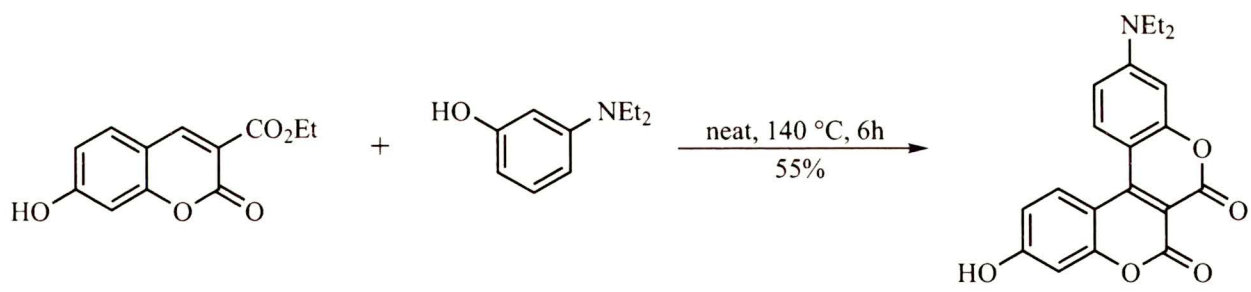


120 **121**

Scheme 3.56

Exploring the subject of π-expanded coumarins, I became interested in an annulated biscoumarin scaffold published by Poronik *et al.*[145] Such biscoumarin express interesting optical properties (strong absorption in blue region) and is promising as a counterpart in corrole-coumarin dyad.

Corresponding biscoumarin derivative **123** with OH group was synthesized following procedure for parent compound described by Poronik. That is, 3-ethoxycarbonylumbelliferone[140] (**109**) was allowed to react with 3-diethylaminophenol (**122**) in a neat giving, after crystallization, desired biscoumarin **123** with good yield (Scheme 3.57).

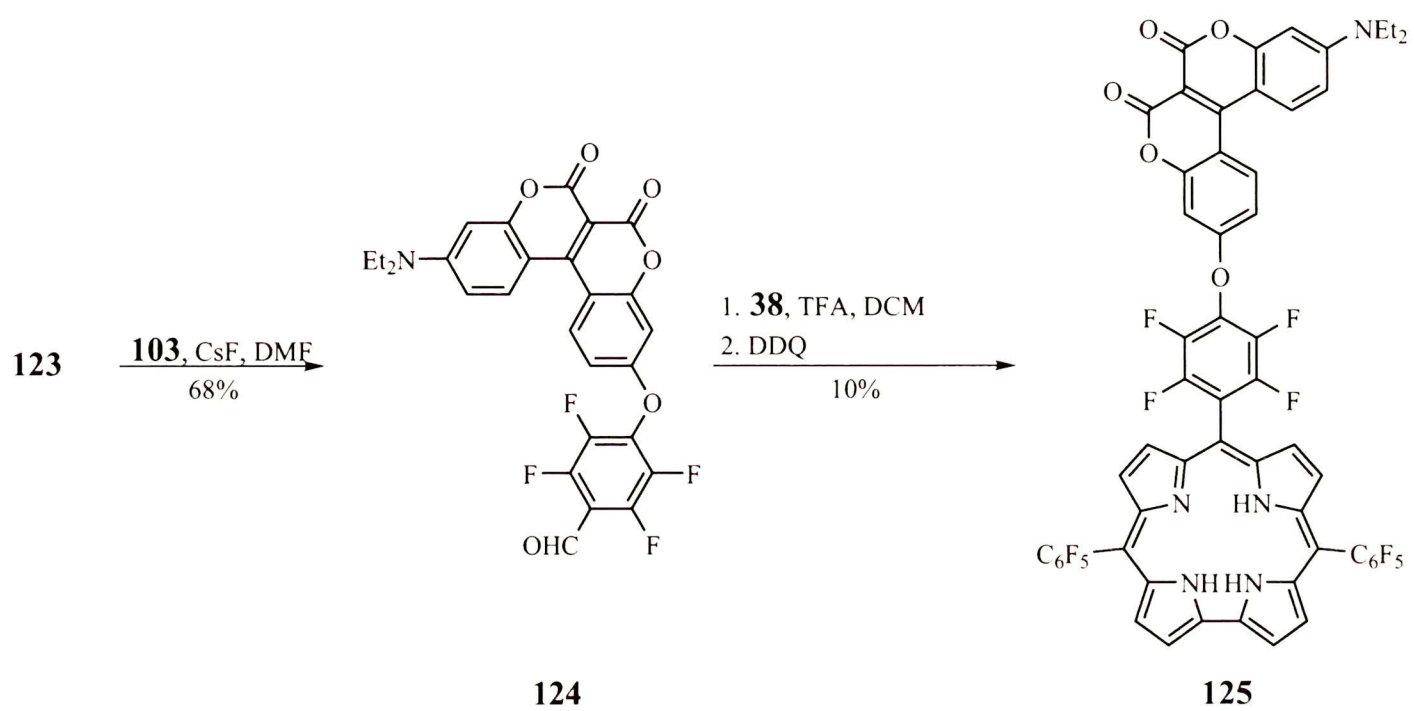


109 **122** **123**

Scheme 3.57

The interesting fact concerning this reaction is, that two equivalents of coumarin derivative should be used since half of it is utilized to oxidize intermediate into final product.

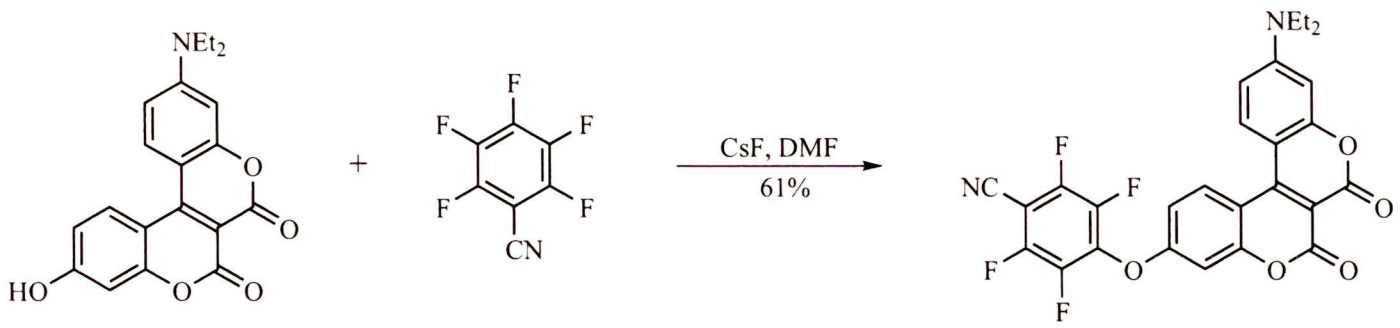
The presence of hydroxyl in biscoumarin **123** allowed me to efficiently transform it into the corresponding aldehyde **124** by reaction with pentafluorobenzaldehyde (**103**) (Scheme 3.58). Its subsequent condensation with 5-(pentafluorophenyl)dipyrrane (**38**) furnishing desired corrole **125** with good, as for such complex structure, yield.



Scheme 3.58

Aldehyde **124** was sparingly soluble in dichloromethane and, similar to previous examples of aldehydes characterized by low solubility, elongated reaction time (40 min) was necessary for condensation reaction. Furthermore, formylcoumarin had diethylamino substituent which can bind the catalyst (TFA), at least partially. That is why concentration of TFA was doubled. As one can predict, small amount of porphyrin can be formed along with corrole and indeed it was the case for corrole **125**. Separation by conventional flash column chromatography failed and I was able to separate the mixture using DCVC.[146] Desired corrole appeared to be quite stable and successfully survived all purification manipulations.

For spectroscopic and electrochemical study, the model compound **126**, based on biscoumarin chromophore, was synthesized by nucleophilic aromatic substitution, reacting biscoumarin **123** with pentafluorobenzonitrile (**107**) in the presence of cesium fluoride (Scheme 3.59).



123 **107** **126**

Scheme 3.59

3.4 Corrole-acridine dyad

Shortly after acridine was first isolated from coal tar by Carl Gräbe and Heinrich Caro in 1871 it became an object of interest in the production of dyes. [147] Further investigations allowed acridine to become a core fragment of various compounds with biological activity (mainly antiseptic agents).

Solutions of acridine absorb UV light and show fluorescence in the blue region of visible spectrum. Modification of its structure and/or introducing substituents into core molecule leads to significant changes of its photophysical properties.

Early studies of acridines in the intermolecular electron transfer processes revealed its capability to form corresponding radical-anions readily [148] and interest in such acridine-based systems is constantly growing. [149] There are numerous, recent publications where acridine moiety is covalently connected to its counterpart, among which are carbon nanotubes, [150] triarylamines, [151] heme. [152] Acridine has ability to intercalate into DNA helices and due to this feature acridine-based systems are widely studied as DNA-binders [153,154] and antitumor agents. [155]

A small number of publications concerning porphyrin-acridine dyads can be found in the literature [156] and only a few corroles bearing acridine moiety were published to date. [7,157]

It was shown during recent studies in our group, [7] that corroles with acridine moiety connected directly at *meso*-position can be obtained in good yields from formylacridines, except for 9-formylacridine.* My plan was to continue studies on corrole-acridine dyads and to prepare new acridine-based chromophores by

*9-formylacridine has very low solubility in chloroform and dichloromethane, and in addition, steric hindrance near aldehyde group makes its condensation with dipyrranes complicated

connecting acridine moiety to corrole through another heterocyclic system – pyrrole or coumarin.

Classical synthetic methods of acridine synthesis involve condensation of α-halobenzoic acids with anilines.[158] It is possible to prepare by this method highly functionalized acridine derivatives by selecting of appropriate starting materials. Acridines can also be prepared by the condensation reactions involving diarylamines[151,159] and sometimes diarylmethanes.[160] However, despite of the variety of methods, in most cases acidic catalysis is used for condensation reaction and in case of pyrrolic substrates, which are acid sensitive, these methods become unsuitable.

Another synthetic approach towards acridine containing building blocks is direct introduction of acridine moiety by aromatic nucleophilic substitution of hydrogen at position 9 of acridine.[161,162]

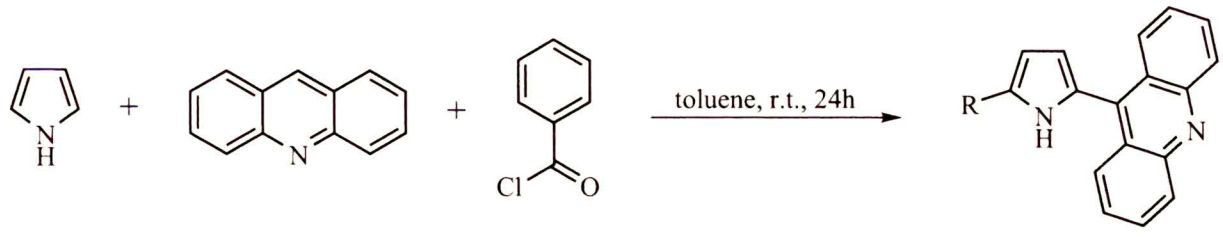
There are numerous examples in the literature[163] describing the reaction of acridine with electron-rich aromatic compounds in the presence of acylating agent, forming corresponding 9-substituted acridines.

I decided to study the reaction of pyrroles with acridine from the viewpoint of preparation of new chromophores for corrole-based dyads. Early studies by Treibs and Fligge clearly showed,[164] that fluorescence properties of adducts formed by direct nucleophilic addition of acridine to pyrrole display somehow unique optical properties: intense fluorescence and bathochromically shifted absorption. I thought that attaching such unit to corrole could be beneficial creating new type of bichromophoric system. Thereby, using published procedure,[165] pyrrole **127** was reacted with acridine (**128**) in the presence of benzoyl chloride (**129**) to give a mixture of mono- and disubstituted pyrroles **130** and **131** (Scheme 3.60) even though excess of pyrrole was used.

It is noteworthy, that additional equivalent of acridine is used to oxidize intermediate, formed after pyrrole addition to *N*-acylacridinium chloride.

The column chromatography was used in order to separate mono- and disubstituted products, which were obtained slightly contaminated with acridine* (visible on TLC) which can be removed by diffusion crystallization. Formation of disubstituted product even when excess of pyrrole is present can be assigned to high reactivity of *N*-acylacridinium salt (and hence low selectivity) along with feebly

*similar hetarylation products are known to form complexes with acridine[164,166]



127 **128** **129**

R = H (**130**), 48%
9-acridinyl (**131**), 17%

Scheme 3.60

marked effect of substituent in the intermediate of monosubstituted acridinopyrrole.*

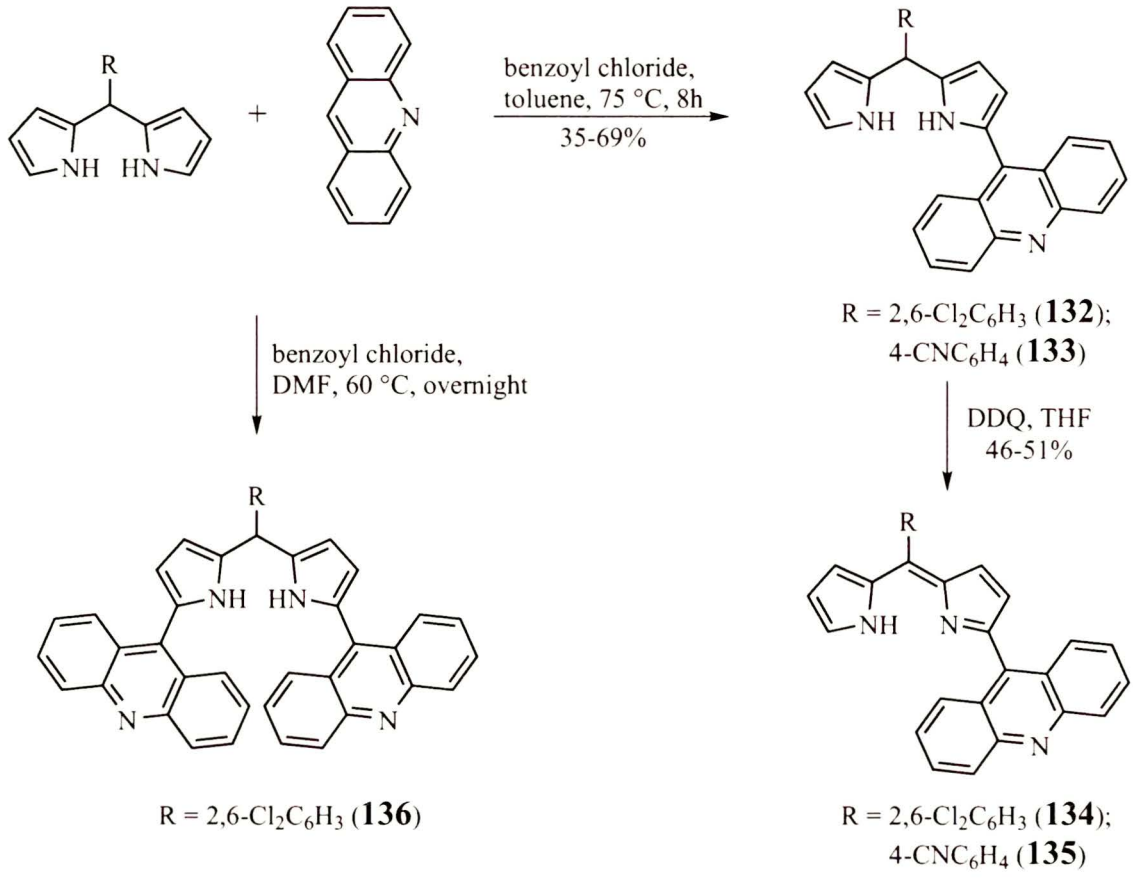
This type of reactivity of pyrrole is interesting and I was curious to study if dipyrrane – a cousin of the pyrrole and at the same time key building block in porphyrinoid chemistry – can react with acridine in a similar manner. Such adducts can show interesting optical properties and can be oxidized then to dipyrrins, altering the electronic properties significantly. The reaction of 5-(2,6-dichlorophenyl)-dipyrrane[97] and 5-(4-cyanophenyl)dipyrrane[167] with acridine was performed using conditions described above but at slightly higher temperatures (Scheme 3.61).

1-(9-Acridinyl)dipyrranes **132** and **133** were formed in good yields and after purification they were transformed into corresponding dipyrrins **134** and **135** *via* oxidation by DDQ in tetrahydrofuran. Comparing to pyrrole, reaction of acridine with dipyrranes appeared to be more selective and in toluene, even at elevated temperature, reaction stopped after first substitution† and even with excess of acridine and benzoyl chloride formation of disubstituted product was not observed. However, after several attempts in different solvents I found, that reactions proceeds very fast in DMF. Thus, I was able to synthesize disubstituted product – 1,9-di(9-acridinyl)-5-(2,6-dichlorophenyl)dipyrrane (**136**) with 88% yield when toluene was substituted with DMF. Optical properties of prepared dipyrrane-acridine adducts are described in section 4.4.

Encouraged by these results I decided to transform acridinepyrrolic chro-

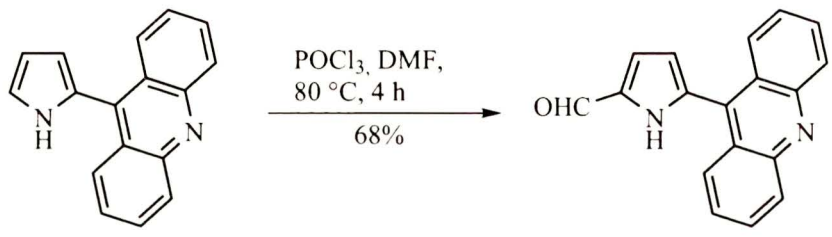
*in the intermediate, before rearomatization of acridine, there is 9-*N*-acylacridanyl substituent which has no pronounced electron withdrawing character

†possible reason for observed selectivity is precipitation of the protonated adduct from the reaction mixture



Scheme 3.61

mophore into the form, suitable for corrole synthesis. The simplest way to achieve this is to introduce formyl group directly into compound **130** (Scheme 3.62).

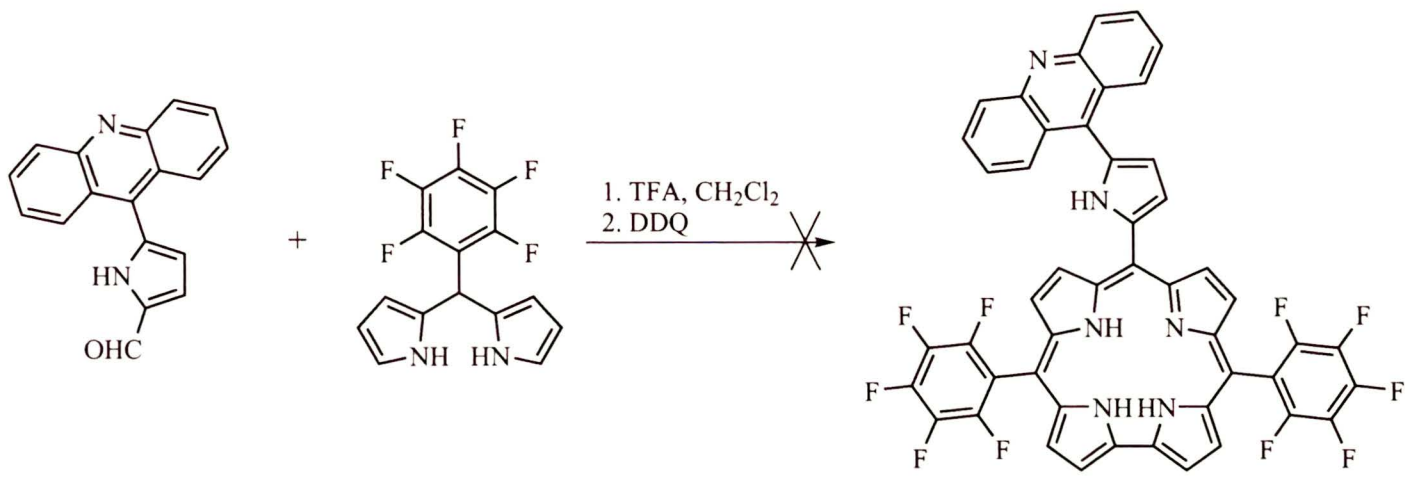


130 **137**

Scheme 3.62

In a first attempt, relatively mild formylation conditions were used, which were considered appropriate for pyrrole derivative (DMF, $POCl_3$, 0 °C), however, only traces of product were formed. When somewhat harsher conditions were used, desired aldehyde was obtained in good yield. The analysis of NMR spectra confirmed monoformylation of **130**. The product was slightly contaminated after two crystallizations and was used in the next step without further purification.

The condensation of aldehyde **137** with 5-(pentafluorophenyl)dipyrrane (**38**) was performed under conditions elaborated for aldehydes bearing basic nitrogen atom[168] (Scheme 3.63).



137 **38**

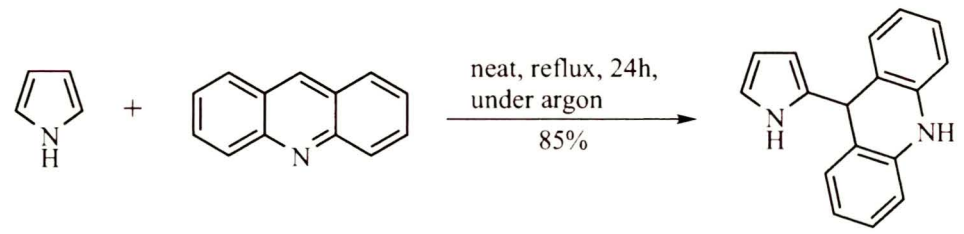
Scheme 3.63

Unfortunately, there were no signs of conversion of aldehyde even after 5 hours and TFA concentration *ca.* 50 mM. After addition of TFA, aldehyde **137** changed its color to deep red and the resulting salt precipitated immediately.

In order to overcome the problem with acridine basicity, I decided to synthesize pyrrole with its reduced analogue (*i.e.* acridane) as a substituent. It was not reported hitherto, however, that it is possible to stop nucleophilic aromatic substitution of hydrogen in acridine itself (or in acridinium salts) on the stage of acridane derivative.[163,164,166,169] The only method of 9-(2-pyrrolyl)acridane synthesis was reported by Treibs and Fligge[164] and involved reduction of corresponding acridine derivative **130** with sodium amalgam. All reported attempts to react pyrrole with acridine in the neat, resulted in a mixture of mono and disubstituted acridinepyrroles,[164,169] but after modification of reaction conditions I was able to prepare monosubstituted acridanylpyrrole **138** in very pure form by increasing pyrrole to acridine ratio dramatically* (Scheme 3.64).

The mixture of pyrrole and acridine was refluxed under inert atmosphere for 24 hours giving desired acridane derivative **138** with good yield after removal of pyrrole excess and silica pad filtration. The product is known to be unstable and

*100-fold excess of pyrrole was used, which than can be recovered by distillation – the trick widely used in dipyrranes syntheses

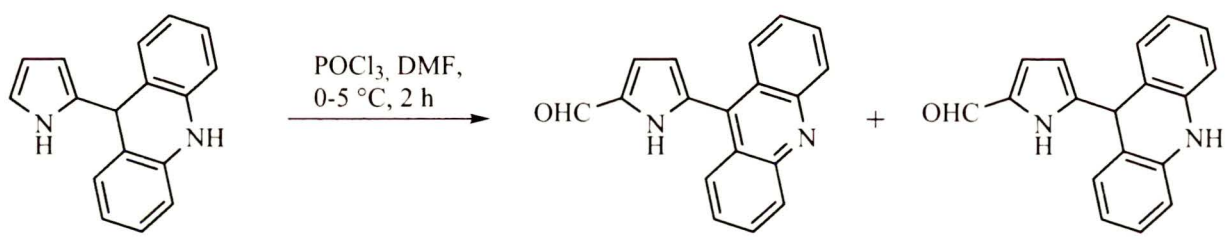


138

Scheme 3.64

oxidize slowly by oxygen present in the air to the corresponding acridine derivative. And indeed, small amount of 9-substituted acridine was formed along with the main product, but purification was straightforward due to the vast difference in polarity of products.

Having prepared derivative **138** bearing dihydroacridine moiety, I decided to attempt Vilsmeier formylation, and after performing the reaction (Scheme 3.65) I found that mixture of aldehydes with similar R_f was formed (TLC).



138 **137** **139**

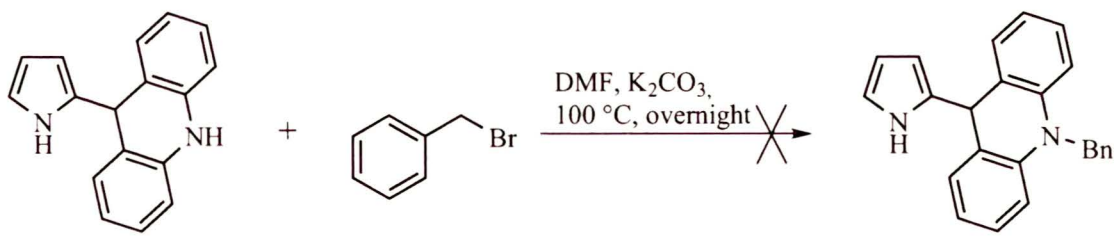
Scheme 3.65

All attempts to separate products failed since reduced aldehyde **139**, similarly to pyrrole **138**, appeared to be unstable and oxidizes by the oxygen from air to aldehyde **137**.

In order to prepare derivative of **138** with "locked" reduced form, I decided to introduce a protective substituent at nitrogen atom of acridane. Consequently, compound **138** was reacted with benzyl bromide in the presence of base and under inert atmosphere (Scheme 3.66).

Unfortunately, desired product was not formed in this reaction* and I decided to introduce benzyl moiety before reacting acridine with pyrrole. That is,

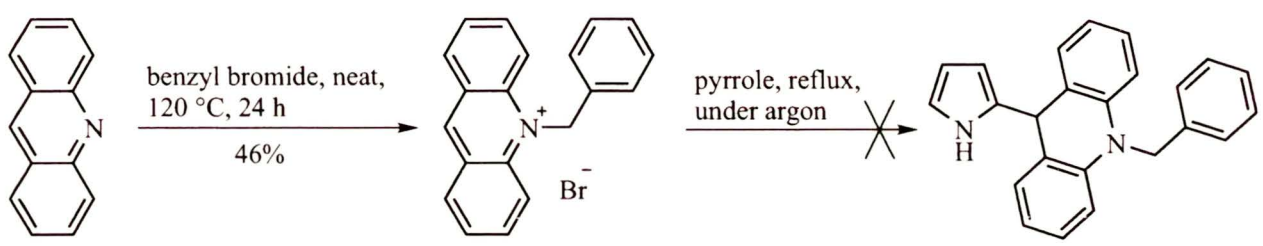
*probably due to low basicity of secondary aromatic amine and possible side reactions on pyrrole ring



138

Scheme 3.66

N-benzylacridinium bromide[170] was refluxed in excess of pyrrole under inert atmosphere for 6 hours (Scheme 3.67).

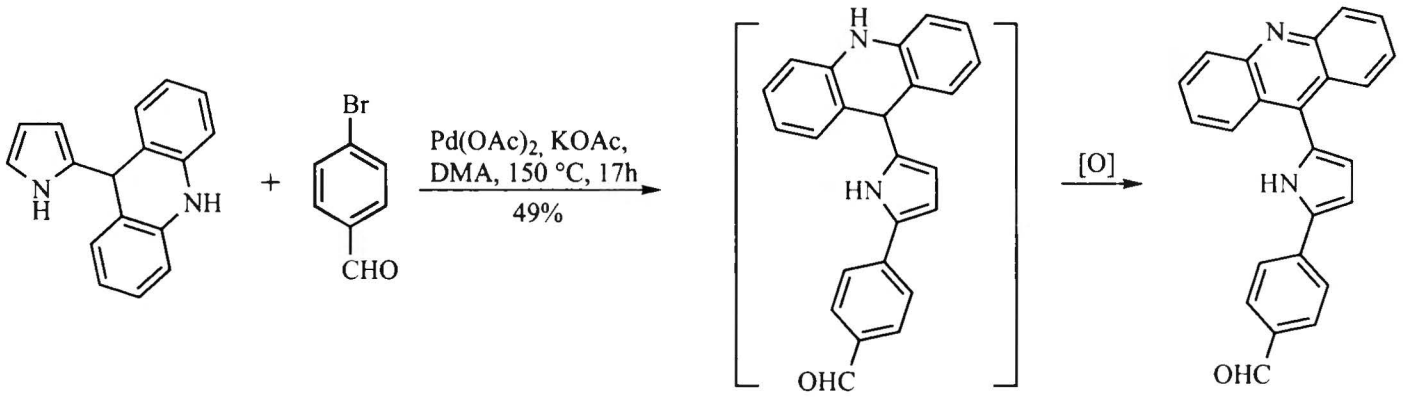


Scheme 3.67

During the reaction, considerable amount of black polymeric material was formed presumably due to pyrrole polymerization in acidic conditions. Surprisingly, after workup, no mono- nor disubstituted product was detected (MS) and as a main product only reduced substrate (10-benzyl-9,10-dihydroacridine) was isolated.

The failure with aldehyde **137** turned my attention to insertion of phenylene linker between pyrrole moiety and corrole core in the final dyad. This can be easily accomplished using recently published procedure for direct pyrrole arylation.[171] Reaction was performed on acridane derivative **138** under Pd-catalyzed conditions with *p*-bromobenzaldehyde (**140**) as haloarene counterpart. After normal workup and chromatographic purification only oxidized product **142** was collected with moderate yield and no acridane derivative **141** was observed on TLC plate (Scheme 3.68).

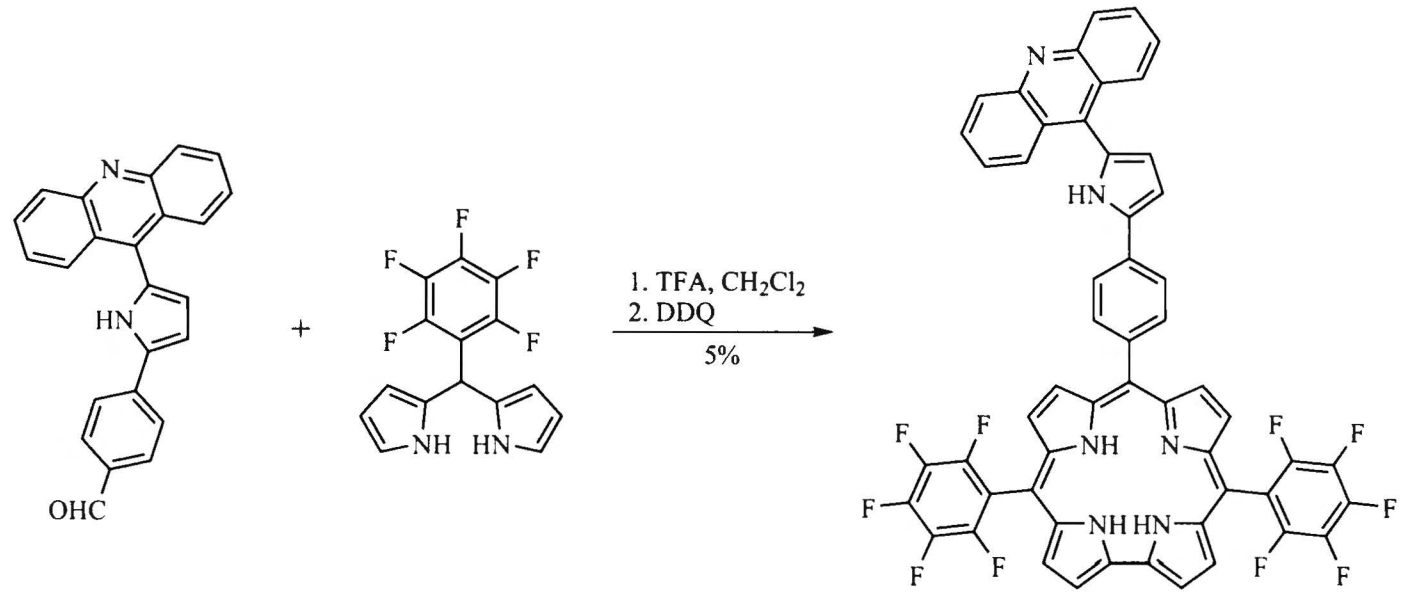
Synthesis of corrole starting from aldehyde **142** was performed using conditions for aldehydes with pyridine-type nitrogen.[168] Condensation of 5-(pentafluorophenyl)dipyrrane (**38**) with aldehyde **142** proceeded as expected and after one hour I was able to observe virtually full conversion of aldehyde (TLC). How-



138 **140** **141** **142**

Scheme 3.68

ever, purification of corrole **143** was not straightforward due to its low solubility in common organic solvents together with the presence of some fluorescent side-products with similar R_f. Consequently, as a final purification step, SEC eluted with THF was used. As a result, I was able to isolate desired corrole **143**, however, with rather low yield (Scheme 3.69). The yields of corroles synthesized from aldehydes containing basic nitrogen atom are known to be relatively low, therefore, I decided to do not optimize further this reaction.



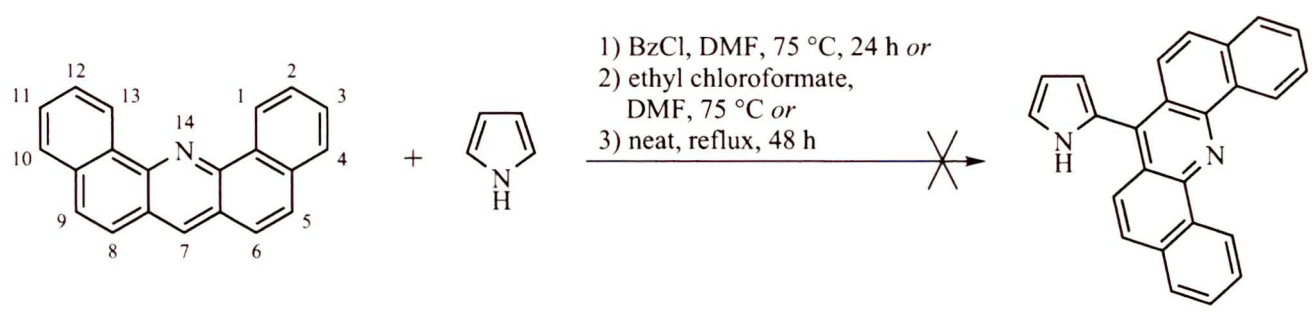
142 **38** **143**

Scheme 3.69

Hetarylation by cyclammonium cations* is known to be quite versatile method-

*acridinium salts are special case of cyclammonium cations (*vide supra*)

ology. Consequently, I decided to study the reaction of π-expanded analogue of acridine – dibenzo[*c,h*]acridine[172] with pyrrole (Scheme 3.70).



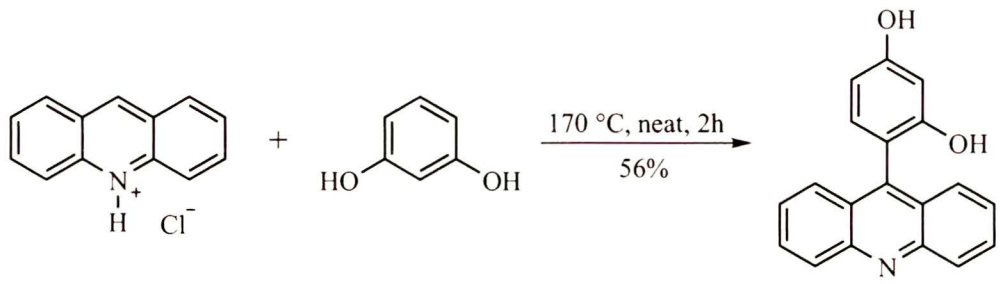
144 **127** **145**

Scheme 3.70

The geometry of dibenzoacridine isomer was chosen among other possible options with intention to avoid steric hindrance near the reaction site – position 7. The same reaction conditions were used as in the case of acridine but, even after prolonged reaction at elevated temperature there was no conversion of the starting material. Refluxing of dibenzoacridine **144** in pyrrole under inert atmosphere also did not give positive results. In the case of acridine derivative activation *via in situ* generation of *N*-acylacridinium salt, the reason for the lack of reaction can supposedly be the crowded position of nitrogen atom (*i.e.* attack of acylating agent on this site can be problematic). Replacement of benzoyl chloride with ethyl chloroformate did not changed reaction outcome. In the light of this failure I can only suggest tentatively, that dibenz[*c,h*]acridine in this case behaves more like pyridine derivative than acridine. That is, based on Clar's theory,[173] electron density is localized mostly on peripheral rings and central pyridine-type ring, while bonds between 5-6 and 8-9 carbons should be considered as rather isolated double bonds. In such situation, disturbing the aromaticity of central pyridine-type ring of dibenzoacridine can require higher activation energy comparing to acridine.

As it was already mentioned on page 94, acridine after activation *via* formation of a salt is able to react with various electron rich aromatic compounds such as dialkylanilines, resorcinol or phloroglucinol. Such adducts might further be transformed into aldehydes for corrole synthesis. I was interested in the adduct of acridine and resorcinol, as it would have two OH groups which can direct introducing of electrophilic reagents in aromatic ring. Corresponding acridine derivative

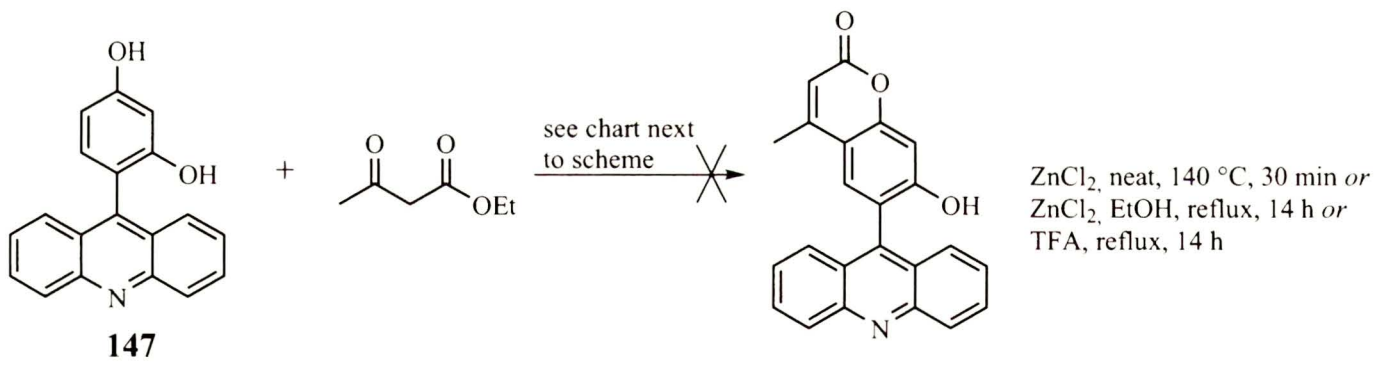
147 was synthesized, as it is shown on scheme 3.71, by reacting acridine hydrochloride (**146**) with resorcinol (**87**) according to procedure proposed by Chupakhin and co-authors.[166a]



146 **87** **147**

Scheme 3.71

The next step of this route would be to form coumarin ring *via* von Pechmann reaction. Second hydroxyl would be suitable site for linking chromophore to pentafluorobenzaldehyde. Consequently, phenol **147** was submitted to condensation reaction with ethyl acetoacetate in the presence of either Lewis or Brønsted acid as a catalyst (Scheme 3.72).



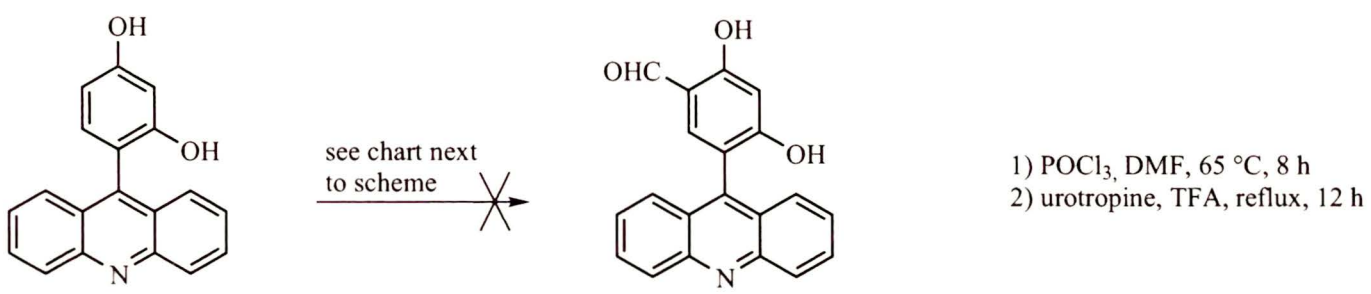
Scheme 3.72

Unfortunately, regardless the type of catalyst and reaction conditions used, I was not able to prepare desired coumarin. The only possible explanation of this reaction outcome can be an electron-withdrawing effect of acridine unit, although the degree of conjugation of both aromatic units can not be high (due to steric hindrance).

Far away from giving up I decided to change the strategy and close the pyranone ring *via* reaction of substituted salicylaldehyde with active methylene compounds. One option was to formylate already prepared phenol **147**. My hopes

regarding this formylation reaction were justified by the fact, that active species in both Vilsmeier and Duff reactions are iminium ions with full positive charge on nitrogen and hence higher reactivity towards electron rich aromatics, comparing to protonated carbonyl group. Problems with regioselectivity should not arise because there is only one unhindered position with two hydroxyls directing concordantly.

Consequently, phenol **147** was submitted to formylation reaction (Scheme 3.73).

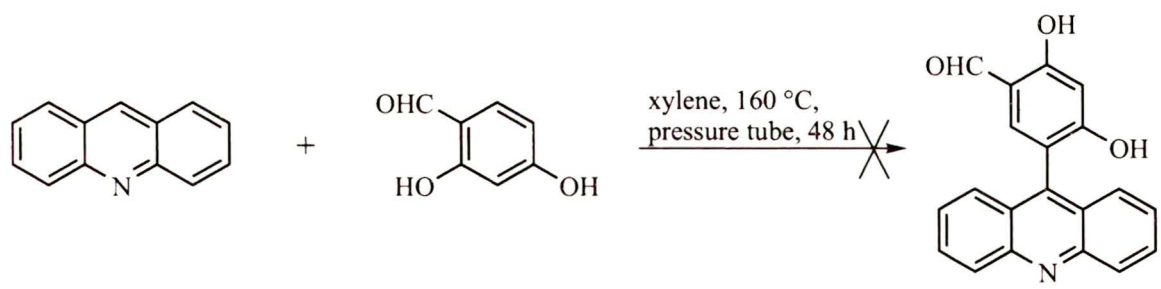


147 **148**

Scheme 3.73

Unfortunately, neither Vilsmeier-Haack nor Duff reaction was successful in transforming phenol **147** to aldehyde **148**.

Alternative pathway which might lead to aldehyde **148** is presented on scheme 3.74.



128 **149** **148**

Scheme 3.74

It involves direct addition of acridine (**128**) to β-resorcylaldehyde (**149**). Initially I decided to start from acridine hydrochloride as it is more reactive than acridine itself, but mixture which was formed was too complex and I was not able to isolate desired aldehyde **148**. Subsequently, reaction was performed with acridine under inert atmosphere in xylene but conversion was slow and finally, after

48 hours, TLC from reaction mixture looked very similar to one from the reaction with acridine hydrochloride. Apparently, β-resorcylaldehyde is not reactive enough for this transformation.

3.5 Corrole-based dyads with other counterparts

A few more corroles have been synthesized which are difficult to subject to systematization from the point of view of current research. These compounds, however, deserve some attention due to the fact, that chromophores incorporated in the dyads, are well established in the world of functional dyes. One can benefit from combination of corrole with this type of chromophores reaching compounds with interesting photophysical properties.

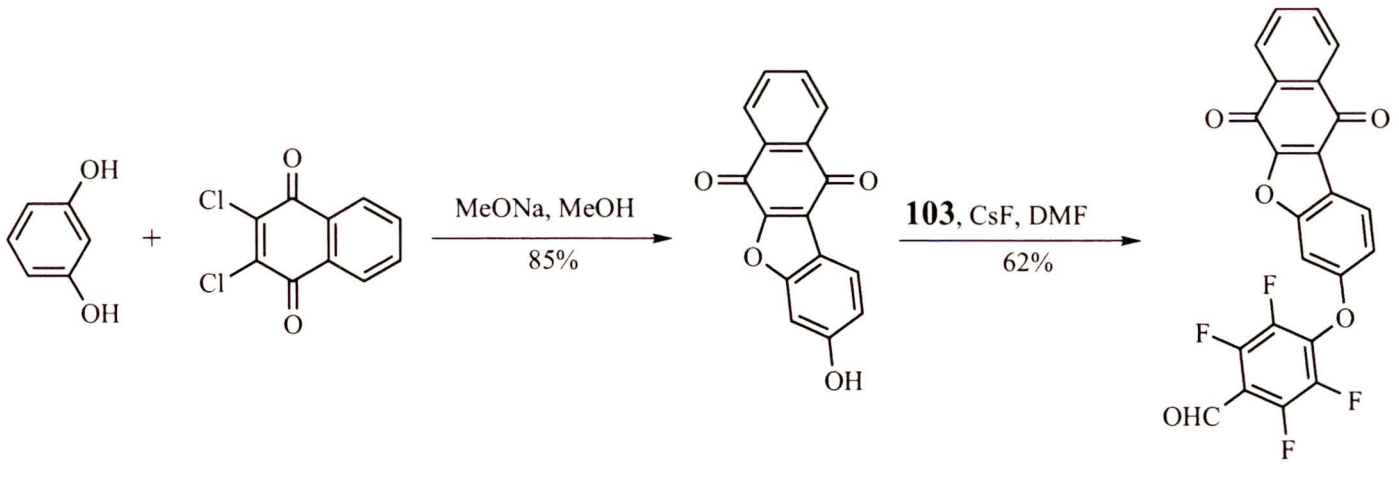
In natural photosynthesis quinones play a crucial role in charge-separation process. Also, in all first dyads and triads, prepared by Gust, Moore or Wasielewski, quinones of various types were utilized.[174] Later on they lost their popularity, since they are often quite reactive, unstable and difficult to incorporate into complex arrays. I decided to try to revitalized this area by introducing complex heterocyclic quinone **151**. I was interested in studying the effect of introduction of the quinone substituent on photophysical properties of corrole-based dyad.

The synthesis of 3-hydroxybenzo[*b*]naphtho[2,3-*d*]furan-6,11-dione – compound discovered more than a century ago – was performed starting from resorcinol and 2,3-dichloronaphthoquinone (**150**) according to known procedure[175] (Scheme 3.75).

Phenol **151** was prepared in good yield and consequently allowed to react with pentafluorobenzaldehyde (**103**) giving desired aldehyde **152** after simple workup and crystallization.

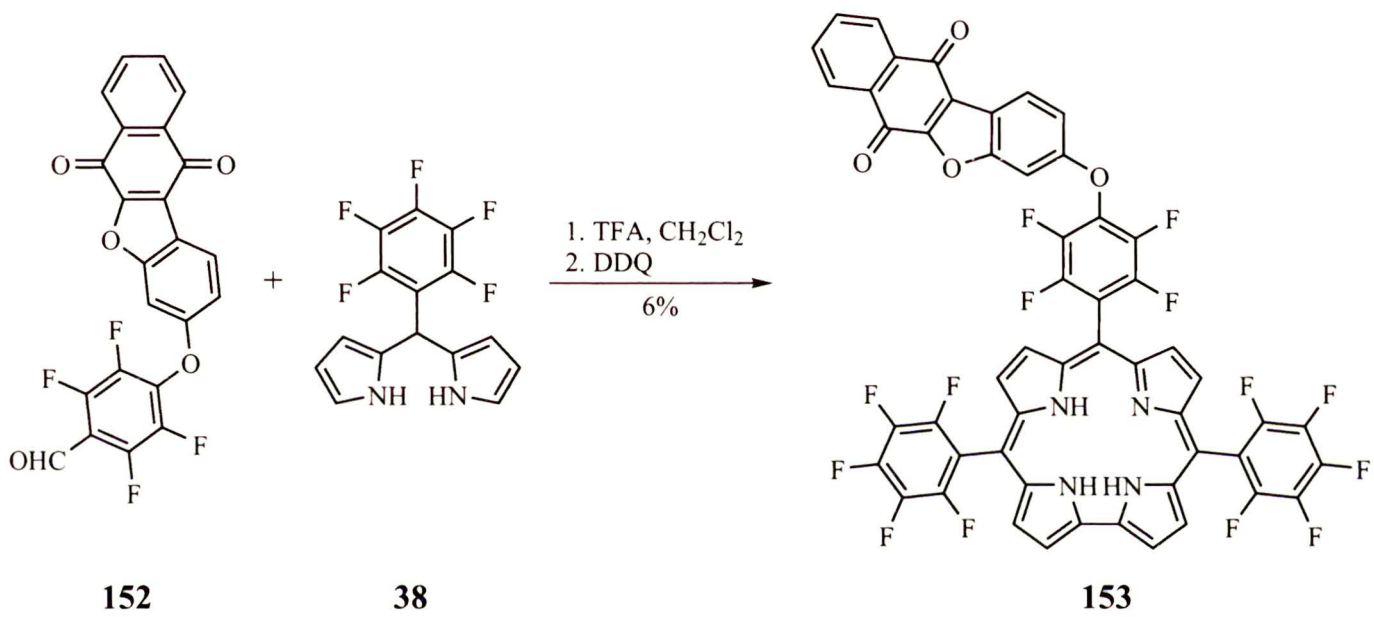
Subsequent condensation of aldehyde **152** with 5-(pentafluorophenyl)dipyrrane (**38**) in the presence of TFA under standard conditions gave desired corrole **153** with relatively low yield (Scheme 3.76).

Even more exciting example of chromophore which can be used to build conjugate with corrole is diketopyrrolopyrrole (DPP).[176] Corresponding DPP derivative was prepared by the reaction of diisopropyl succinate (**154**) with the mixture of aromatic nitriles **155** and **156** (Scheme 3.77).



150 **151** **152**

Scheme 3.75



152 **38** **153**

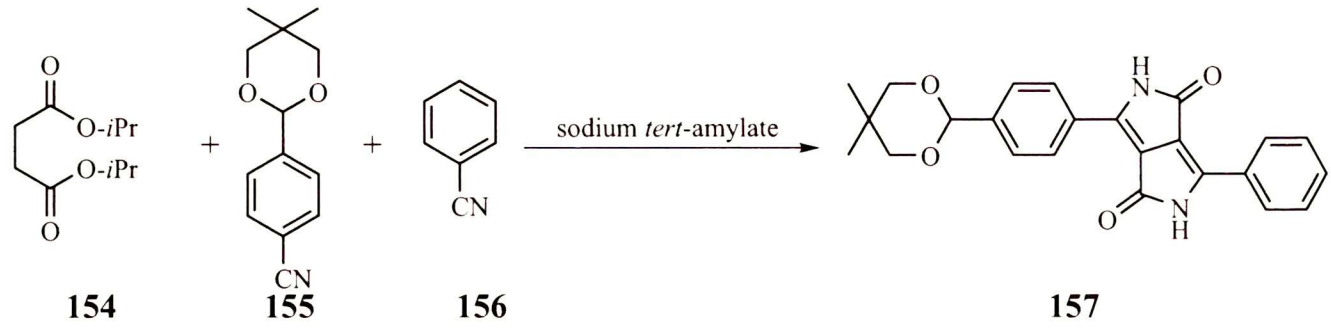
Scheme 3.76

The reaction had statistical character and mixture of symmetrical and unsymmetrical DPPs was formed.*

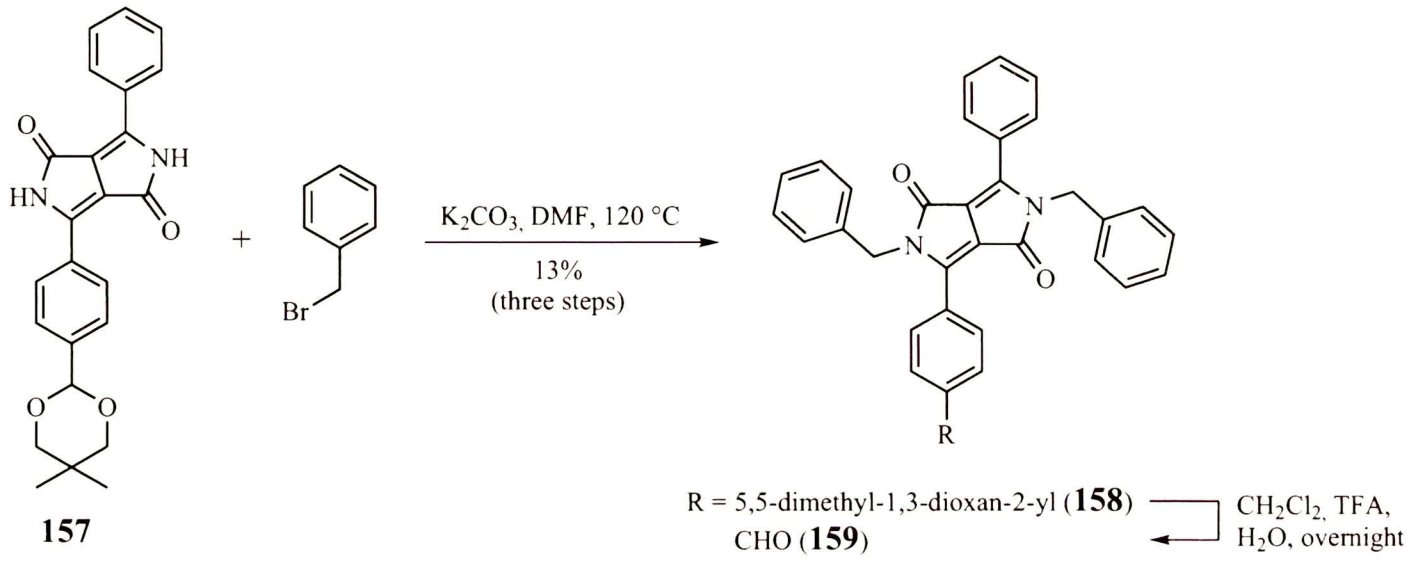
The solubility of products was very low (they are pigments actually) and in order to transform them into the form, suitable for column chromatography purification, I performed alkylation of the crude reaction mixture with benzyl bromide (Scheme 3.78).

After alkylation step and initial purification (rough separation on short column) acetal **158** was cleaved in DCM/TFA/H_2O mixture to form aldehyde **159**

*only one isomer is shown on the scheme for simplicity



Scheme 3.77



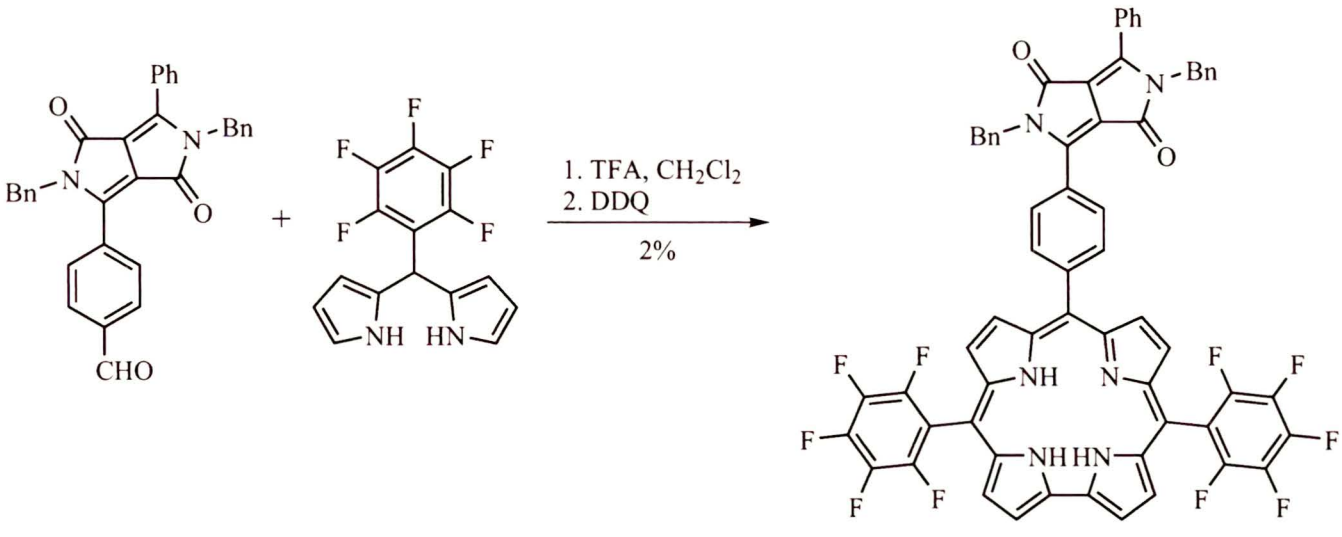
Scheme 3.78

as a shiny orange crystals. The overall yield of **159** after three steps was 13%.*

Consequently, aldehyde **159** was submitted to the condensation reaction with 5-(pentafluorophenyl)dipyrrane (**38**) in the presence of TFA (Scheme 3.79).

After 40 min aldehyde was consumed, reaction was quenched with triethylamine and oxidized with DDQ. To my disappointment, judging from TLC it was obvious that yield will not be too high. Moreover, there were numerous additional fluorescent spots with similar R_f. The product was painstakingly purified by passing it three times through SEC, alternating eluents and one from collected fluorescent fractions was proved to be desired corrole **160**, which was isolated with 2% yield.

*counting the theoretical maximum yield of the key step (statistical cross-condensation) *ca.* 50%



159 **38** **160**

Scheme 3.79

3.6 Corrole-based triads

3.6.1 Introduction

Brief survey of corrole-related literature can reveal constant interest in the corrole scaffold in the context of eT studies.[98,177] The synthesis of corroles from various "imidoaldehydes" was studied in section 3.2 and these results show, that corroles with imide substituents can be synthesized efficiently from the corresponding aldehydes. Most of studied acceptors, however, where not perfectly suitable, based on their electrochemical properties, for eT investigations. From the other side, perylene diimides (PDI) have reputation of good component in multichromophoric systems due to their outstanding physicochemical properties such as intense absorption in green region of visible spectrum, extremely high photostability, fluorescence quantum yield ≈ 1 and characteristic "spectral signature" of anion radicals. As a drawback, very low solubility of simple PDIs in common organic solvents can be mentioned. It is possible, however, to increase solubility by using "swallow-tail" amines.

As a donor counterpart I chose electron-rich triarylamine. Its nitrogen center can be oxidized easily to highly stable radical cation species.[178] The target triad is schematically represented on figure 3.1.

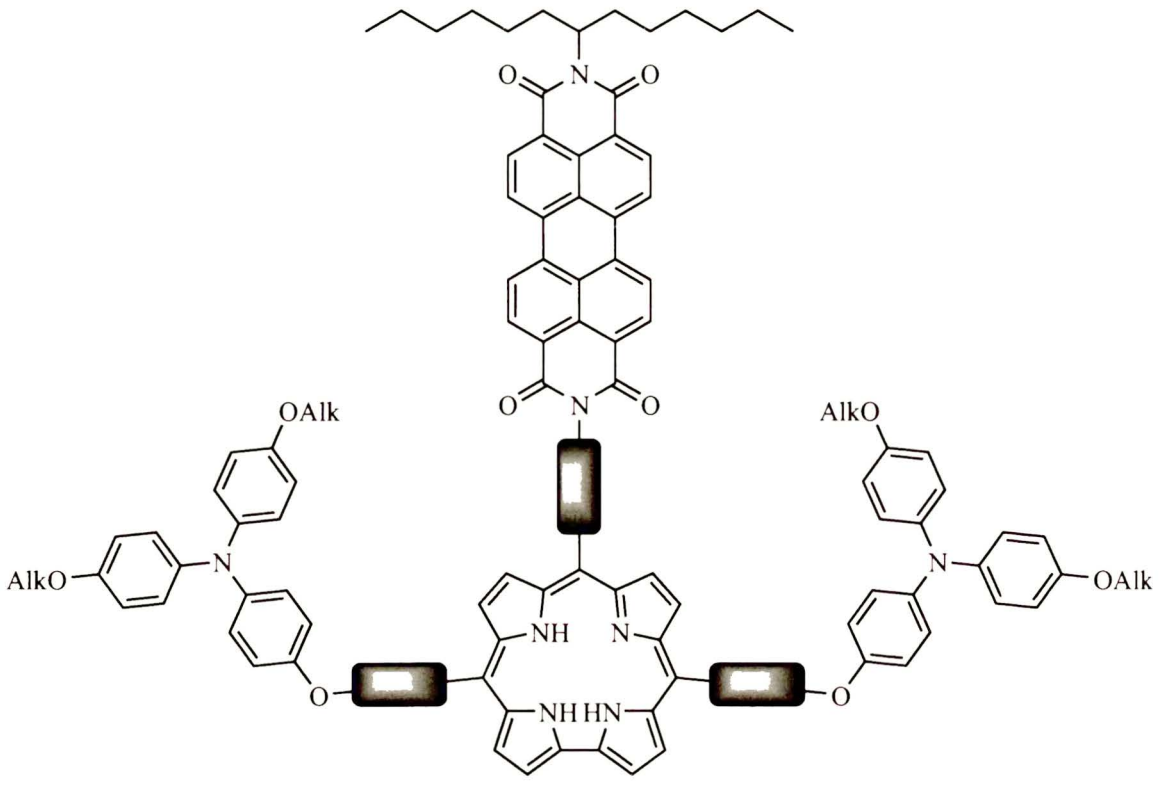


Figure 3.1

3.6.2 Synthesis of primary electron donor

The analysis of possible disconnections and reaction pathways towards donor-bearing dipyrrane is presented on figure 3.2.

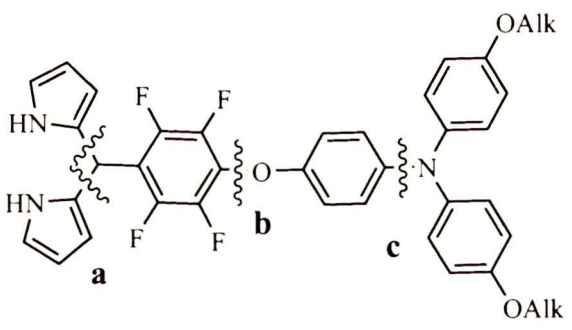
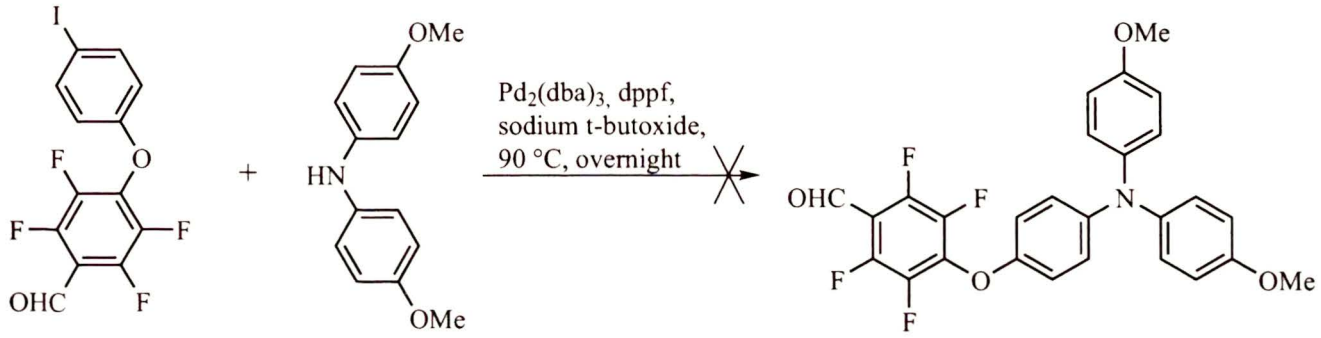


Figure 3.2

Tetrafluorophenylene linker was chosen due to stabilizing effect of fluorine substituents on final corrole. It was also important for me to have reliable method of connecting chromophore to a linker. Reaction of phenols with pentafluorobenzaldehyde, judging from previously described research, can be considered as sufficient for my needs. It is noteworthy, that formation of bond **b** should always precede synthesis of dipyrrane (bonds **a**). This requirement is based on directing

and activating influence of formyl group in pentafluorobenzaldehyde compared to 5-(pentafluorophenyl)dipyrrane.

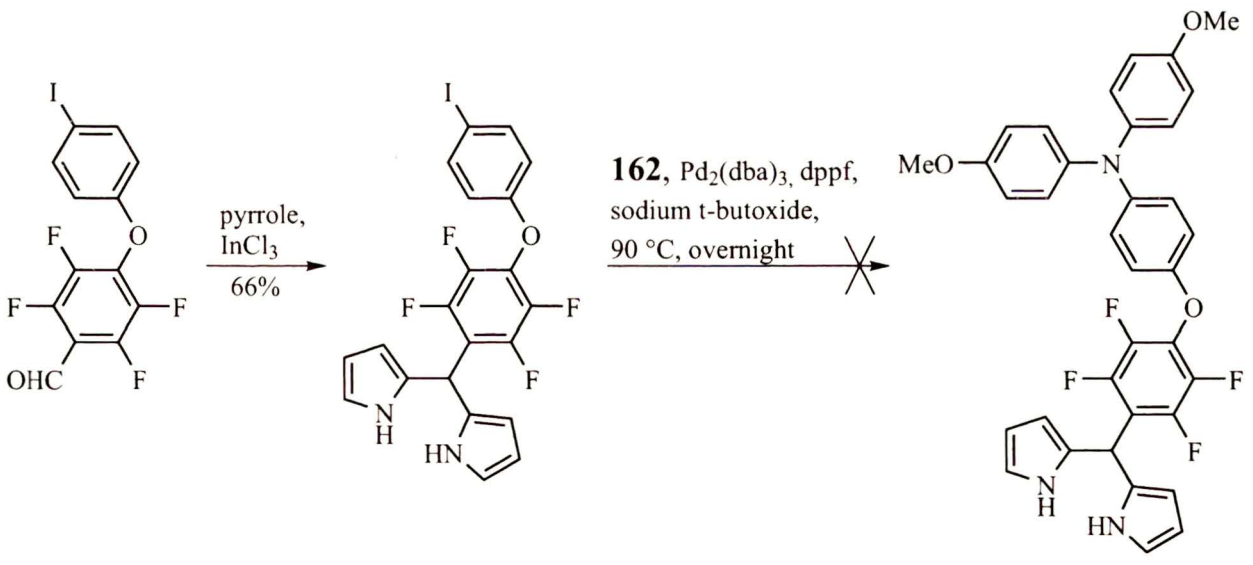
The logical approach towards triarylamine moiety is to start from commercially available diarylamine and to react it with corresponding aryl halide according to Buchwald-Hartwig protocol. Consequently, appropriate iodoaldehyde **161**, which was synthesized according to literature procedure, [126] was reacted with bis(4-methoxyphenyl)amine (**162**) in the presence of Pd-catalyst [179] (Scheme 3.80).



161 **162** **163**

Scheme 3.80

Surprisingly, this reaction failed. I decided to convert aldehyde **161** to corresponding dipyrrane and then repeat attempt of the Buchwald-Hartwig amination. Iodoaldehyde **161** was condensed with pyrrole using indium chloride as a catalyst, [180] giving dipyrrane **164** with good yield (Scheme 3.81).

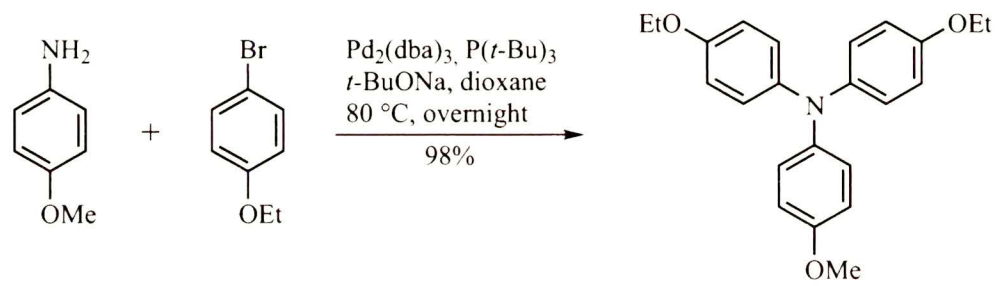


161 **164** **165**

Scheme 3.81

Next step – the reaction with bis(4-methoxyphenyl)amine (**162**) – however, also failed. Discouraged by negative results from aldehyde **161** and dipyrrane **164** aminations, I decided to reverse the order of synthetic steps.

The new target molecule was, in my opinion, 4-(bis-[4-alkoxyphenyl]amino)-phenol because it can be reacted with pentafluorobenzaldehyde to give desired aldehyde. One of the possible ways toward this building block is to synthesize tris-(4-alkoxyphenyl)amine and then cleave one ether bond in order to obtain corresponding monophenol. To improve selectivity and hence the yield of monodeprotection I decided to differentiate alkoxy substituents, that is, to synthesize amine with two 4-ethoxyphenyl units and one 4-methoxyphenyl substituent. Consequently, two molecules of *p*-bromophenetole were reacted with *p*-anisidine using slightly modified procedure proposed by Lamanna *et al.*[181] resulting in formation of desired triarylamine **166** in nearly 100% yield (Scheme 3.82).



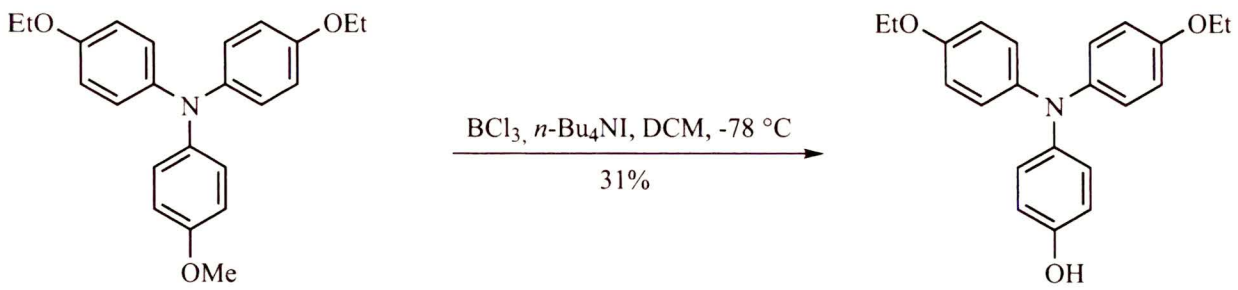
166

Scheme 3.82

Second step, according to the plan, would be selective cleavage of methoxy group. I was expecting that slightly more sterically hindered ethoxy group will react slower under applied conditions. And indeed, after treating trisalkoxyphenylamine **166** with boron trichloride[182] as it is shown on scheme 3.83 I was able to isolate desired diarylaminophenol **167**.

Reaction appeared to be not selective enough and along with monodeprotected product, the presence of considerable amounts of products of further deprotection were detected on the TLC. Overall yield of monophenol **167** was far from satisfactory for the current stage of synthesis of target dipyrrane and I decided to seek for another way towards this type of hydroxytriarylamine.

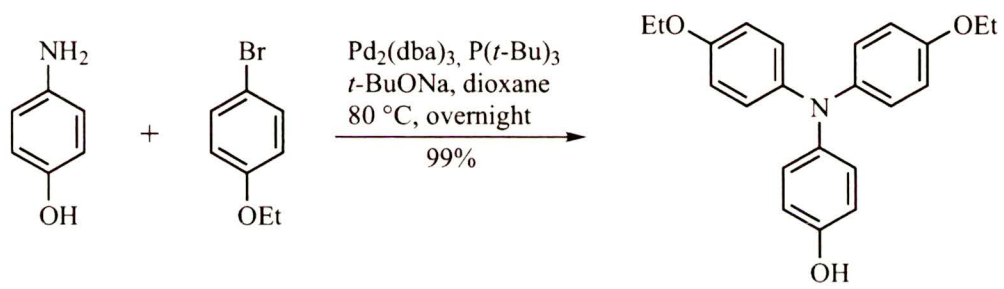
During Buchwald-Hartwig aminations, carried out previously, I was usually avoiding combination of base-sensitive groups and sodium *tert*-butoxide. However,



166 **167**

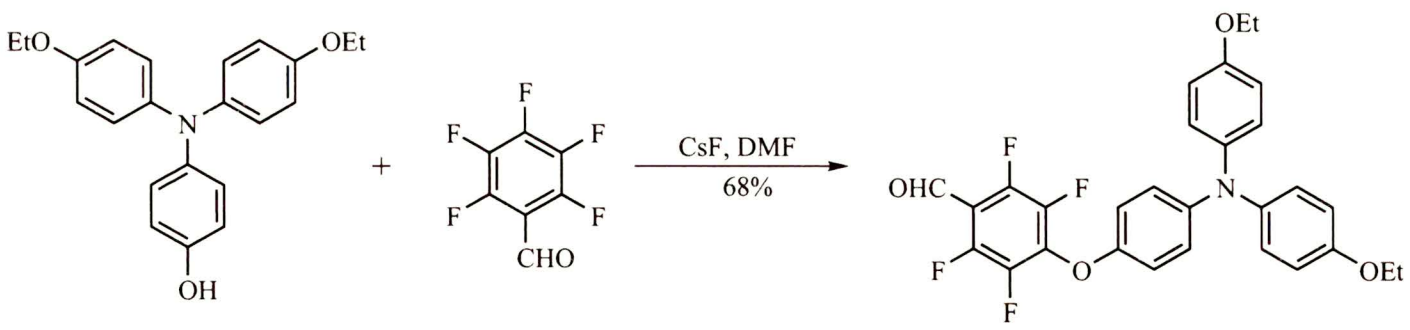
Scheme 3.83

when similarly to transformation shown on scheme 3.82, instead of *p*-anisidine 4-aminophenol was used, desired hydroxytriarylamine **167** was formed with excellent yield (Scheme 3.84). Subsequent reaction of **167** with pentafluorobenzaldehyde in the presence of cesium fluoride gave aldehyde **168** with good yield (Scheme 3.85).



167

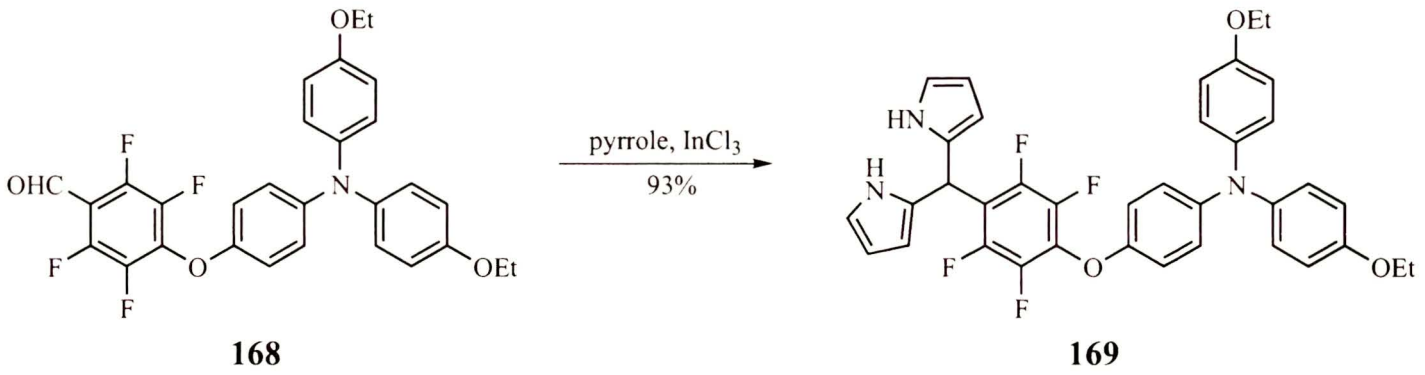
Scheme 3.84



167 **168**

Scheme 3.85

Using standard conditions aldehyde **168** was condensed with pyrrole in the presence of indium chloride giving desired dipyrrane **169** with surprisingly high yield (Scheme 3.86).

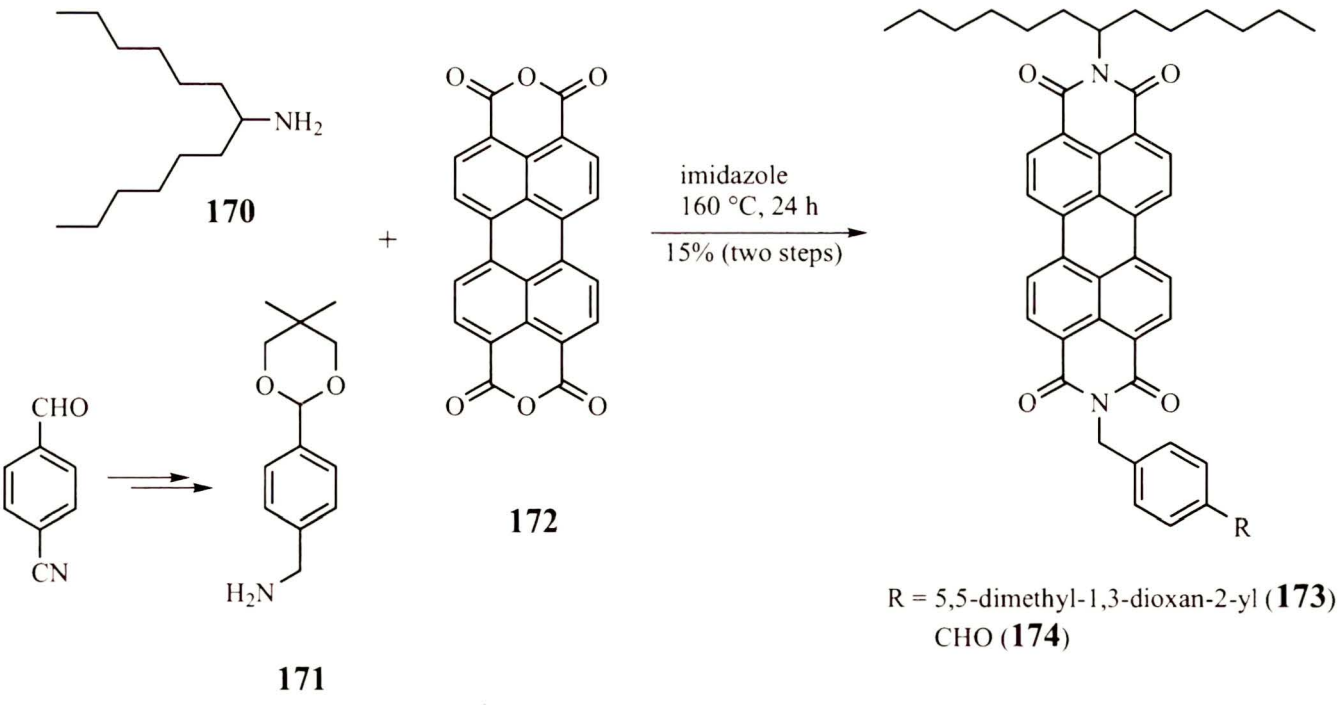


Scheme 3.86

I was not able to crystallize product and it was obtained in the form of dried foam. All analysis data, however, showed satisfactory purity.

3.6.3 Synthesis of perylene diimide possessing formyl group

There are only three examples of corrole-PDI dyads published to date.[177e] In my investigation I decided to build up upon previously developed routes as well as reaction conditions. The plan was to attach PDI-based acceptor to corrole core by α,4-dehydrotoluene linker. Desired aldehyde was synthesized using known procedure (Scheme 3.87).



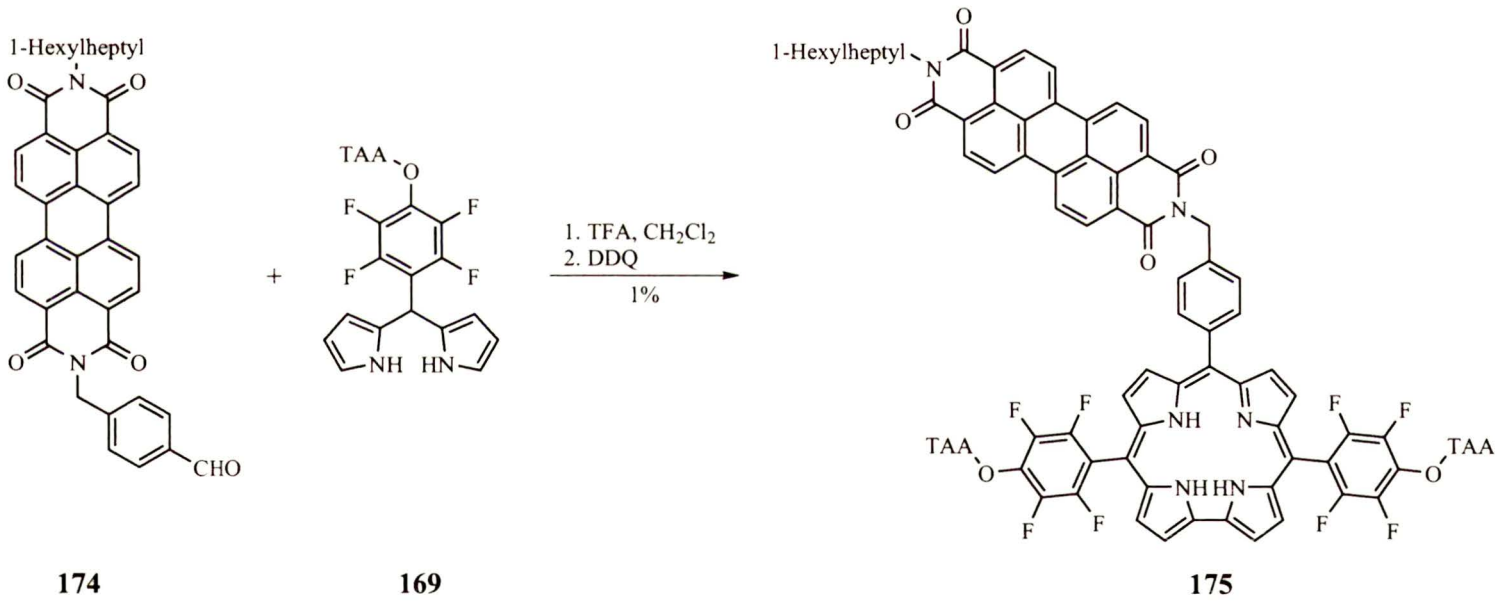
Scheme 3.87

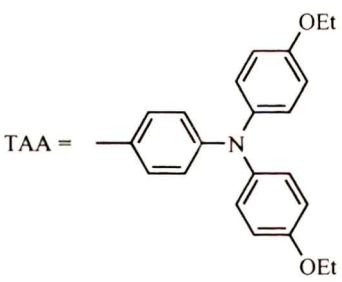
3,4,9,10-Perylenetetracarboxylic dianhydride (**172**) was condensed with 1-

hexylheptylamine (**170**), which was prepared by reductive amination of corresponding ketone, and amine **171**, prepared in two steps from commercially available *p*-cyanobenzaldehyde. It is noteworthy, that condensation reaction proceeds in statistic regime and the mixture of comparable amounts of three diimides is formed. It is possible, however, to separate all components by column chromatography. It is important to emphasize here, that amino group of protected aldehyde has to be benzylic (aromatic amines are much less reactive comparing to aliphatic amines in a condensation reaction with this anhydride).

The acetal protection of aldehyde was not cleaved under condensation reaction conditions and additional deprotection step was necessary to convert **173** to aldehyde **174**.

The next step, according to the plan, was condensation of aldehyde **174** with dipyrrane **169** (Scheme 3.86 on the facing page), containing triarylamine fragment – here and further abbreviation TAA will be used for convenience (Scheme 3.88).





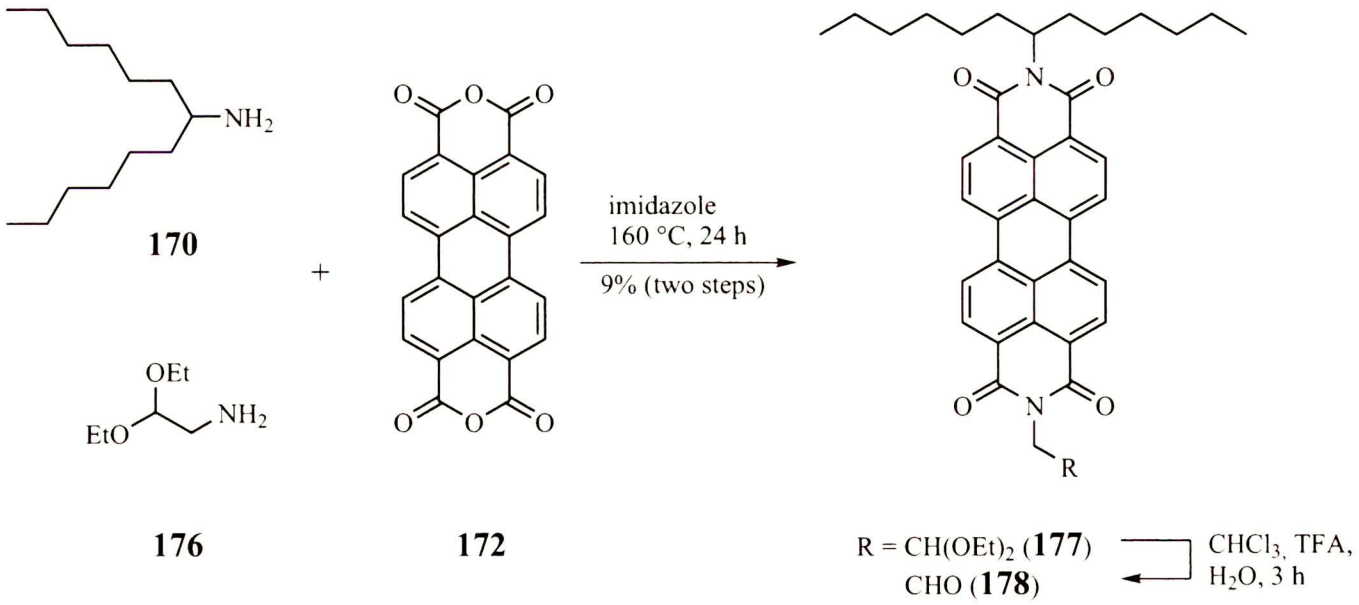
Scheme 3.88

The reaction conditions were standard for this type of aldehyde ($C_{TFA} \approx$

27 mM) but, to my disappointment, desired corrole **175** was isolated with really miniscule yield. It appeared to be very unstable on TLC and light sensitive. Moreover, MS measurement with such mild ionization method as field desorption, showed molecular peak of very low intensity and recognizable fragmentation pattern.

This behavior of corrole **175** was interesting and I decided to study, if there is any correlation between linker type and triad stability. My plan was to find the most stable arrangement of chromophores and then develop that structure to the set of models (dyads), required for photochemical investigations of charge transfer processes.

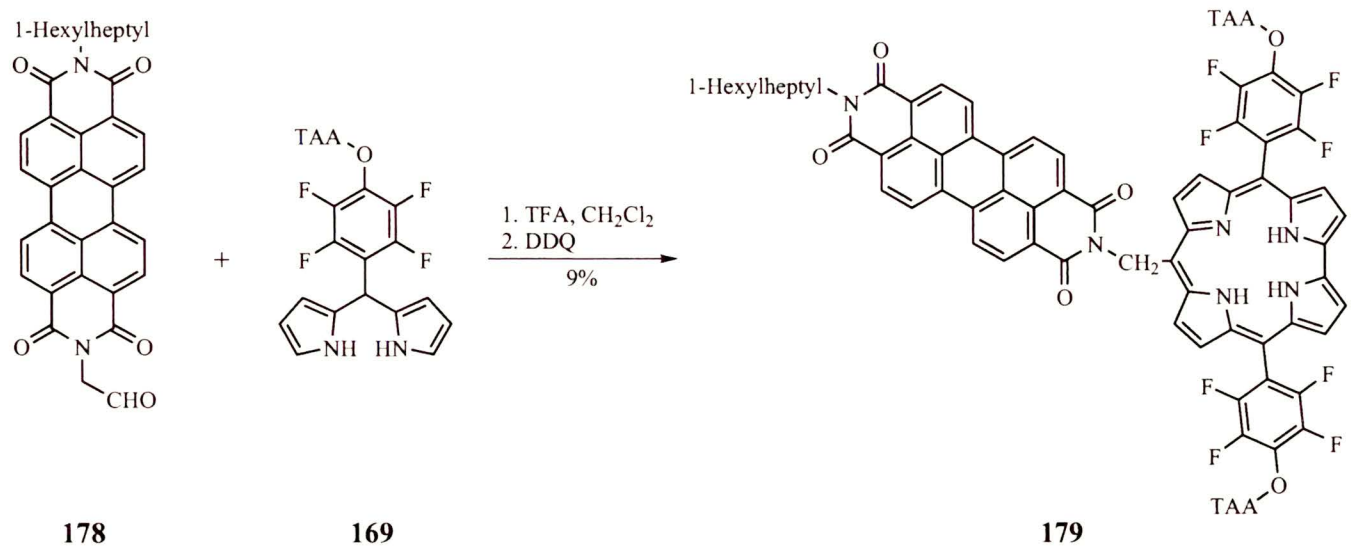
The next linker between PDI and corrole which I studied was methylene unit. The target corrole synthesis has to start from corresponding, substituted acetaldehyde. Thus, perylenetetracarboxylic dianhydride **172** was condensed with 1-hexylheptylamine (**170**) and aminoacetaldehyde diethyl acetal (**176**) under conditions used for aldehyde **174** (Scheme 3.87 on page 112) as it is shown on scheme 3.89.



Scheme 3.89

As a result, after straightforward purification, acetal **177** was isolated, though, with somewhat lower yield. Apparently, the reaction conditions, used for condensation of amines with anhydride **172**, were quite mild, since diethyl acetal remained untouched. The unsuccessful attempt was made to submit acetal **177** directly to reaction with dipyrrane hoping that under acidic catalysis deprotection of aldehyde and condensation step will proceed "one pot". Consequently, the reaction of

dipyrrane was repeated with deprotected aldehyde **178** according to scheme 3.90.



178 **169** **179**

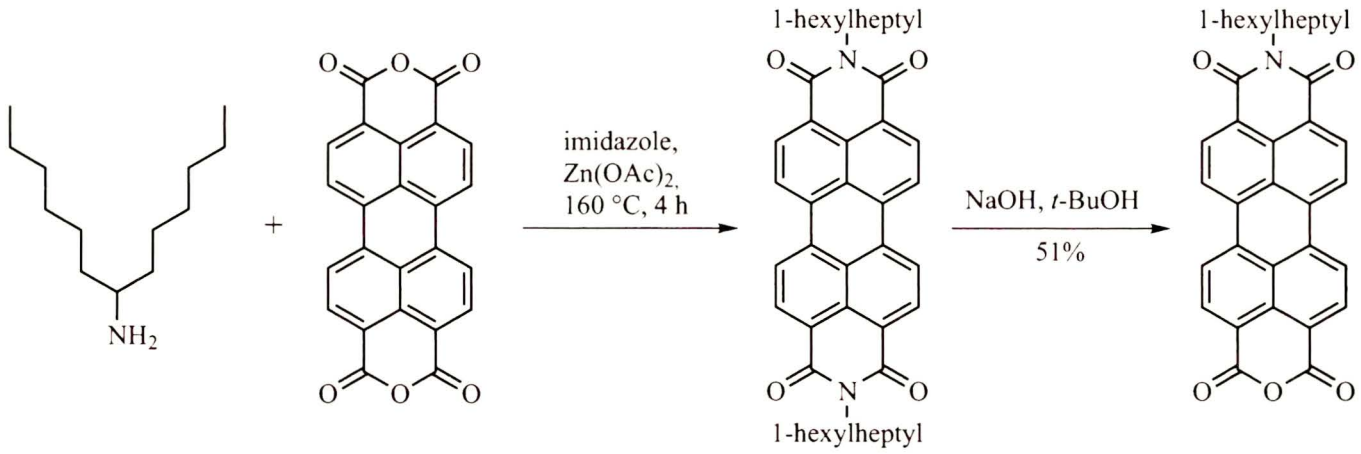
Scheme 3.90

The reaction was started at 0 °C and concentration of TFA ≈ 13 mM to gain better control on the reaction progress. Reaction mixture was allowed to warm to ambient temperature but after one hour there were still no signs of reaction. Concentration of TFA was raised up to *ca.* 50 mM but during next hour there were no changes (judging from TLC). To my great surprise, after 24 h reaction mixture clarified completely and there were almost no aldehyde on TLC. After oxidation and common workup I was able to isolate desired corrole **179** with good (as for aliphatic aldehyde) yield.

I also decided to synthesize triad with acceptor connected to corrole *via* *p*-phenylene linker. It is, however, difficult to prepare corresponding mixed PDI in one step from 3,4,9,10-perylenetetracarboxylic dianhydride because of wast difference in reactivity of aliphatic and aromatic amines.

I started the synthesis of desired PDI-based aldehyde from preparation of monoanhydride **181** which was synthesized by partial saponification of symmetrical diimide (**180**) using known procedure[183,184] (Scheme 3.91).

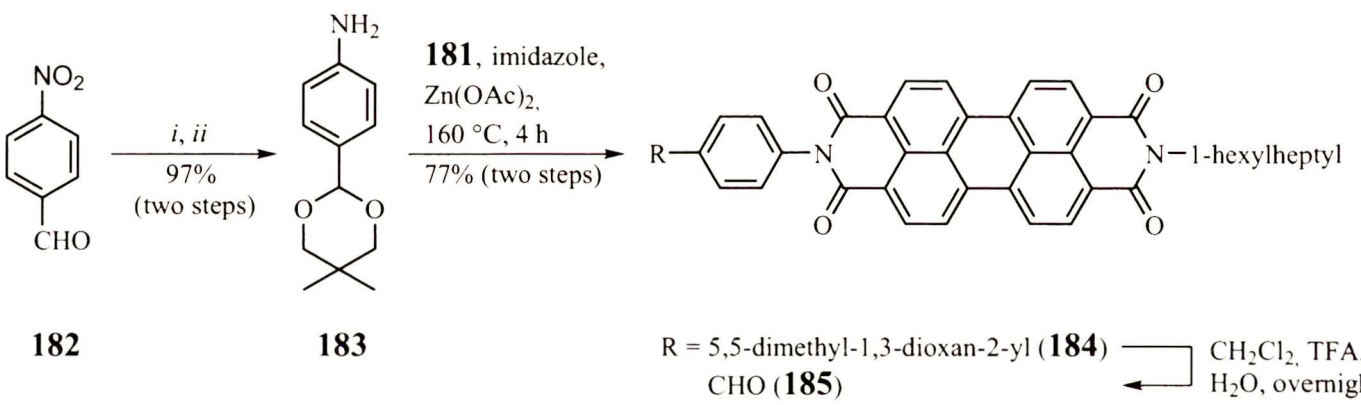
Monoanhydride **181** now can be reacted with aromatic amine giving mixed PDI. Protected 4-aminobenzaldehyde (**183**) was derived in two steps from *p*-nitrobenzaldehyde (**182**) and subsequently reacted with anhydride **181** under published conditions[185] giving, after deprotection, desired aldehyde **185** with good yield



170 **172** **180** **181**

Scheme 3.91

(Scheme 3.92).



182 **183**

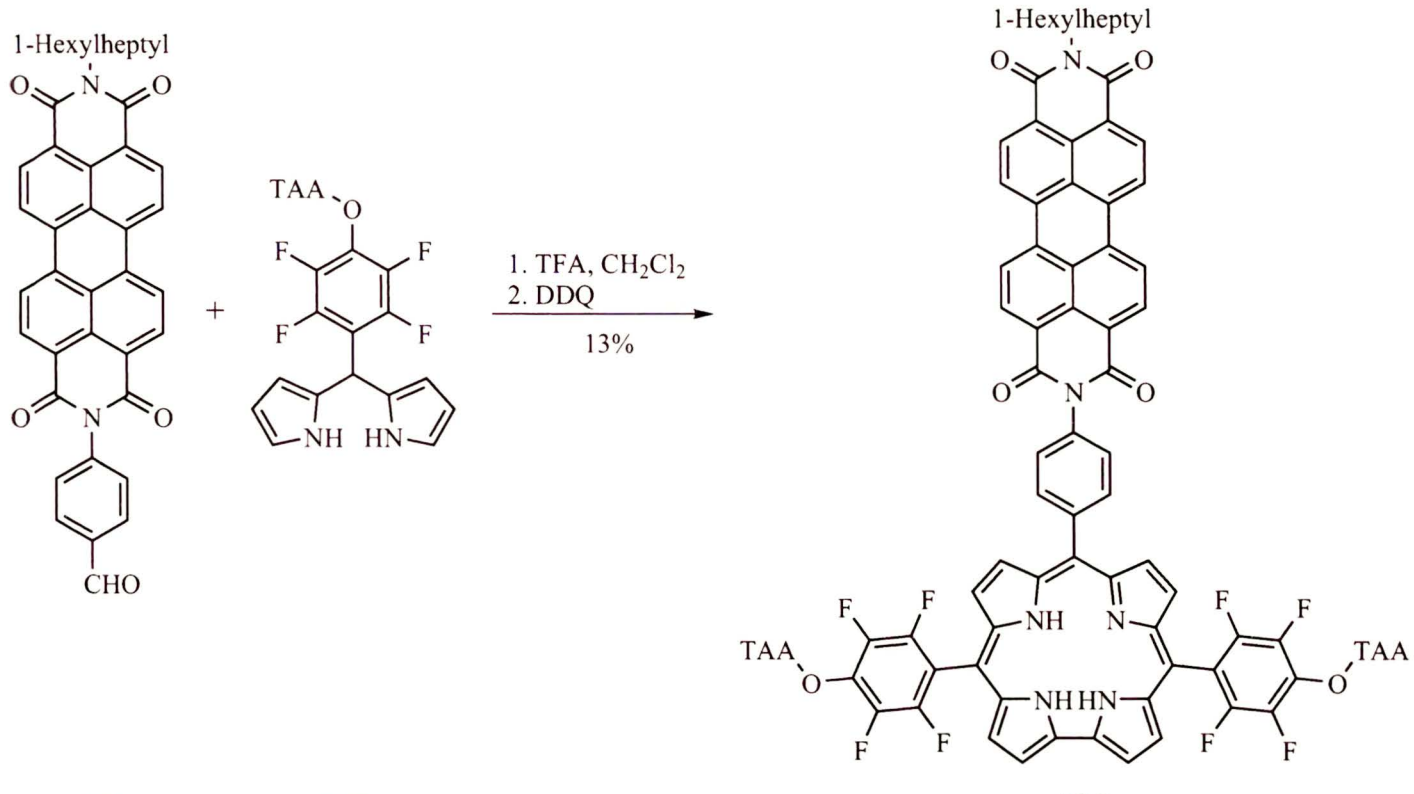
i. 2,2-dimethylpropane-1,3-diol; *ii*. H_2, Pd/C

Scheme 3.92

Consequently, aldehyde **185** was condensed with dipyrrane **169** in the presence of TFA (Scheme 3.93).

The condensation of TFA in starting solution was *ca.* 13 mM, but after 20 min no signs of reaction were observed on TLC. After increasing TFA concentration to 27 mM and stirring for one hour I noticed that aldehyde partially disappeared along with starting spot formation (TLC). To diminish side reactions I decided to quench the reaction at this point and after oxidizing with DDQ I was able to isolate desired corrole **186** with 13% yield. Stability of product was satisfactory and purification was straightforward.

Having positive result in triad synthesis I decided to synthesize group of model compounds, necessary for its photochemical investigation. Firstly, hydroxytriary-



178 **169** **186**

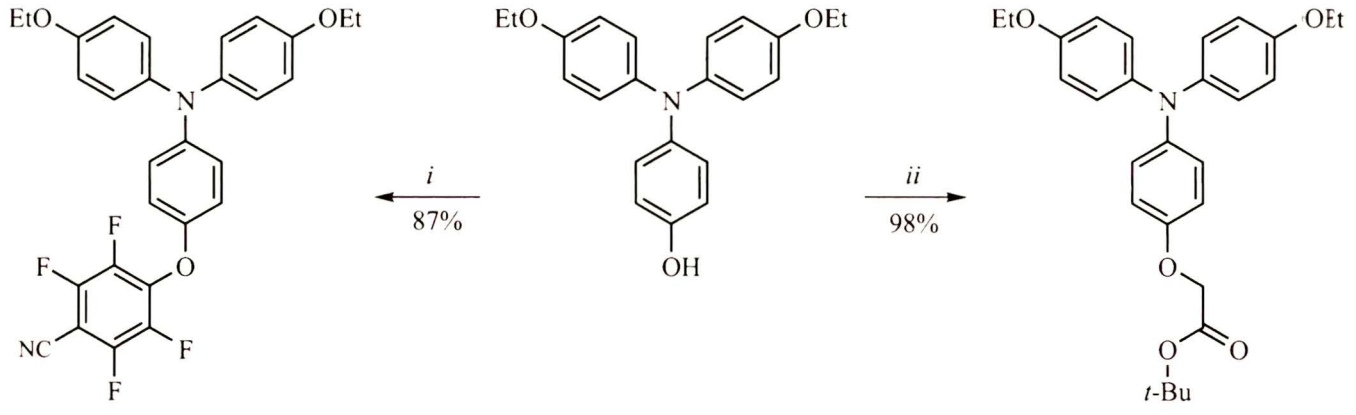
Scheme 3.93

lamine **167** was reacted with pentafluorobenzonitrile (**107**) under standard conditions (Scheme 3.94) giving desired triarylamine derivative **187**.

The product appeared, however, to have rather weak fluorescence and, due to this fact, measurements of fluorescence decay were complicated. Endeavouring to solve this issue, I decided to synthesize triarylamine derivative with substituent, which has not so prominent electron withdrawing properties as *p*-cyanotetrafluorophenyl. Consequently, phenol **167** was alkylated with *tert*-butyl chloroacetate (**188**) in the presence of a base, giving desired triarylamine derivative **189** with excellent yield.

The model compound, containing only two types of chromophores (corrole core and triarylamine substituents) was synthesized by condensation of dipyrrane **169** with *p*-tolylaldehyde under standard conditions. After simple workup and purification corrole **190** was isolated with good yield (Scheme 3.95). It is worth to mention that mainly porphyrin formed when increased concentration of TFA was used.

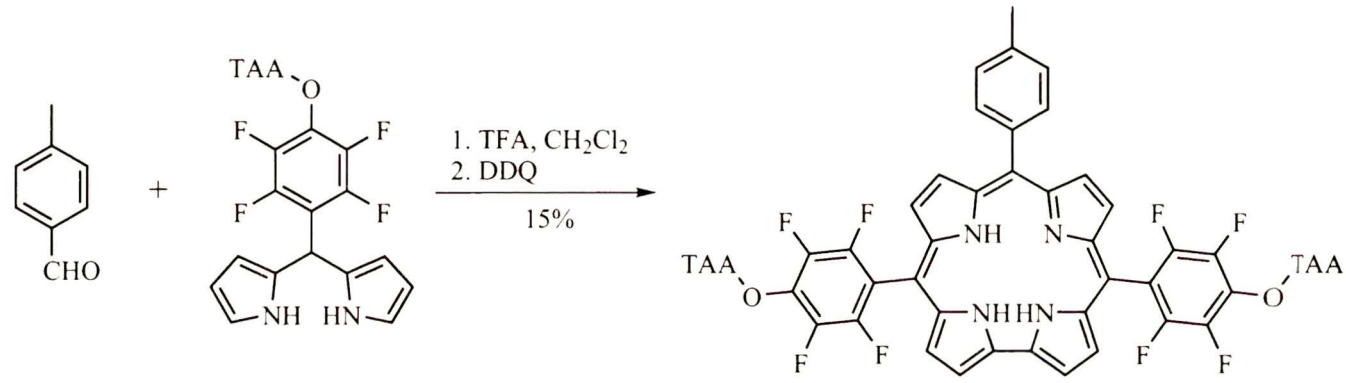
Inasmuch as photochemical properties of perylene diimides are widely studied in the literature, there was no need to synthesize separate model compound with



187 **167** **189**

i. pentafluorobenzonitrile (**107**), CsF, DMF; *ii*. *tert*-butyl chloroacetate (**188**), $CsCO_3$, DMF, 70 °C

Scheme 3.94



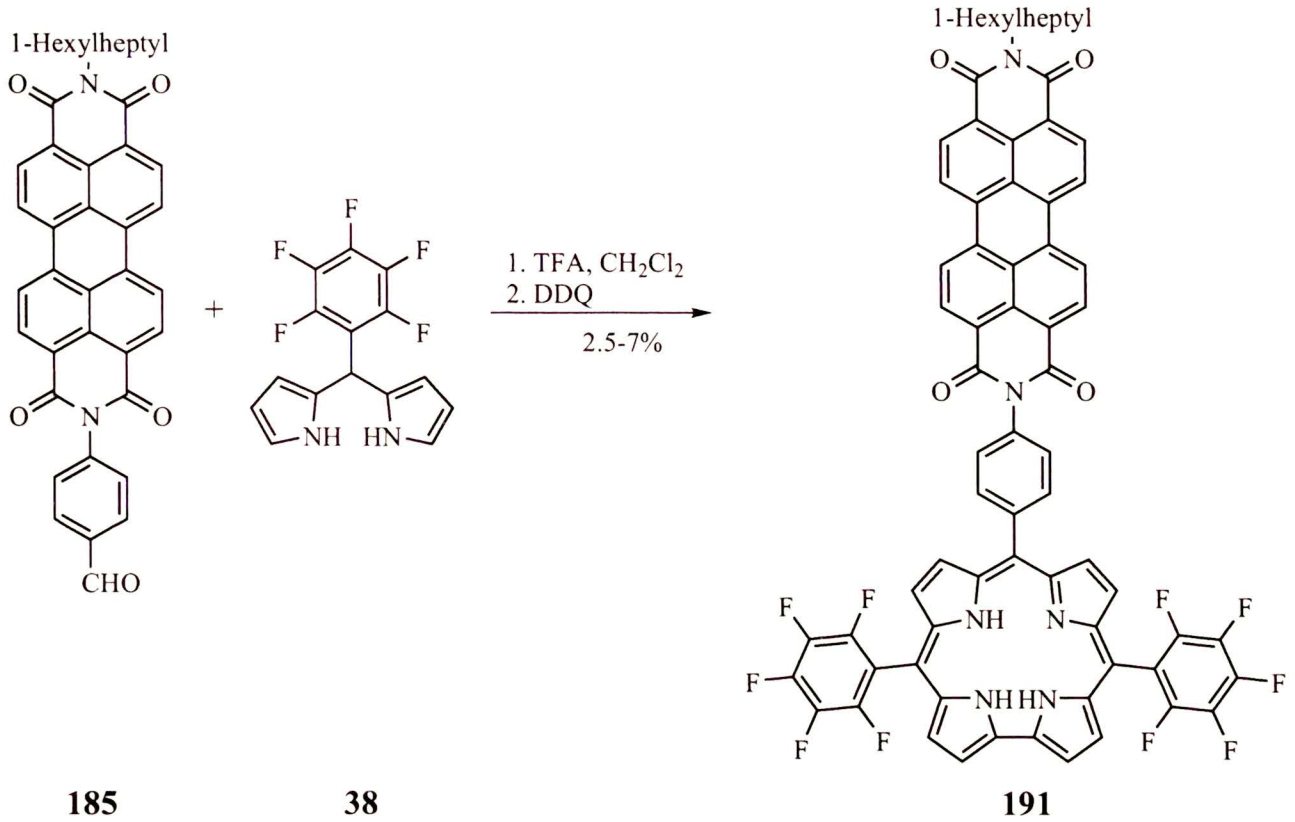
169 **190**

Scheme 3.95

only PDI chromophore thereafter.

The corrole-PDI dyad **191** was synthesized by the condensation of aldehyde **185** with 5-(pentafluorophenyl)dipyrrane (**38**), catalyzed by TFA (Scheme 3.96). Regardless relative simplicity of substrates, reaction appeared to be capricious. That is, under classical conditions ($C_{TFA} \approx 13\,mM$), after 20 min some reaction progress was visible on TLC but, after quenching and oxidation step, only traces of corrole were detected. When reaction was allowed to proceed for one hour without changing TFA concentration, corrole **191** was isolated in 2.6% yield. Doubling of TFA concentration allowed to increase the yield up to 7% but on TLC many spots appeared, indicating the presence of side reactions. Corrole **191** itself appeared unexpectedly to be very unstable and its fluorescence decay on TLC was very fast.

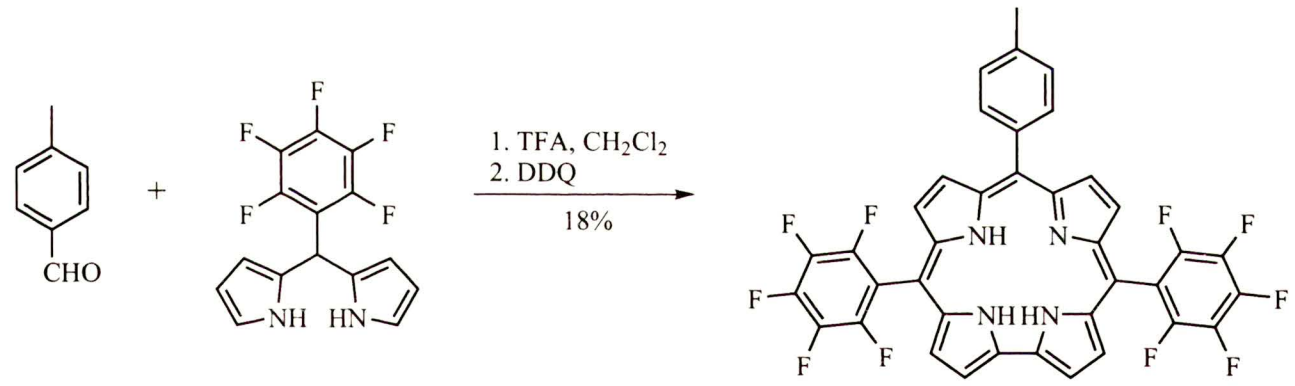
Finally, the model compound **192**, possessing corrole as a sole chromophore,



185 **38** **191**

Scheme 3.96

was synthesized following published procedure [91] from *p*-tolualdehyde and 5-(pentafluorophenyl)dipyrrane (**38**, Scheme 3.97).



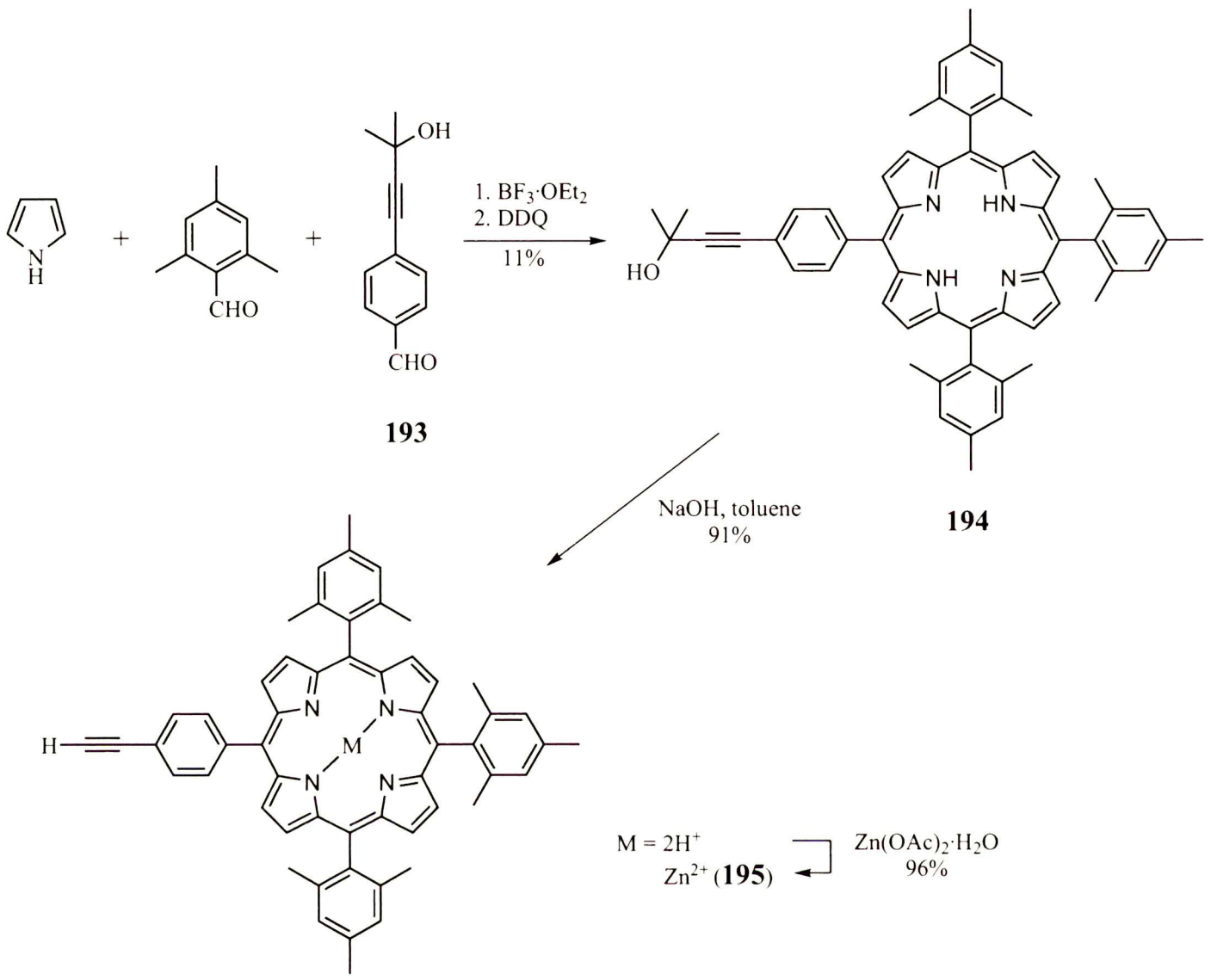
38 **192**

Scheme 3.97

3.7 Corrole-porphyrin triad

Among other possible combinations of chromophores I have chosen to synthesize triad possessing both corrole and electron-rich Zn-porphyrin, accompanied

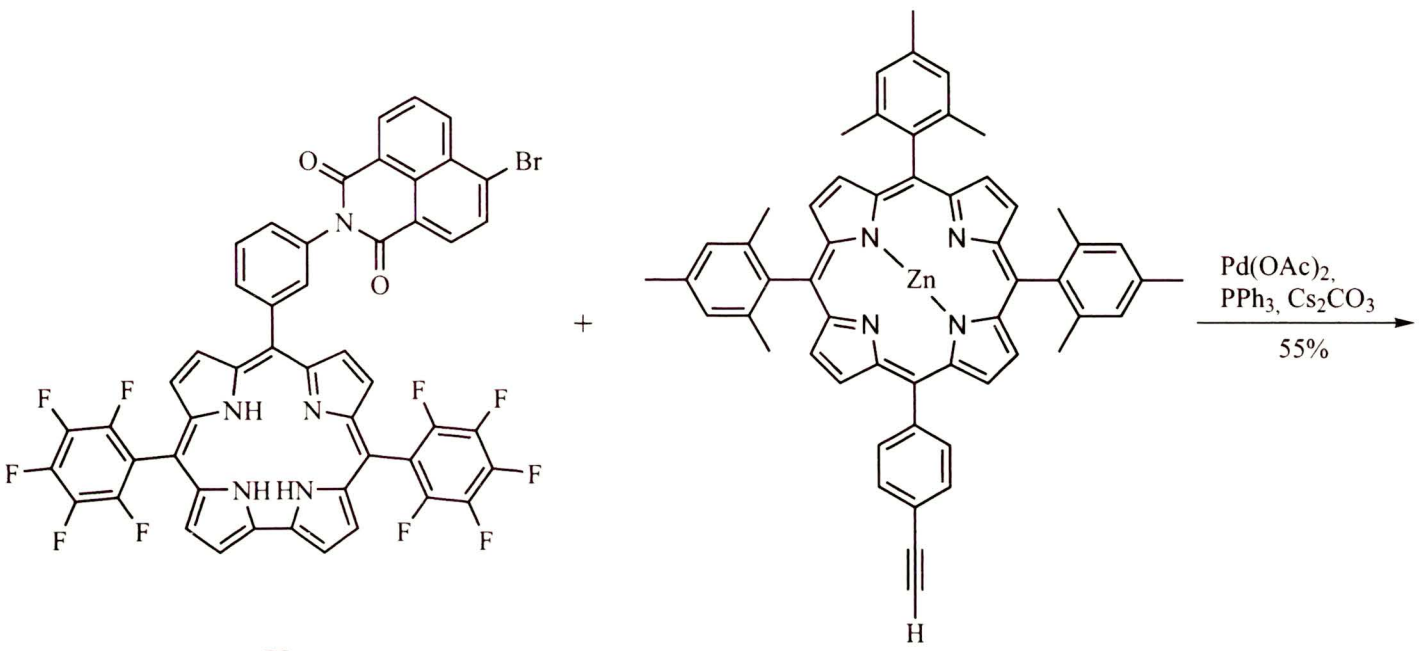
with imide moiety. Zn-Porphyrin counterpart was synthesized following published procedure[186] (Scheme 3.98). Mix-condensation of aldehyde **193**,[187] pyrrole, and



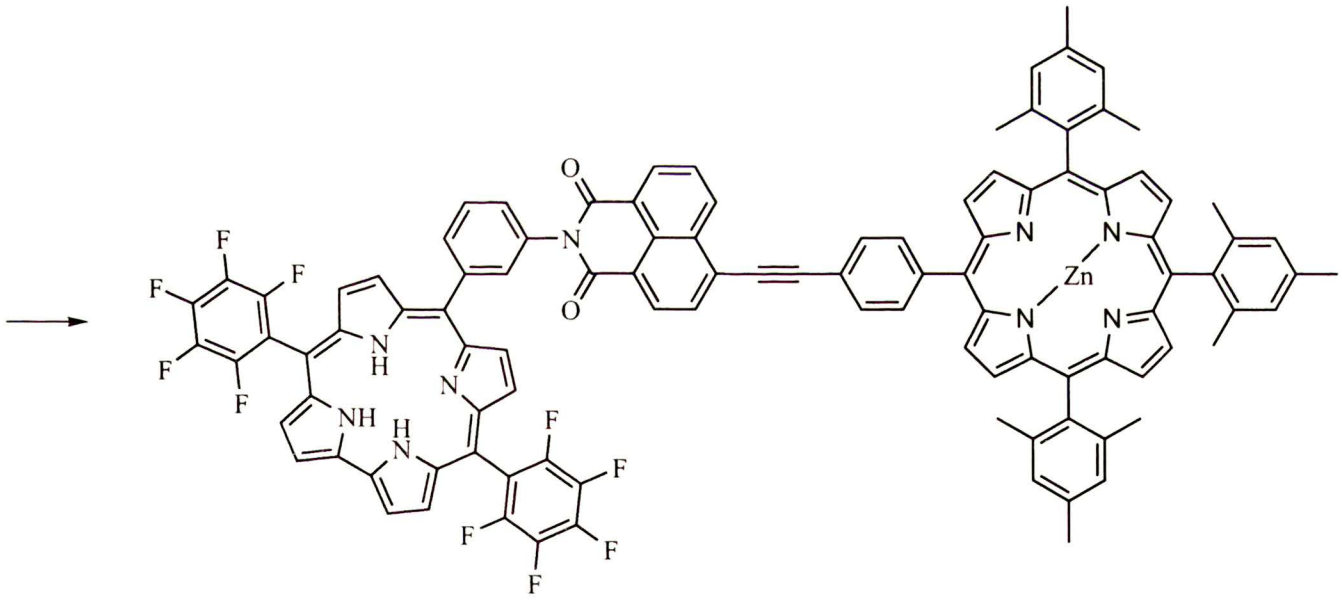
Scheme 3.98

mesityl aldehyde in the presence of BF_3-etherate afforded corresponding A_3B-porphyrin **194** with acceptable yield. Subsequent deprotection of triple bond and treatment with zinc acetate gave desired ethynyloporphyrin **195** with excellent yield.

Based on success with copperless Sonogashira coupling of corrole **50** with phenylacetylene, I decided to study its reactivity with acetylene of incomparable complexity. To my delight, reaction proceeded smoothly and desired triad **196** was formed in good yield (Scheme 3.99).



50



196

Scheme 3.99

4 Spectroscopic and photophysical properties

4.1 Introduction

For fast majority of compounds which I synthesized, the UV-vis absorption and emission spectra were measured. Electrochemistry and spectroelectrochemistry of selected compounds was measured by Dr Maciej Chotkowski (Faculty of Chemistry, Warsaw University). The most interesting compounds, including triads, were sent to Bologna (Italy) where they will be studied from the point of view of occurrence of electron- and energy-transfer.

4.2 Photophysical characteristics of imides and imide-corrole dyads

The absorption spectra of naphthalenedicarboximide-corrole dyads **58**, **39** and **54** display two absorption bands. The short-wavelength band (around 410 nm) consists of two overlapped electronic transitions, one being localized in the naphthalenedicarboximide "antenna" and the Soret band of the corrole framework. At the same time, the long-wavelength Q-bands are localized around 550–650 nm. It appears that positions at which the phenylene linker is incorporated into the dyad molecules hardly influence the spectral properties of these dyes (Figure 4.1). In the case of DPP-based dyad **160** (Figure 4.2, top) the electronic spectrum shows the absorption curve as a superposition the Soret and Q-bands of corrole and the absorption band related to the DPP chromophore. However the absorption maximum corresponded to the DPP π-system ($\lambda_{max} = 470$ nm) is somewhat red-shifted

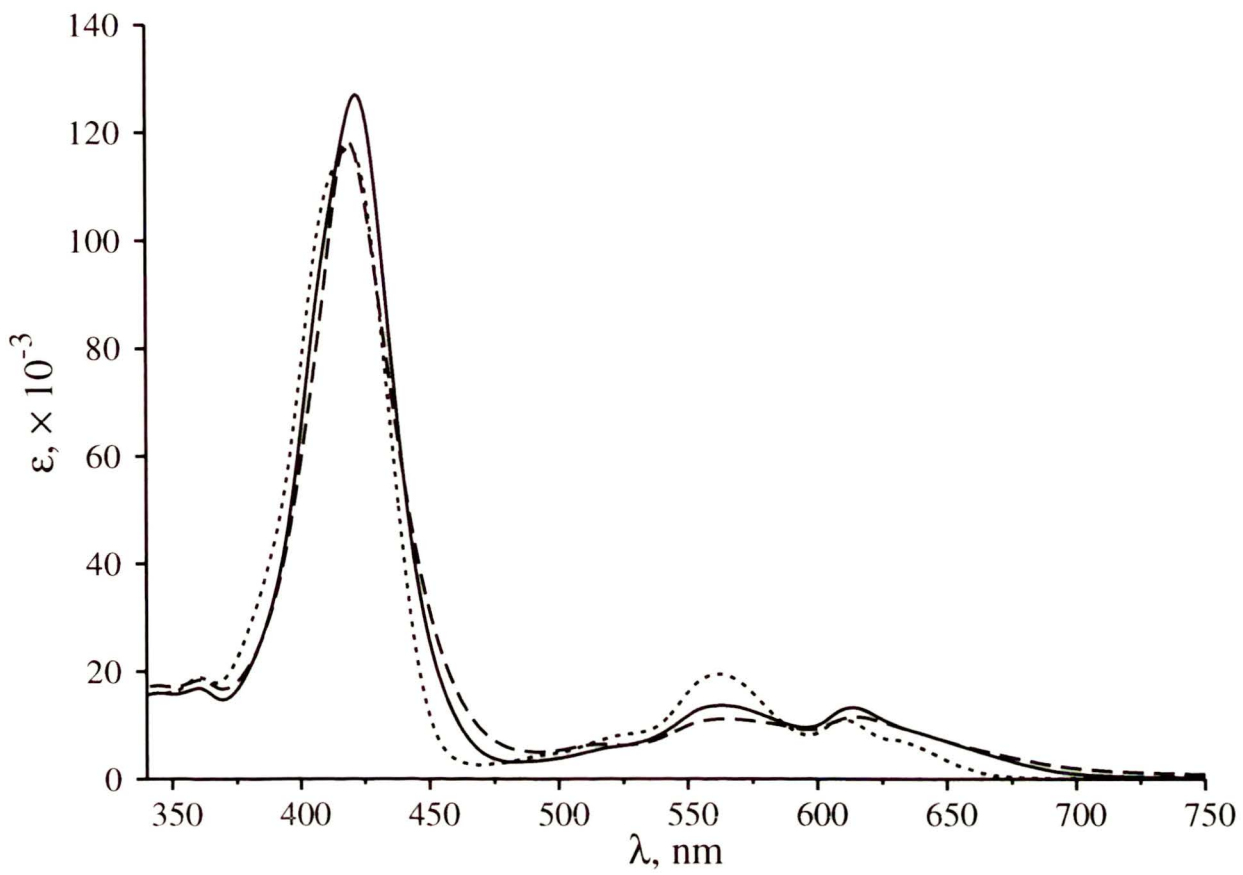
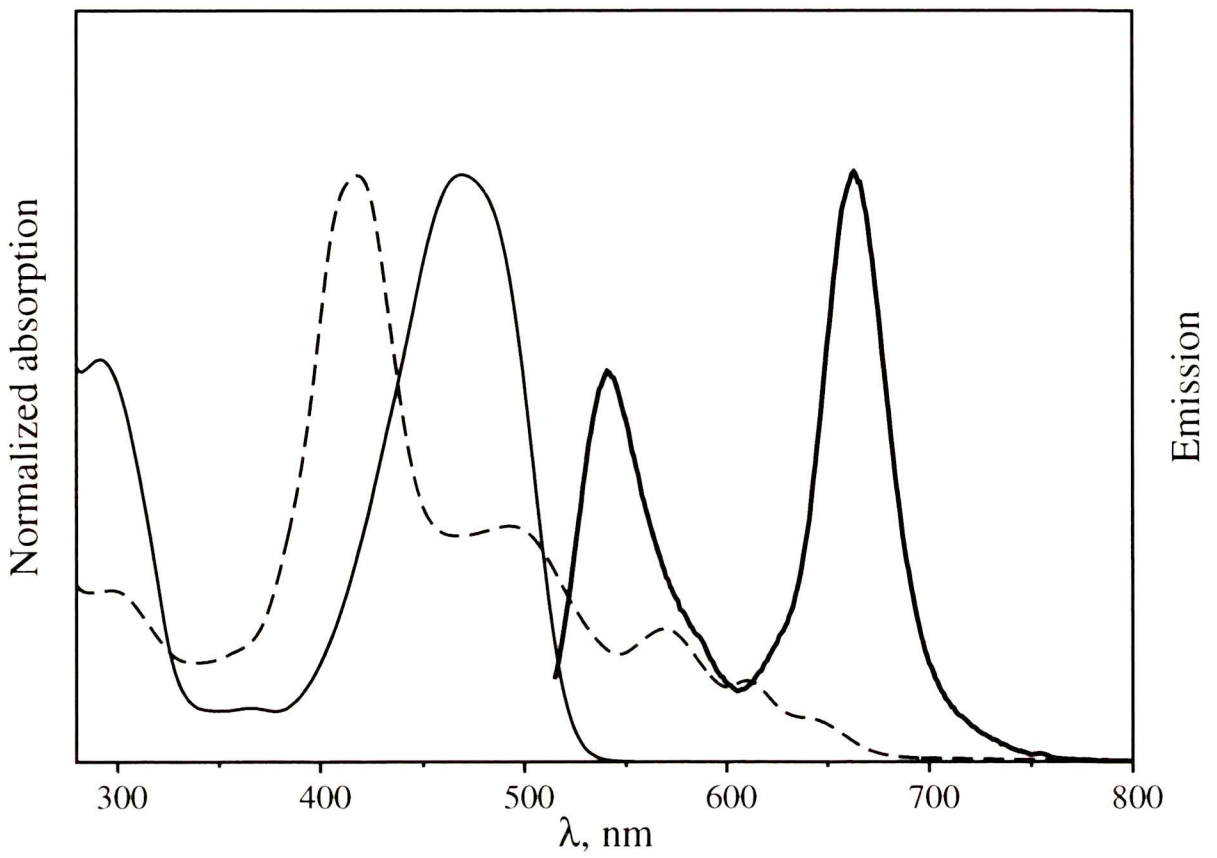


Figure 4.1. Absorption spectra of imide-corrole dyads: **39** (solid line), **58** (dashed line) and **54** (dotted line)

compared to the absorption of the "parent dye" **158** (418 nm). Emission of DPP-corrole dyad shows two narrow bands with maxima at 541 and 663 nm indicating limited electronic coupling and hence (energy transfer) between counterparts of dyad.

The absorption spectrum of imide-corrole dyad **85** displays two bands. The Soret band occurs around 410 nm, overlapped with the absorption band of imide moiety, resolved as a long-wavelength shoulder. On the other hand, the Q-bands are localized within the range of 550–650 nm (Figure 4.2, bottom).



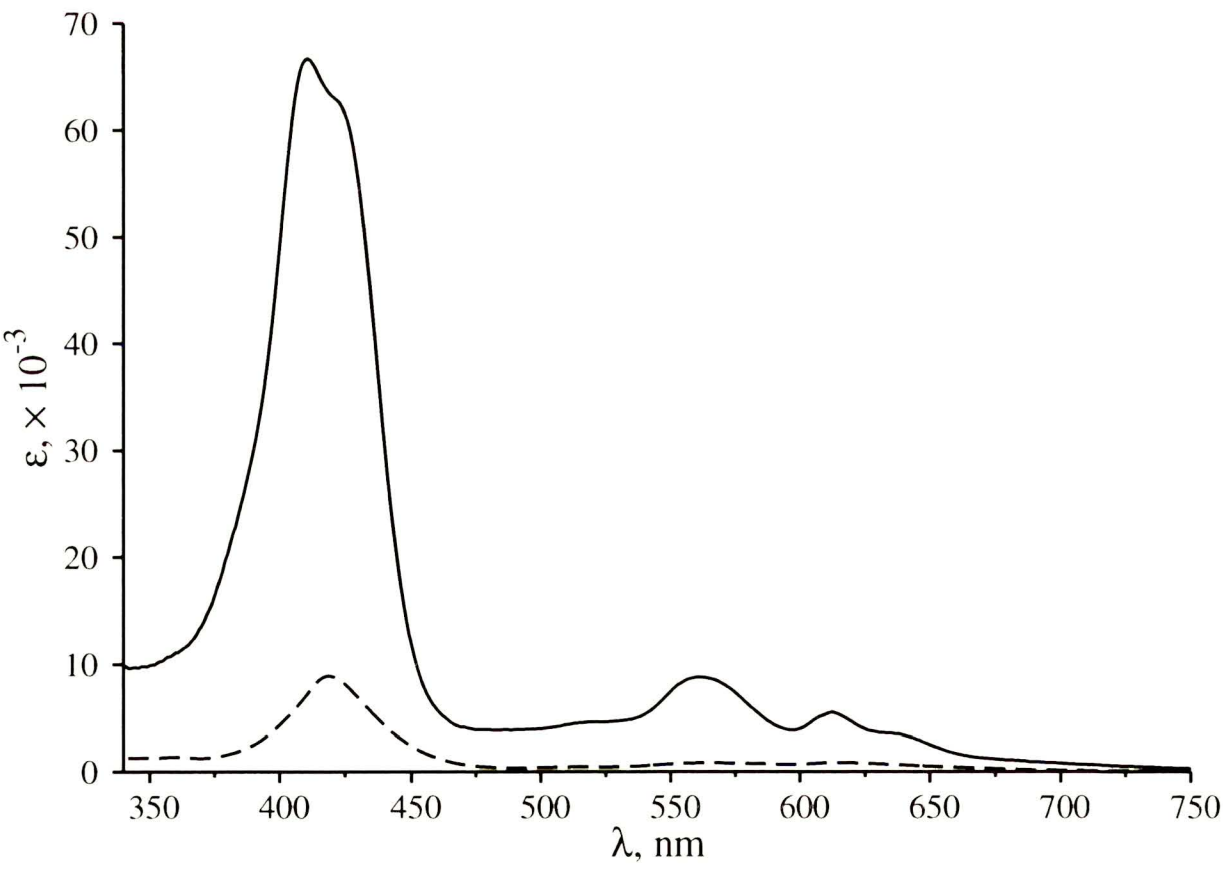


Figure 4.2. Top: Normalized absorption spectra of compounds **160** (solid line), **158** (dashed line) and emission of **160** (bold solid line). Bottom: Absorption spectra of imide-corrole dyad **85** (solid line) and model compound **86** (dashed line).

4.3 Optical properties of coumarins and coumarin-corrole dyads

The spectroscopic properties of the prepared compounds are collected in Table 4.1. The absorption of π-expanded coumarins is very strong, especially for compounds

Table 4.1. Spectroscopic data for coumarins and coumarin-corroles.

Compound	Solvent	λ_{abs}/nm	$\varepsilon \times 10^{-3}$ [a]	λ_{em}/nm
114	DCM	301	18.0	380
116	DCM	301, 408, 562, 604	145.4	645
93 [b]	DCM	363	9.9	433
95 [c]	THF	400	8	494
98	DCM	341	41.9	430, 550
96	DCM	305, 413, 563, 612	417	658
99	DCM	413, 652, 613	35	573
100	THF	475	32	574
102	CH_3CN	308	22	491
104	DMSO	432	2.5	457
105	DCM	308, 408, 562, 604	123	645
123	CH_3CN	367, 444	32.7	508
124	CH_3CN	342, 455	32.1	527
125	DCM	408, 459, 562, 604	983.1	646

[a] for corroles ε refers to intensity of Soret band
[b] data from Ref.[188]
[c] data from Ref.[137]

98 and **123** ($\varepsilon > 30000$, Figure 4.3). The absorption of coumarins **95**, **98** and **104** although very intense, was not so bathochromically shifted as that of coumarin **123** (Table 4.1).

The influence of the presence of coumarin units on the absorption spectra of dyads depended on the type of linkage as well as on the absorption maximum of the coumarin counterpart. For corroles **116**, **105** and **125**, where both units are not directly linked but are separated by a moderately flexible linker, the influence was not so pronounced. Still, there was a characteristic hypsochromic shift in the Soret band in the absorption spectra all these corroles ($\lambda_{max} = 408\,nm$), which originated from the overlap of the spectra of the corrole and coumarin units (Figure 4.3, Table

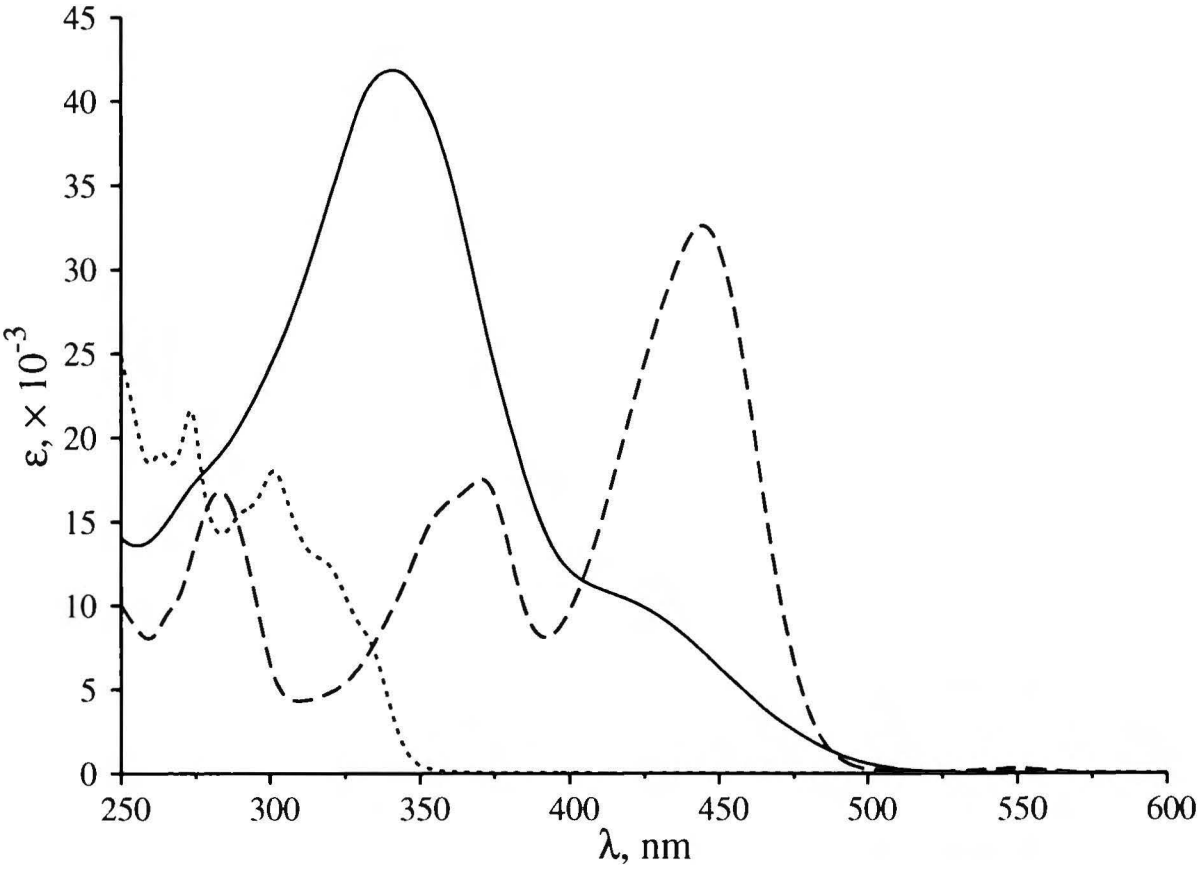


Figure 4.3. Absorption spectra of compounds **98** (solid line), **123** (dashed line) and **114** (dotted line).

4.1). The analysis of the spectra of corroles **96** and **99**, where modified coumarins were directly attached to the *meso*-10 position of the corrole core, confirmed the previous observation that due to substantial steric hindrance, there is no direct electronic communication between both units.

The novel annelated biscoumarins **124** and **125** displayed intriguing spectroscopic properties, since the addition of the auxochrome group (OH) resulted in a hypsochromic rather than a bathochromic shift of absorption (λ_{max} of the analogous biscoumarin lacking a hydroxyl group was around 455 nm).[145] In a way, these compounds behaved like a push-pull system. Replacing the strongly electron-donating hydroxyl group with a weaker electron-donating OC_6F_4CHO group (**124** $\longrightarrow$ **125**) resulted in a 16 nm bathochromic shift of absorption and emission (Table 4.1) which further confirmed this conclusion. Strong absorption of coumarin **124** in the blue region was also clearly visible on the spectrum of dyad **125**.

4.4 Optical properties of acridinyl-pyrrole derivatives

Spectral characteristics of compounds **132**–**136** were examined and compared to those of the known simple acridine and dipyrrin derivatives (Figures 4.4 to 4.5 on pages 128–129, Table 4.2).

Table 4.2. Spectroscopic data for compounds **132**–**136**.

Compound	Solvent	λ_{abs}/nm	$\varepsilon \times 10^{-3}$	λ_{em}/nm	Φ^a
132	THF	415	8.1	512	0.19
		362	7.4		
	MeOH	429		526	
		360			
	toluene	407		518	0.04
		362			
	DCM	414		525	0.06
		363			
136	THF	400	11.1	501	0.13
		363			
133	THF	400	8	494	0.09
		363	8.9		
134	THF	472	35	573	
135	THF	475	32	574	

[a]determined using fluorescein in 1N NaOH as a standard

The most notable feature of adducts **133** and **134** is an intense absorption band at λ_{max}405–415 nm with $\varepsilon \sim 8000$ (Figure 4.4).

This represents the significant bathochromic shift versus parent acridine and is in general agreement with an electron donating effect of pyrrole moiety on chromophores (9-aminoacridine absorbs at 401 nm).[189] The absorption spectra of adducts **132**and **133** are similar to that of simple adducts of pyrrole and acridine,[164,165,169,190,191] and are sensitive to solvent polarity with the bathochromic shift occurring in polar solvents (see Table 4.2). Furthermore, the emission maxima of adducts **132**and **133** occur at $\lambda_{max} = 501$–512 nm with $\Phi = 0.09$–0.19 (in THF). The Stokes shifts of dipyrranes **132** and **133** are large (4600 cm^{-1} and 4800 cm^{-1}

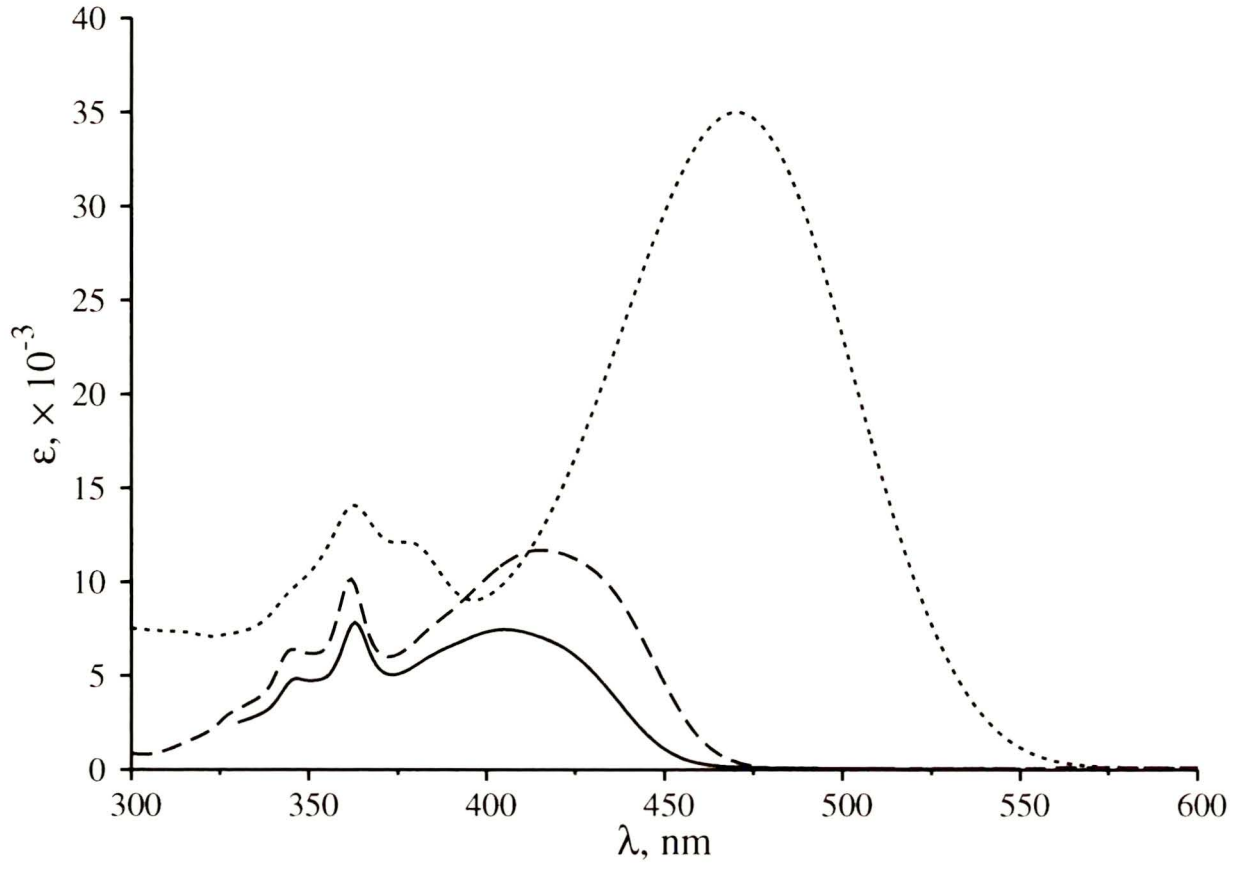


Figure 4.4. Absorption spectra of compounds **98** (solid line), **123** (dashed line) and **114** (dotted line).

respectively in THF) and they are significantly higher than for acridines bearing simple electron-donating groups (9-aminoacridine). This large Stokes shift is one notable characteristic of the present skeleton; presumably it can be attributed to the change from the twisted structure to the planar structure in the excited state. Interestingly, the fluorescence quantum yield for **132** is sensitive to solvent polarity: $\Phi_{\mathrm{THF}} = 0.19, \Phi_{\mathrm{DCM}} = 0.06, \Phi_{\mathrm{toluene}} = 0.04, \Phi_{\mathrm{MeOH}} = 0.00$, which indicates polarized excited state. The absorption and emission spectra of **132** are presented in Figure 4.5. The electronic spectrum of adduct **133** resembles that of **132**. The emission is less intense ($\Phi = 0.13$) and hypsochromically shifted.

The dipyrrins **134** and **135** display very different properties. The absorption maxima are located around 470–475 nm which is significantly bathochromically shifted in comparison to simple 5-aryl substituted dipyrrins ($\sim$ 430 nm).[192,193] It indicates that both chromophores are conjugated to certain extent. The absorption is much more intense (ε = 32000–35000) than for adducts **132**,**133** and **136**. Although the emission is very red shifted, its quantum yield is below the measure-

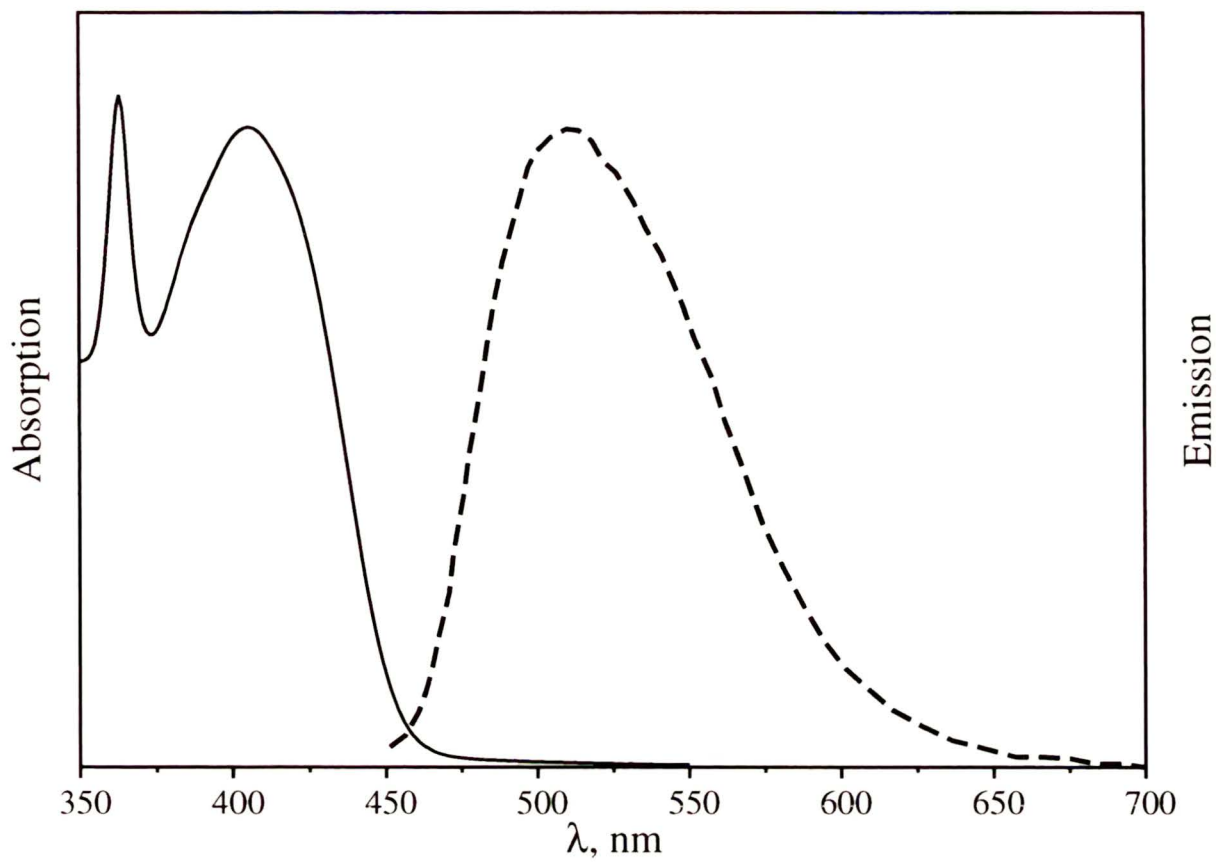


Figure 4.5. Normalized absorption (solid line) and emission (dashed line) spectra of compound **132** in THF.

ments limit. In the case of dipyrrins **134** and **135** Stokes shift is also significant (3600–3700 cm^{-1} in THF). Interestingly, compound **135** displays intense orange fluorescence in the solid state. Whereas a number of molecules are known to be highly fluorescent in dilute solutions, most of them tend to show a decreased fluorescence in the solid state due to the certain intermolecular interactions that result in significant quenching of the emission. Compounds possessing more intense fluorescence in the solid state than in the solution are rather rare.

4.5 Optical properties of triads

Triarylamine-arylimide-corrole triads **179** and **186** differ by the linker between the arylimide part and the corrole framework and their absorption bands consist of three components: the short-wavelength band around 300 nm related to the triarylamine moiety, the Soret band localized around 420 nm, along with overlapping Q-bands and PDI absorption occurred within the range of 450–650 nm (Figure

4.6). It appears that changing the type of linker hardly influence the spectral properties of the above dyes. However, in the case of arylimide-porphyrin-corrole based triad **196**, the absorption spectrum appears to be a superposition of arylimide, corrole and porphyrin chromophores. The short-wavelength band corresponds with the chromophore localized within the arylimide system, the intensive absorption band around 420 nm ($\varepsilon = 3.5 \times 10^5$) originates from the overlapped Soret bands of porphyrin and corrole. The weakly intensive Q-bands occur within the range of 530–650 nm (Figure 4.6).

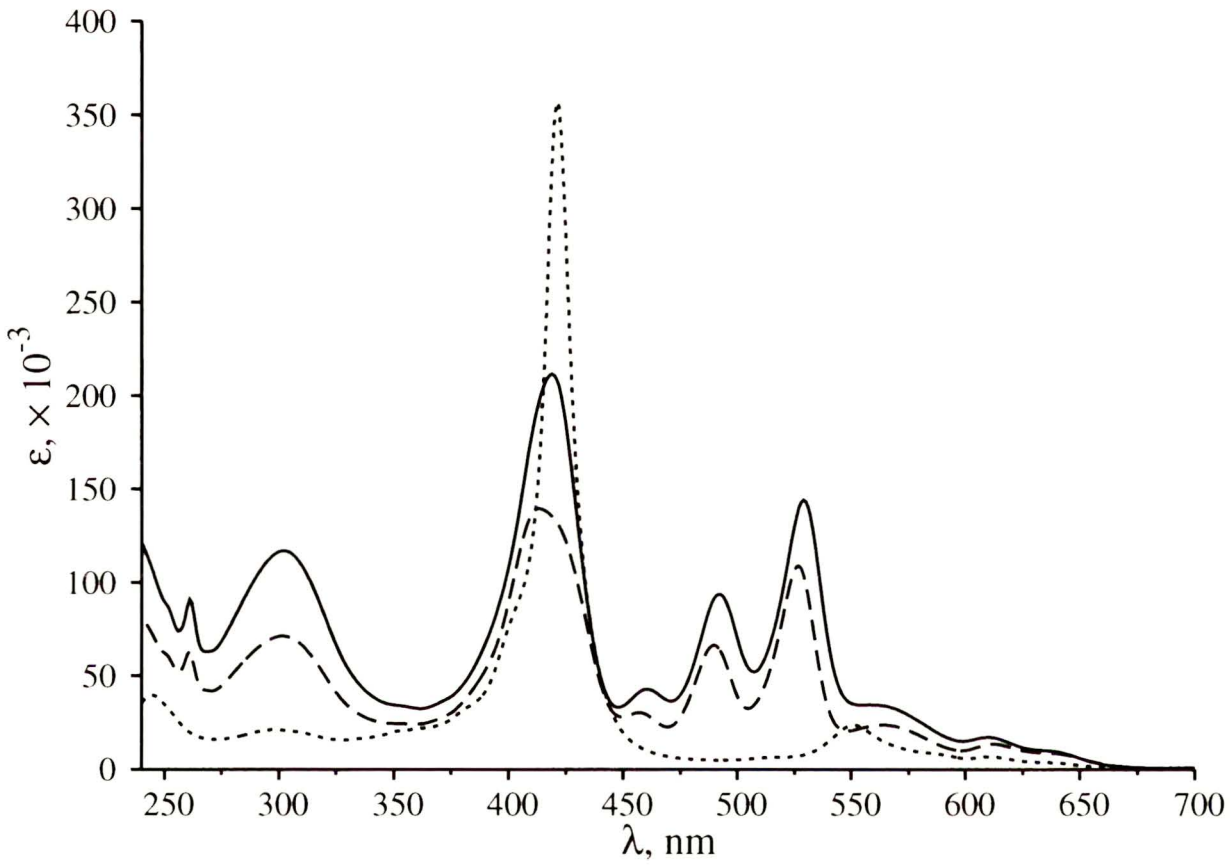


Figure 4.6. Absorption spectra of triarylamine-imide-corrole triads **179** (solid line), **186** (dashed line) and imide-corrole-porphyrin triad **196** (dotted line).

4.6 Electrochemistry and spectroelectrochemistry of selected molecules

Voltammetry experiments for all studied compounds were performed using standard three-electrode setup: platinum working electrode, auxilary electrode (plat-

inum mesh) and reference electrode – saturated calomel electrode (SCE; 0.240 V relative to SHE). Basic electrolyte – 0.1 M $TBAPF_6$ in DCM.

Analyzing the behaviour of compounds **158**, **64**, **86** and **79** it can be noticed that in all cases quasi-reversible redox system appeared within the range from −1.2 to −1.4 V. Compound **158** has additional redox system near the potential about 1.4 V (Figure 4.7).

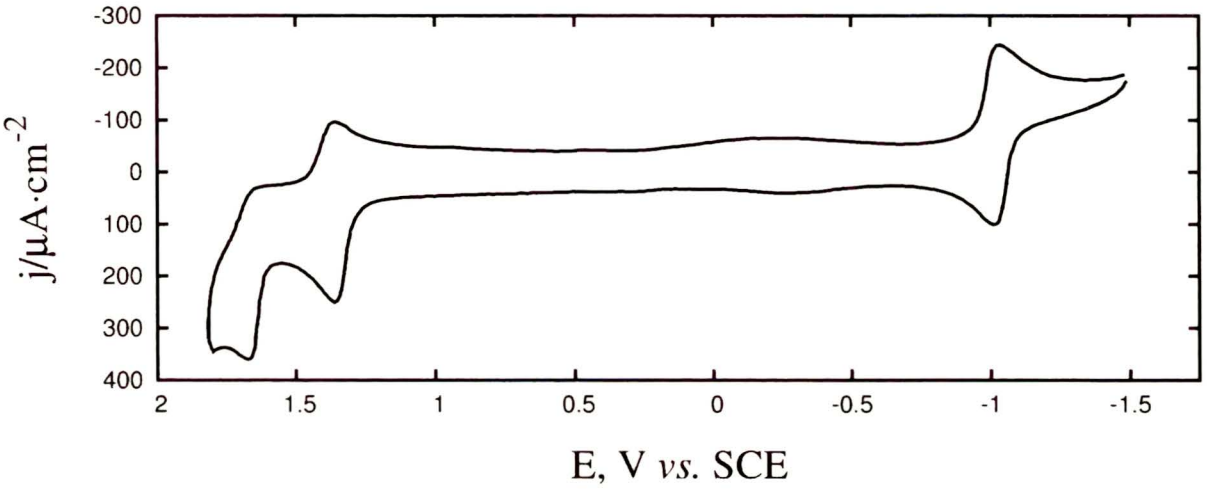


Figure 4.7. Voltammogram of compound **158**.

Spectroelectrochemical experiments were performed on the similar setup, except for working electrode platinum mesh was used (for transparency). The optical path length was 1 mm. Electrochemical data for compounds **158**, **64**, **86** and **79** is summarized in table 4.3.

Table 4.3. Half-wave potentials and absorption maxima of electrochemically generated anion-radicals (DCM).

Compound	$E_{1/2}$	λ_{abs}/nm
158	−1.201, 1.247	616
64	−1.162	447, 491, 796
86	−1.158	591
79	−1.408	

For compounds **158**, **64** and **86** the formation of visible light absorbing anion-radicals was observed. Additionally, for the sample **86** there is growing band in UV region (362 nm). However, in the case of compound **79** there were no changes of spectrum observed during the experiment.

Electrochemical investigation of the triarylamine-corrole-imide dyad **186** and the set of related model compounds (**189**, **190** and **191**) revealed, that electrochemical behaviour generally presents the superposition of the electrochemical characteristics of dyad's components. However, according to the data shown in table 4.4, there is some interaction between counterparts.

Table 4.4. Half-Wave Potential (V *vs.* SCE) for the Oxidation/Reduction processes of corresponding counterparts of triad **186** and model compounds **189**–**192** in DCM.

Compound	Corrole (Ox)	Triarylamine (Ox)	PDI (Red)
189		0.616	
190	0.194, 0.856, 1.045	0.700	
191	0.254, 0.954		−0.350, −0.568
192	0.114, 0.691, 0.778, 0.959		
186	0.229, 0.911, 1.112	0.716	−0.559

For example, the calculated half-wave potential for corrole's redox system shifts from 0.954 V for **191**, to 1.045 and 1.112 V for **190** and **186** respectively (Figure 4.8). The redox wave of triarylamine is very intensive and occurs at potentials between 0.616 and 0.716 V. The half-wave of PDI, according to my expectations, appeared near −0.565 V. There is somewhat unexpected redox wave detected near 0.2 V. After careful examination of the work on corroles' electrochemistry published by Shen *et al.*[194] it becomes clear that this peak is caused by electrode reactions, *i.e.* formation of $(^{\cdot}\mathrm{Cor})\mathrm{H}_2$ species.

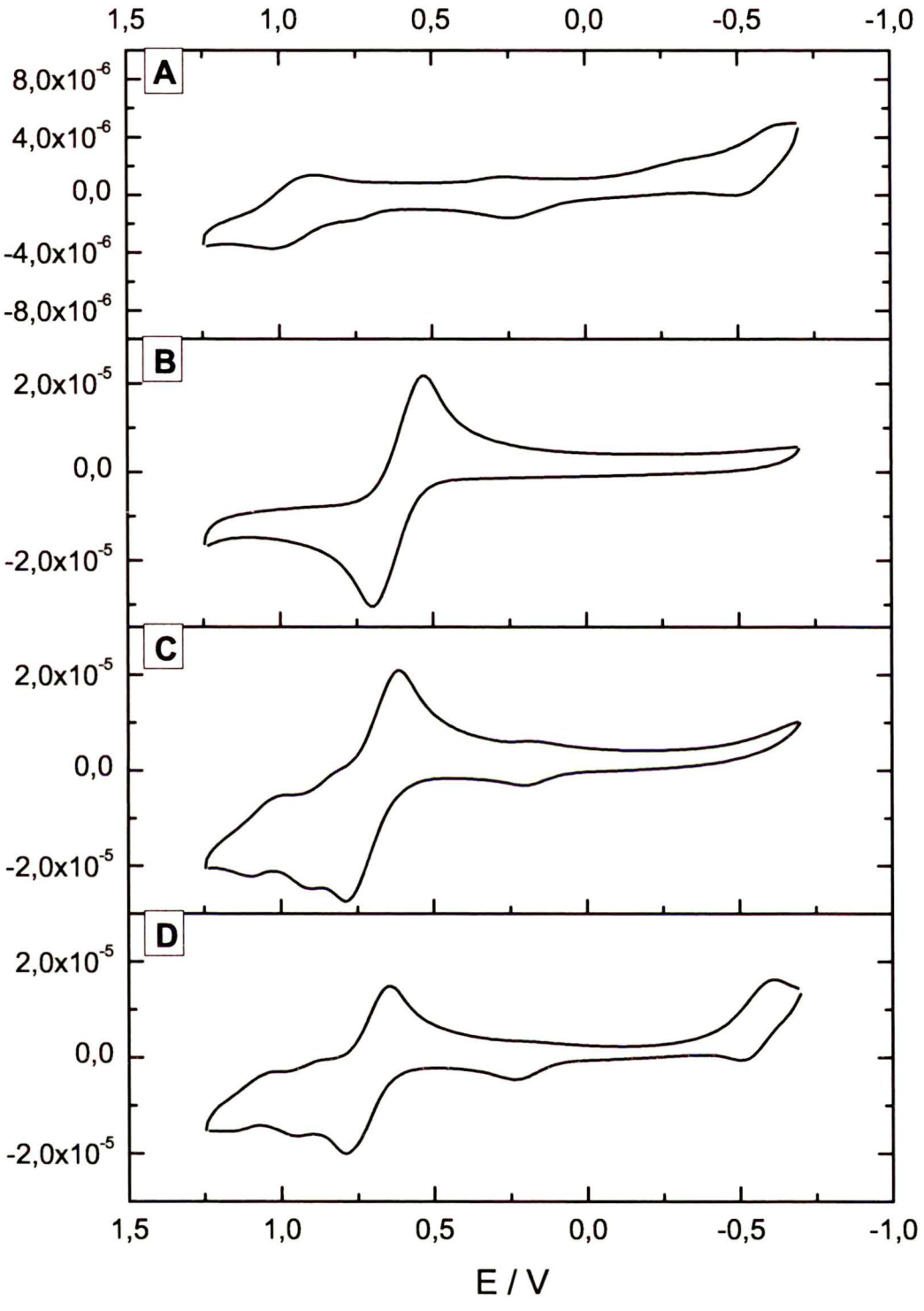


Figure 4.8. Voltammograms of triarylamine-corrole-imide triad **186** (D) and model compounds **191** (A), **189** (B) and **190** (C).

5 Experimental part

5.1 General notes

All commercially available compounds were used without additional purification, unless otherwise noted. Organic solvents were purified according to generally accepted literature methods.[195]

Reactions involving air and/or moisture sensitive reagents were performed under inert atmosphere (argon).

Reactions progress was controlled by thin layer chromatography (TLC), performed on commercially available aluminium plates covered with silica gel or neutral aluminium oxide (60 F_{254}, Merck). All R_f values are referred to SiO_2.

For the purification by the means of column chromatography silica gel 60 (Merck) was used. Dry column vacuum chromatography was performed on MN-Silica gel P/UV_{254} for preparative chromatography. Size exclusion column (SEC) was filled with BioRad Bio-Beads SX-1 and eluted with either THF or toluene.

Melting points were measured on Automatic Melting Point Apparatus (EZ-Melt, Stanford Research Systems) and are presented without correction.

Structure and purity of synthesized compounds was confirmed using ^{1}H,^{13}C-NMR, MS and quantitative analysis.*

NMR spectra were obtained on Varian Mercury 400 MHz, Bruker DRX 500 MHz, Varian VNMRS 500 MHz or 600 MHz. Reported chemical shifts (δ, ppm) were determined relative to TMS as the internal reference.

Mass spectra were obtained on AMD-604 (AMD Intectra GmbH), Mariner (Perseptive Biosystems, Inc.), 4000 Q-TRAP (Applied Biosystems) or GCT Premier (Waters).

*all values are given as percentages

UV/vis spectra were recorded on Lambda 25 Spectrometer (Perkin Elmer) and fluorescence measurements were performed on Hitachi Fluorescence Spectrometer F-7000.

5.2 Starting materials for syntheses

Some compounds were synthesized following literature procedures: **38**,[180] **43**,[99] **44**,[100] **63**,[106] **83**,[111] **89**,[128] **91**,[136] **93**,[196] **95**,[137] **97**,[197] **100**,[134] **109**,[140] **113**,[143] **120**,[144] **147**,[166a] **151**,[175] **155**,[198] **161**,[126] **170**,[199] **171**,[200] **174**,[177e] **178**,[201] **193**.[187]

Compounds **34**, **40**, **46**, **55**, **56**, **59**, **65**, **87**, **88**, **101**, **103**, **107**, **117**, **122**, **128**, **140**, **150**, **162** were commercially available and used without further purification.

5.3 Syntheses and characterization of obtained compounds

2-(3-(Hydroxymethyl)phenyl)-benzo[*f*]isoindole-1,3-dione (36). The solution of 2,3-naphthalenedicarboxylic acid anhydride (**34**, 1.98 g, 10 mmol) and 3-aminobenzyl alcohol (**35**, 1.23 g, 10 mmol) in DMF (50 mL) was heated under reflux for 6 h. After cooling the reaction mixture to ambient temperature water (50 mL) was added. The precipitate was filtered off, washed with small amount of EtOH and chromatographed (SiO_2, CH_2Cl_2 + 2 %MeOH) affording **36** (2.11 g, 70%) as colorless crystals. Mp 214–5 °C; ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 4.59 (2H, d, J = 5.8 Hz, CH_2), 5.35 (1H, t, J = 5.8 Hz, OH), 7.36 (1H, d, J = 8.0 Hz, C_6H_4), 7.42 (1H, d, J = 8.0 Hz, C_6H_4), 7.45 (1H, s, C_6H_4), 7.51 (1H, t, J = 8.0 Hz, C_6H_4), 7.81 (2H, m, naphth), 8.30 (2H, m, naphth), 8.60 (2H, s, naphth); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 62.9, 125.2, 125.7, 126.1, 126.6, 127.8, 129.0, 129.8, 130.7, 132.4, 135.6, 144.0, 167.2; Anal. Calcd for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62; Found: C, 75.23; H, 4.45; N, 4.54; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{19}H_{13}NO_3$, 303.0895; found, 303.0900.

3-(1,3-Dioxo-1,3-dihydrobenzo[*f*]isoindol-2-yl)benzaldehyde (37).

Method A. Alcohol **36** (660 mg, 2.18 mmol) was suspended in the solution of TEMPO (34 mg, 10% mol) in DCM (5 mL). Subsequently, BAIB (772 mg, 2.4 mmol) was added and reaction was stirred until the alcohol was fully consumed (nearly 3 h). The reaction mixture was diluted with DCM to dissolve solid product, washed with $Na_2S_2O_{3(aq,sat)}$ and extracted with DCM (3×10 mL). The combined organic extracts were washed with $NaHCO_{3(aq)}$ and brine, dried over Na_2SO_4 and concentrated under reduced pressure. Flash column chromatogrtaphy (silica, DCM/hexanes 4:1) afforded title compound as a colorless crystalline solid (610 mg, 92%).

Method B. 2,3-Naphthalenedicarboxylic acid anhydride (991 mg, 5 mmol) and 3-aminobenzaldehyde polymer (605 mg, 5 mmol) were suspended in acetic acid (12 mL) and stirred at reflux overnight. The precipitate, formed after cooling to rt, was filtered off, washed with AcOH and dried under vacuum (1.18 g, 78%).

R_f 0.4 (DCM); mp 281 °C (dec); ^{1}H NMR (600 MHz, DMSO-d_6, TMS, δ): 7.78–7.85 (3H, m, C_6H_4 + naphth), 7.87 (1H, m, C_6H_4), 8.02 (1H, m, C_6H_4), 8.07 (1H, m, C_6H_4), 8.33 (2H, m, naphth), 8.67 (2H, s, naphth), 10.10 (1H, s, CHO); ^{13}C NMR (150 MHz, DMSO-d_6, TMS, δ): 124.9, 127.3, 127.3, 129.3, 129.7, 130.2, 132.9, 133.0, 135.1, 136.7, 166.4, 192.5; Anal. Calcd for $C_{19}H_{11}NO_3$: C, 75.74; H, 3.68; N, 4.65; Found: C, 75.63; H, 3.71; N, 4.58; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{19}H_{11}NO_3$, 301.0739; found, 301.0724.

Corrole 39. Aldehyde **37** (0.6 g, 2 mmol) and 5-(pentafluorophenyl)dipyrrane (**38**, 1.25 g, 4 mmol) were suspended in 30 mL of DCM and 330 μL of preprepared TFA solution* (10 mL of TFA in 100 mL DCM) was added. Reaction course was controlled by TLC and after 30 min reaction was quenched by triethylamine addition (60 μL). Reaction mixture was diluted to 200 mL with DCM and poured into solution of DDQ (1.18 g, 5.2 mmol) in 300 mL of DCM stirred vigorously. After 2 h reaction mixture was slightly concentrated and passed through 2 cm silica pad. Product-containing fractions (contaminated by dipyrrin) were combined and solvent was removed under reduced pressure. Residue was washed with small amount of methanol, suspended in boiling cyclohexane and after cooling, crystals were filtered off and dried under vacuum giving 288 mg of corrole **39** (16%). R_f 0.4 (DCM/hexanes 3:2); ^{1}H NMR (500 MHz, THF-d_8, TMS, δ): (−4)–(−1.5) (3H,

*from now on this solution will be referred as "TFA stock solution"

br s, NH), 7.72 (2H, m, naphth.), 7.90–7.97 (2H, m, C_6H_4), 8.19 (2H, m, naphth.), 8.25 (1H, m, C_6H_4), 8.47 (1H, m, C_6H_4), 8.55 (2H, s, naphth.), 8.59 (2H, br s, β-H), 8.84 (2H, br s, β-H), 8.87 (2H, d, $J = 4.5$ Hz, β-H), 9.09 (2H, d, $J = 3.7$ Hz, β-H); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{49}H_{22}N_5O_2F_{10}$, 902.1608; found, 902.1646; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 613 (13.5), 563 (13.5), 422 (127.7).

3-(6-Bromo-1,3-dioxo-1*H*,3*H*-benzo[*de*]isoquinolin-2-yl)benzaldehyde (45).

Method A. 4-Bromo-1,8-naphthalenedicarboxylic anhydride (**40**, 554 mg, 2 mmol) was dissolved in boiling AcOH (5 mL) and the solution of 3-aminobenzaldehyde ethylene acetal (**44**, 375 mg, 2.2 mmol) in ether (2 mL) was added dropwise while stirring. Solvent was removed under reduced pressure, residue was dissolved in DCM, washed with $NaHCO_{3(aq)}$, dried over $MgSO_4$ and chromatographed (silica, DCM). Evaporation of product-containing fractions and drying the residue under vacuum gave 466 mg of **45** (60%) as a colorless crystalline solid.

Method B. 4-Bromo-1,8-naphthalenedicarboxylic anhydride (1.38 g, 5 mmol), 3-aminobenzaldehyde ethylene acetal (1.24 g, 7.5 mmol) and imidazole (6.8 g, 0.1 mol) were loaded into 100 mL round-bottom flask and chloroform (40 mL) was added. The mixture was stirred at gentle reflux for 7 h and then cooled to rt. The solvent was removed on rotary evaporator and the residue was taken up in small amount of absolute ethanol. The resulting suspension was sonicated for 15 min,* filtered, washed with cold ethanol and air-dried. NMR analysis revealed the mixture of aldehyde and acetal. In consequence, the sample was fully deprotected by stirring with excess of acetone in the presence of p-TsOH (35 mmol/L) and passing the mixture through silica pad. At this point the yield was 1.85 g, (96%) and analytically pure sample was obtained after crystallization (chloroform/hexanes).

R_f 0.6 (1% MeOH in DCM); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 7.60 (1H, m, C_6H_4), 7.74 (1H, t, $J = 7.8$ Hz, C_6H_4), 7.86 (1H, s, C_6H_4), 7.92 (1H, m, naphth.), 8.02 (1H, m, C_6H_4), 8.11 (1H, d, $J = 7.6$ Hz, naphth.), 8.47 (1H, d, $J = 7.6$ Hz, naphth.), 8.64–8.76 (2H, m, naphth.), 10.08 (1H, s, CHO); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, δ): 122.0, 122.9, 128.3, 129.3, 129.9, 130.1, 130.1, 130.9, 131.1, 131.3, 131.8, 132.7, 134.0, 134.7, 136.0, 137.6, 163.6, 163.6, 191.1; Anal.

*several heating-cooling cycles can be applied to a suspension to facilitate filtration

Calcd for $C_{19}H_{10}BrNO_3$: C, 60.02; H, 2.65; N, 3.68; Br, 21.02; Found: C, 60.10; H, 2.91; N, 3.65; Br, 20.90; HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{10}BrNO_3Na$, 401.9736; found, 401.9720.

2-[2-(5,5-Dimethyl-[1,3]dioxan-2-yl)-phenyl]-benzo[de]isoquinoline-1,3-dione (47). 1,8-naphthalenedicarboxylic anhydride (**46**, 535 mg, 2.7 mmol), 2-aminobenzaldehyde 2,2-dimethyl-1,3-propylene acetal (**43**, 840 mg, 4.05 mmol) and imidazole (3.67 g, 54 mmol) were loaded into 50 mL round-bottom flask and chloroform (20 mL) was added. The mixture was stirred at gentle reflux for 1.5 h and then cooled to rt. The solvent was removed on rotary evaporator and the residue was taken up in small amount of absolute ethanol. The resulting suspension was sonicated for 15 min and then filtered. Filter cake was washed with cold ethanol and air-dried (1.03 g, 98%). Analytically pure sample was obtained by column chromatography (DCM/hexanes 3:1). R_f 0.5 (DCM/hexanes 4:1); ^{1}H NMR (600 MHz, DMSO-d_6, δ): 0.52 (3H, s, CH_3), 0.99 (3H, s, CH_3), 3.29 (2H, d, $J = 10.8$ Hz, CH_2), 3.40 (2H, d, $J = 10.9$ Hz, CH_2), 5.29 (1H, s, CH), 7.39 (1H, m, C_6H_4), 7.53 (2H, m, C_6H_4), 7.72 (1H, m, C_6H_4), 7.92 (2H, t, $J = 7.7$ Hz, naphth.), 8.52 (4H, m, naphth.); ^{13}C NMR (150 MHz, DMSO-d_6, δ): 21.5, 23.0, 30.1, 76.9, 98.5, 122.9, 127.5, 127.7, 128.4, 128.9, 129.8, 130.4, 131.2, 132.0, 134.5, 134.9, 135.6, 136.4, 163.9; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{24}H_{21}NO_4$, 387.1471; found, 387.1465.

2-[2-(5,5-Dimethyl-[1,3]dioxan-2-yl)-phenyl]benzo[*f*]isoindole-1,3-dione (48).

Method A. The mixture of 2,3-naphthalenedicarboxylic anhydride (420 mg, 2.12 mmol) and acetal **43** (482 mg, 2.33 mmol) in AcOH (5 mL) was stirred at 110 °C overnight. After cooling to rt and solvent evaporation, the residue was dissolved in DCM, washed with $NaHCO_{3(aq)}$, dried over Na_2SO_4 and chromatographed (AcOEt/hexanes 1:3) giving 273 mg (33%) of acetal **48**.

Method B. 2,3-naphthalenedicarboxylic anhydride (990 mg, 5 mmol), 2-aminobenzaldehyde acetal **43** (1.55 g, 7.5 mmol) and imidazole (6.8 g, 0.1 mol) were loaded into 100 mL round-bottom flask and chloroform (40 mL) was added. The mixture was stirred at gentle reflux for 2 h and then cooled to rt. The solvent was removed on rotary evaporator and the residue was taken up in small amount of absolute ethanol. The resulting suspension was sonicated for 15 min and then filtered.

Filter cake was washed with cold ethanol and air-dried. Column chromatography (DCM/hexanes 3:1) afforded 838 mg (43%) of **48** as a colorless solid.

R_f 0.5 (DCM/hexanes 3:1); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 0.61 (3H, s, CH_3), 1.10 (3H, s, CH_3), 3.39 (2H, d, $J = 10.9$ Hz, CH_2), 3.55 (2H, d, $J = 11.1$ Hz, CH_2), 5.42 (1H, s, CH), 7.29 (1H, m, C_6H_4), 7.51 (2H, m, C_6H_4), 7.74 (2H, m, naphth.), 7.85 (1H, m, C_6H_4), 8.11 (2H, m, naphth.), 8.47 (2H, s, naphth.); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 21.7, 23.0, 30.1, 77.6, 99.0, 125.2, 127.7, 127.9, 129.3, 129.4, 129.5, 129.6, 129.7, 130.3, 135.6, 136.2, 167.2; Anal. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62; Found: C, 74.13; H, 5.36; N, 3.58; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{24}H_{21}NO_4$, 387.1471; found, 387.1478.

Corrole 50. Aldehyde **45** (1.5 g, 3.94 mmol) and 5-(pentafluorophenyl)dipyrrane (2.46 g, 7.88 mmol) were suspended in 60 mL of DCM and 650 μL TFA stock solution (see footnote on page 136) was added. Reaction course was controlled by TLC and after 1 h reaction was quenched by triethylamine addition (110 μL). Reaction mixture was diluted to 1 L with DCM and DDQ (2.68 g, 10.24 mmol), dissolved in minimal amount of toluene, was added during vigorous stirring. After 2 h reaction mixture was slightly concentrated and passed through 2 cm silica pad. Product containing fractions were combined, concentrated, and mixture* was passed through SEC eluting by toluene and collecting second (less polar on TLC) fraction. The solvent was removed on rotary evaporator and residue was recrystallized from DCM/MeOH. Dark violet solid was dried under vacuum (508 mg, 13%). R_f 0.5 (DCM/hexanes 4:1); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 7.71 (1H, d, $J = 7.7$ Hz, C_6H_4), 7.88 (1H, t, $J = 8.0$ Hz, naphth.), 7.95 (1H, t, $J = 7.7$ Hz, C_6H_4), 8.06 (1H, d, $J = 7.9$ Hz, naphth.), 8.17 (1H, s, C_6H_4), 8.29 (1H, d, $J = 7.1$ Hz, C_6H_4), 8.49 (1H, d, $J - 7.9$ Hz, naphth.), 8.56 (2H, s, β-H), 8.60 (1H, d, $J = 8.3$ Hz, naphth.), 8.72–8.79 (3H, m, β-H+C_6H_4), 8.94 (2H, d, $J = 4.5$ Hz, β-H), 9.10 (2H, d, $J = 3.8$ Hz, β-H); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{49}H_{21}BrF_{10}N_5O_2$, 980.0713; found, 980.0722.

General method for acetal cleavage (47, 48 ⟶ 51, 52).

TFA (8 mL) and 5% $H_2SO_{4(aq)}$ were added to acetal (1 mmol) dissolved in 20 mL of chloroform and reaction was stirred for 24 h at rt. Reaction mixture was diluted with water (50 mL) and allowed to stirr for the next 30 min. The

*there was a mixture of two products with similar R_f on TLC

mixture was extracted with chloroform (3×10 mL), washed with 2M $NaHCO_3$, dried over $MgSO_4$ and concentrated. Residue was recrystallized from chloroform to give crystalline product (92–96%).

2-(1,3-Dioxo-1,3-dihydro-benzo[*f*]isoindol-2-yl)-benzaldehyde (52). ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 7.67 (1H, d, $J = 7.8$ Hz, C_6H_4), 7.76 (1H, t, $J = 7.5$ Hz, C_6H_4), 7.83 (2H, m, naphth.), 7.89 (1H, m, C_6H_4), 8.08 (1H, m, C_6H_4), 8.33 (2H, m, naphth.), 8.67 (2H, s, naphth.), 10.04 (1H, s, CHO); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 125.6, 128.0, 130.0, 130.1, 130.7, 130.8, 131.5, 132.5, 132.7, 135.2, 135.7, 167.4, 191.7; HRMS–EI (*m/z*): $[M]^{+\cdot}$ calcd for $C_{19}H_{11}NO_3$, 301.0739; found, 301.0743.

Aldehyde **51** was used in further transformations without purification.

Corrole 53. Aldehyde **51** (600 mg, 2 mmol) and 5-(pentafluorophenyl)dipyrrane (1.25 g, 4 mmol) were dissolved in 30 mL of DCM and 330 μL of stock TFA solution (see page 136) was added while stirring. Reaction course was controlled by aldehyde consumption (TLC) and after 20 min reaction was quenched by triethylamine (60μL) addition. Reaction mixture was diluted with dichloromethane to 300 mL and *p*-chloranil (1.28 g, 5.2 mmol) was added. After 12 h reaction mixture was passed through 2 cm silica pad and then chromatographed (silica, toluene). Product-containing fractions were combined, solvent was removed under reduced pressure. Dark residue was recrystallized from DCM and vacuum dried, giving 409 mg of **53** (23%). R_f 0.5 (DCM/hexanes 3:2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 7.15 (2H, m, naphth.), 7.50 (2H, m, naphth.), 7.81 (1H, d, $J = 7.8$ Hz, C_6H_4), 7.87 (1H, t, $J = 7.2$ Hz, C_6H_4), 7.95 (2H, d, $J = 7.2$ Hz, naphth.), 7.99 (1H, m, C_6H_4), 8.19 (1H, d, $J = 7.3$ Hz, C_6H_4), 8.40 (2H, m, β-H), 8.60 (2H, d, $J = 4.7$ Hz, β-H), 8.83 (2H, d, $J = 4.5$ Hz, β-H), 8.91 (2H, m, β-H); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{49}H_{22}N_5O_2F_{10}$, 902.1608; found, 902.1602.

Corrole 54. The mixture of aldehyde **52** (311 mg, 1.03 mmol) and 5-(pentafluorophenyl)dipyrrane (645 mg, 2.06 mmol) in 15 mL of DCM was treated with 170 μL of TFA stock solution (see page 136). After 20 min reaction was quenched with 30 μL of triethylamine, diluted with DCM to 130 mL and DDQ (608 mg, 2.68 mmol) dissolved in a minimal amount of toluene was added. After 2 h of stirring, reaction mixture was passed through silica pad, evaporated with Celite and chromatographed (DCM/hexanes 1:4 ⟶ 1:1). Product-containing fractions

were collected and evaporated. Crystallization from DCM afforded 157 mg (17%) of corrole **54** as a crystalline solid. R_f 0.4 (DCM/hexanes 3:2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 7.27 (solv. overlap, m, naphth.), 7.48 (2H, m, naphth.), 7.61 (2H, s, naphth.), 7.82 (1H, m, C_6H_4), 7.89 (1H, m, C_6H_4), 7.97 (1H, m, C_6H_4), 8.25 (1H, m, C_6H_4), 8.42 (2H, br s, β-H), 8.66 (2H, d, $J = 5.9$ Hz, β-H), 8.81 (2H, d, $J = 6.0$ Hz, β-H), 8.91 (2H, br s, β-H); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{49}H_{22}N_5O_2F_{10}$, 902.1608; found, 902.1579; UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 296 (22.9), 419 (11.7), 561 (19.4), 611 (11.0).

4-(1,3-Dioxo-1,3-dihydrobenzo[*f*]isoindol-2-yl)benzaldehyde (57). 2,3-Naphthalenedicarboxylic acid anhydride (1.98 g, 10 mmol) and 4-aminobenzaldehyde polymer (1.21 g, 10 mmol) were suspended in acetic acid (25 mL) and stirred at reflux overnight. Orange color disappeared (reaction mixture becomes yellow). The precipitate, formed after cooling to rt, was filtered off, washed with AcOH and dried under vacuum (2.38 g, 79%). R_f 0.3 (DCM); ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 7.79 (2H, d, $J = 8.4$ Hz, C_6H_4), 7.82 (2H, m, naphth.), 8.10 (2H, d, $J = 8.4$ Hz, C_6H_4), 8.33 (2H, m, naphth.), 8.67 (2H, s, naphth.), 10.09 (1H, s, CHO); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 125.5, 127.7, 128.0, 130.0, 130.4, 130.8, 135.6, 135.7, 137.8, 166.7, 192.9; Anal. Calcd for $C_{19}H_{11}NO_3$: C, 75.74; H, 3.68; N, 4.65; Found: C, 75.68; H, 3.68; N, 4.63; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{19}H_{11}NO_3$, 301.0739; found, 301.0729.

Corrole 58. Aldehyde **57** (0.6 g, 2 mmol) and 5-(pentafluorophenyl)dipyrrane (**38**, 1.25 g, 4 mmol) were suspended in 30 mL of DCM and 330 μL of TFA stock solution (see page 136) was added. Reaction course was controlled by TLC and after 30 min reaction was quenched by triethylamine addition (60 μL). Reaction mixture was diluted to 200 mL and poured into solution of DDQ (1.18 g, 5.2 mmol) in 300 mL DCM stirred vigorously. After 2 h reaction mixture was slightly concentrated and passed through 2 cm silica pad. Product-containing fractions were combined and solvent was removed under reduced pressure. Residue was washed with small amount of methanol, suspended in boiling cyclohexane and after cooling, crystals were filtered off and dried under vacuum giving 244 mg of corrole **58** (14%). R_f 0.33 (DCM/hexanes 2:1); ^{1}H NMR (500 MHz, THF-d_8, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 7.78 (2H, m, naphth.), 8.02 (2H, m, C_6H_4), 8.25 (2H, m, naphth.), 8.35 (2H, m, C_6H_4), 8.63 (4H, m, naphth.+β-H), 8.74 (2H, br s, β-H),

8.82 (2H, br s, β-H), 9.10 (2H, br s, β-H); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{49}H_{22}N_5O_2F_{10}$, 902.1608; found, 902.1618; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 615 (12.4), 564 (11.3), 419 (118.3).

3-(4,5,6,7-Tetrabromo-1,3-dioxo-1,3-dihydroisoindol-2-yl)benzaldehyde (60). The target compound was synthesized following the procedure described for **37** (Method B, page 136); Yield 94%. R_f 0.43 (DCM); ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 7.76–7.83 (2H, m, C_6H_4), 7.99 (1H, m, C_6H_4), 8.03 (1H, m, C_6H_4), 10.08 (1H, s, CHO); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 120.8, 127.4, 130.0, 130.0, 131.0, 132.4, 133.2, 136.7, 136.9, 162.8, 192.4; Anal. Calcd for $C_{15}H_5Br_4NO_3$: C, 31.78; H, 0.89; N, 2.47; Br, 56.39; Found: C, 31.85; H, 1.15; N, 2.54; Br, 56.25; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{15}H_5Br_4NO_3$, 562.7003; found, 562.6991.

4-(4,5,6,7-Tetrabromo-1,3-dioxo-1,3-dihydroisoindol-2-yl)benzaldehyde (61). The target compound was synthesized following the procedure described for **57** (page 141); Yield 56%. R_f 0.43 (DCM); ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 7.69 (2H, d, $J = 8.4$ Hz, C_6H_4), 8.09 (2H, d, $J = 8.5$ Hz, C_6H_4), 10.08 (1H, s, CHO); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 121.4, 128.2, 130.5, 131.5, 136.0, 137.0, 137.2, 163.0, 192.9; Anal. Calcd for $C_{15}H_5Br_4NO_3$: C, 31.78; H, 0.89; N, 2.47; Br, 56.39; Found: C, 31.66; H, 1.11; N, 2.47; Br, 56.56; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{15}H_5Br_4NO_3$, 562.7003; found, 562.6993.

3-(1,3-Dioxo-6-phenylethynyl-1*H*,3*H*-benzo[*de*]isoquinolin-2-yl)benzaldehyde (62). A Schlenk flask with a teflon stirring bar was flame-dried and loaded with aldehyde **45** (617 mg, 1.62 mmol), $Pd(PPh_3)_2Cl_2$ (11.4 mg, 16 μmol, 1% mol) and anhydrous CuI (1.6 mg, 8 μmol). Air was evacuated and flask was purged with argon. Diisopropylamine (10 mL) was added, followed by phenylacetylene (230 μL, 2.11 mmol) and the reaction was stirred at 25 °C overnight. The reaction mixture was filtered through Celite and the solvent was removed under vacuum. Residue was chromatographed (DCM) and crystallized from chloroform/hexanes to give 585 mg (90%) of title compound as a yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 7.46 (3H, m, Ph), 7.61 (1H, m, C_6H_4), 7.67–7.77 (3H, m, C_6H_4+Ph), 7.89 (2H, m, C_6H_4+naphth.), 8.02 (2H, m, C_6H_4+naphth.), 8.61 (1H, d, $J = 7.6$ Hz, naphth.), 8.70 (1H, m, naphth.), 8.83 (1H, m, naphth.), 10.07 (1H, s, CHO); ^{13}C NMR (100 MHz, $CDCl_3$, TMS,

δ): 121.8, 122.1, 122.8, 127.6, 128.4, 128.7, 129.6, 129.8, 130.1, 130.2, 130.9, 131.8, 131.9, 132.2, 133.1, 134.8, 136.2, 137.6, 163.7, 164.0, 191.1; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{27}H_{15}NO_3$, 401.1052; found, 401.1044.

6-Phenylethynyl-2-*p*-tolyl-benzo[*de*]isoquinoline-1,3-dione(64). The mixture of 4-phenylethynyl-1,8-naphthalenedicarboxylic anhydride [106] (**63**, 150 mg, 0.5 mmol), *p*-toluidine (80 mg, 0.75 mmol) and imidazole (0.68 g, 10 mmol) in 7 mL of chloroform was stirred overnight at gentle reflux. Solvent was evaporated off and residue was triturated with small amount of absolute ethanol, filtered and air dried. The yield at this point was 183 mg (94%). Analytically pure sample was obtained after crystallization from chloroform. ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 2.45 (3H, s, CH_3), 7.20 (2H, d, $J = 8.1$ Hz, C_6H_4), 7.36 (2H, d, $J = 8.0$ Hz, C_6H_4), 7.45 (3H, m, Ph), 7.69 (2H, m, Ph), 7.87 (1H, t, $J = 7.8$ Hz, naphth.), 7.99 (1H, d, $J = 7.6$ Hz, naphth.), 8.60 (1H, d, $J = 7.6$ Hz, naphth.), 8.68 (1H, d, $J = 7.1$ Hz, naphth.), 8.80 (1H, d, $J = 8.1$ Hz, naphth.); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 21.3, 86.3, 99.3, 122.2, 122.2, 123.2, 127.5, 127.9, 128.2, 128.5, 128.7, 129.5, 130.1, 130.8, 130.8, 131.8, 131.9, 132.0, 132.6, 132.7, 138.7, 164.0, 164.3; Anal. Calcd for $C_{27}H_{17}NO_2$: C, 83.70; H, 4.42; N, 3.62; Found: C, 83.87; H, 4.59; N, 3.79; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{27}H_{17}NO_2$, 387.1259; found, 387.1250.

Corrole 66.

Method A. To the mixture of aldehyde **62** (456 mg, 1.14 mmol) and 5-(pentafluorophenyl)dipyrrane (709 mg, 2.27 mmol) in 17 mL of DCM 190 μL of TFA stock solution (see page 136) was added while stirring. After 20 min reaction was quenched with 30 μL of triethylamine, diluted with DCM to 200 mL and DDQ (0.67 g, 2.95 mmol) dissolved in a minimal amount of toluene was added. After 4 h of stirring, reaction mixture was passed through silica pad, evaporated with Celite and chromatographed (DCM/hexanes 1:1 ⟶ 2:1). Product-containing fractions were collected and evaporated. Crystallization from DCM/hexanes afforded 180 mg (16%) of corrole **66** as a crystalline solid.

Method B. A flame-dried Schlenk flask with a stirring bar was loaded with corrole **50** (196 mg, 0.2 mmol), palladium(II) acetate (2.2 mg, 10 μmol), triphenylphosphine (10.5 mg, 40 μmol) and Cs_2CO_3 (78 mg, 0.24 mmol). Air was evacuated and flask was purged with argon. Dry DMSO (1 mL) was added, followed by pheny-

lacetylene (26 μL, 0.24 mmol), and reaction was stirred for 24 h at 80 °C. After cooling to rt, reaction mixture was diluted with DCM, washed thoroughly with water and brine. Organic layer was separated and dried over Na_2SO_4. Solvent was evaporated and the residue was chromatographed on silica (toluene). Collected fractions were evaporated and residue dried under vacuum, giving 157 mg (78%) of desired corrole. The product and the substrate can not be distinguished on TLC (there is only minor difference in color) and the product formation was confirmed by NMR.

R_f 0.6 (DCM/hexanes 4:1); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 7.45 (3H, m, Ph), 7.68 (2H, m, Ph), 7.75 (1H, m, C_6H_4), 7.87–7.99 (2H, m, C_6H_4+naphth.), 8.02 (1H, d, $J = 8.0$ Hz, naphth.), 8.21 (1H, m, C_6H_4), 8.30 (1H, m, C_6H_4), 8.57 (2H, br s, β-H), 8.69 (1H, d, $J = 8.0$ Hz, naphth.), 8.74–8.85 (4H, m, naphth.+β-H), 8.97 (2H, d, $J = 4.4$ Hz, β-H), 9.11 (2H, m, β-H); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{57}H_{26}F_{10}N_5O_2$, 1002.1921; found, 1002.1918.

4-(6-Methoxynaphthalen-2-ylethynyl)-1,8-naphthalenedicarboxylic anhydride (68). A 100 mL round-bottom flask containing a magnetic stir bar was charged with 4-bromo-1,8-naphthalic anhydride (830 mg, 3 mmol), triphenylphosphine (16 mg, 0.06 mmol), copper(I) iodide (5.7 mg, 0.03 mmol), bis(triphenylphosphine)palladium dichloride (2.1 mg, 3 μmol), and 15 mL of triethylamine. 2-Ethynyl-6-methoxynaphthalene (656 mg, 3.6 mmol) was added to the flask with 30 mL of toluene. A condenser containing a nitrogen inlet was placed attached, and the reaction mixture was heated to reflux for 14 h. The reaction was cooled and filtered. The filtercake was washed with toluene and dried at 80 °C under vacuum. At this point the yield of a crude product,* yellow amorphous solid, was 1.11 g (98%) and it was used without further purification. HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{25}H_{14}O_4$, 378.0892; found, 378.0900

Aldehyde 69. The mixture anhydride **68** (756 mg, 2 mmol), 3-aminobenzaldehyde ethylene acetal (396 mg, 2.4 mmol) and imidazole (6.8 g, 0.1 mol) in chloroform (40 mL) was stirred at gentle reflux for 12 h and then cooled to rt. The solvent was removed on rotary evaporator and the residue was taken up in small amount of absolute ethanol. The resulting suspension was sonicated for 10 min, filtered,

*judging by NMR it is slightly contaminated with starting anhydride

washed with cold ethanol and dried under vacuum. NMR analysis revealed the mixture of aldehyde and acetal and the sample was fully deprotected by stirring it with excess of acetone in the presence of *p*-TsOH (35 mmol/L). The product was purified by gravity column chromatography (DCM/acetone 98:2), furnishing aldehyde **69** as a bright yellow solid (811 mg, 84%); mp 222–3 °C. Anal. Calcd for $C_{34}H_{23}NO_5$: C, 77.70; H, 4.41; N, 2.68; Found: C, 77.85; H, 4.34; N, 2.66 HRMS–EI (*m/z*): $[M]^{+\cdot}$ calcd for $C_{34}H_{23}NO_5$, 525.1576; found, 525.1564.

Corrole 71. To the mixture of aldehyde **69** (770 mg, 1.6 mmol) and 5-(pentafluorophenyl)dipyrrane (1 g, 3.2 mmol) in 24 mL of DCM, 260 μL of TFA stock solution (see page 136) was added while stirring. Reaction was very slow and it was left to stirr overnight, then quenched with 45 μL of triethylamine. After dilution with DCM to 300 mL, DDQ (944 mg, 4.16 mmol), dissolved in a minimal amount of toluene, was added and reaction was stirred for 2 h. Subsequently, the reaction mixture was passed through silica pad, evaporated with Celite and chromatographed (DCM/hexanes 3:1). There were additional spots with similar polarity and the sample was submitted to SEC purification (eluted with THF). Product-containing fractions were collected and evaporated. Crystallization from DCM afforded 320 mg (18%) of corrole **71** as a crystalline solid. R_f 0.4 (DCM/hexanes 3:1); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 3.95 (3H, s, OCH_3), 7.15 (1H, m, $C_{10}H_6$), 7.20 (1H, m, $C_{10}H_6$), 7.67 (1H, m, $C_{10}H_6$), 7.76 (3H, m, C_6H_4+$C_{10}H_6$), 7.89–8.00 (2H, m, C_6H_4+naphth.), 8.04 (1H, d, $J = 7.6$ Hz, naphth.), 8.13 (1H, s, $C_{10}H_6$), 8.22 (1H, m, C_6H_4), 8.30 (1H, m, C_6H_4), 8.57 (2H, br s, β-H), 8.70 (1H, d, $J = 7.6$ Hz, naphth.), 8.78 (4H, m, naphth.+β-H), 8.97 (2H, d, $J = 4.4$ Hz, β-H), 9.11 (2H, d, $J = 4.4$ Hz, β-H); MS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{62}H_{30}F_{10}N_5O_3$, 1082.2; found, 1082.5.

5,8-Dibromo-naphtho[2,3-*c*]furan-1,3-dione (73). The suspension of 2,3-naphthalenedicarboxylic anhydride (1.65 g, 8.3 mmol) and iodine (60 mg, 0.23 mmol) in 10 mL of water was heated to 50–60 °C and bromine (4.84 g, 30.3 mmol) was added dropwise while stirring. The temperature was increased and the reaction was stirred at gentle reflux for 3 h. After cooling to rt, the reaction mixture was poured in ice, precipitate was filtered off, washed with water and dried. The yield at this point was 92% and recrystallization from methanol afforded pure sample of diacid with mp 220–1 °C (lit.[109] 217-20 °C).

Anhydride function can be recovered in essentially quantitative yield by refluxing diacid in excess of acetic anhydride for 2 h. After solvent removal and drying under vacuum, crude product **73** was used without further purification. HRMS–EI (m/z): $[M+H]^{+\cdot}$ calcd for $C_{12}H_4Br_2O_3$, 353.8527; found, 353.8531.

3-(5,8-Dibromo-1,3-dioxo-1,3-dihydrobenzo[*f*]isoindol-2-yl)-benzaldehyde (75). The mixture of dibromoanhydride **73** (591 mg, 1.66 mmol) and 3-aminobenzaldehyde polymer (413 mg, 2 mmol) was refluxed in glacial acetic acid (10 mL) overnight. After solvent removal, residue was chromatographed (AcOEt/hexanes 3:2) to give 226 mg (25%) of title compound as a colorless solid. R_f 0.4 (THF/hexanes 1:2); ^{1}H NMR (400 MHz, DMSO-d_6, TMS, δ): 7.85 (2H, m, C_6H_4), 8.06 (2H, m, C_6H_4), 8.13 (2H, s, naphth.), 8.65 (2H, s, naphth.), 10.10 (1H, s, CHO); HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{19}H_9Br_2NO_3$, 303.0895; found, 303.0900.

Corrole 77. Aldehyde **75** (226 mg, 0.5 mmol) and 5-(pentafluorophenyl)dipyrrane (312 mg, 1 mmol) were suspended in DCM (8 mL). TFA stock solution* was added (85 μL) and the reaction was stirred for 20 min. Aldehyde was virtually insoluble in DCM. After addition of an acid, white suspension slowly transformed into a grey-black solution. Reaction was quenched with triethylamine (14 μL) and diluted to 120 mL with DCM, followed by DDQ† (295 mg, 1,3 mmol) addition. After 2 h of stirring at rt, reaction mixture was filtered through silica pad, evaporated with Celite and chromatographed on DCVC (DCM/hexanes 1:2 ⟶ 2:1). Product-containing fractions were collected, solvent was evaporated off and the residue was recrystallized from DCM giving 81 mg (15%) of **77**. R_f 0.5 (DCM/hexanes 3:2); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 7.87 (2H, s, naphth.), 7.96 (2H, m, C_6H_4), 8.30 (1H, br s, C_6H_4), 8.41 (1H, br s, C_6H_4), 8.57 (2H, br s, β-H), 8.77 (2H, br s, β-H), 8.96 (4H, m, β-H+naphth.), 9.12 (2H, br s, β-H);
MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{49}H_{19}^{79}Br^{81}BrF_{10}N_5O_2$, 1058.97; found, 1058.93;
UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 269 (53.8), 411 (140.1), 562 (21.4), 612 (12.1).

5,8-Dibromo-2-*p*-tolylbenzo[*f*]isoindole-1,3-dione (78). The mixture of dibromoanhydride **73** (356 mg, 1 mmol) and *p*-toluidine (130 mg, 1.2 mmol) was

*see page 136
†dissolved in minimal amount of toluene

refluxed in glacial acetic acid (5 mL) overnight. Solvent was removed in vacuum, residue was dissolved in DCM, washed with $NaHCO_3$, water and brine. Organic layer was separated and dried over $MgSO_4$. Purification by flash column chromatography (DCM/hexanes 3:1) furnished title compound as amorphous solid (331 mg, 74%). R_f 0.4 (DCM/hexanes 3:1); mp 271–2 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 2.44 (3H, s, CH_3), 7.37 (4H, m, C_6H_4), 7.85 (2H, s, naphth.), 8.88 (2H, s, naphth.) ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 21.3, 124.6, 125.2, 126.4, 128.9, 129.4, 129.9, 133.4, 135.9, 138.6, 166.3 Anal. Calcd for $C_{19}H_{11}Br_2NO_2$: C, 51.27; H, 2.49; N, 3.15; Br, 35.90; Found: C, 51.18; H, 2.69; N, 3.20; Br, 35.82 HRMS–EI (*m/z*): $[M]^{+\cdot}$ calcd for $C_{19}H_{11}{}^{79}Br^{81}BrNO_2$, 444.9136; found, 444.9126

5,8-Bis-phenylethynyl-2-*p*-tolylbenzo[*f*]isoindole-1,3-dione (79). Dry Schlenk flask was charged with dibromoimide **78** (250.4 mg, 0.59 mmol), bis(benzonitrile)palladium(II) chloride (13.5 mg, 0.035 mmol) and copper(I) iodide (4.5 mg, 0.023 mmol; stored under argon) and then purged with argon, followed by addition of anhydrous dioxane (1 mL). Reaction was allowed to stirr under inert atmosphere for 10 min at rt. Keeping the flask secure from air, P(*t*-Bu)$_3$ (290 μL of a 0.25 M solution in dioxane; 0.073 mmol), HN(*i*-Pr)$_2$ (0.2 mL, 1.4 mmol) and phenylacetylene (160 μL, 1.46 mmol) were added *via* syringe to the stirred reaction mixture. During the process, precipitation of $[H_2N(i\text{-}Pr)_2]Br$ was observed and after 14 h at 35 °C reaction mixture was diluted with chloroform and washed with water and brine. Organic layer was dried over $MgSO_4$ and then the solution was evaporated with Celite. The flash column chromatography (toluene) afforded pure **79** as a pale yellow solid (262 mg, 92%). R_f 0.3 (toluene); mp 271–2 °C; ^{1}H NMR (500 MHz, C_6D_6, δ): 2.06 (3H, s, CH_3), 6.98–7.03 (8H, m, C_6H_4+Ph), 7.45–7.47 (2H, m, Ph), 7.49 (2H, s, naphth.), 7.51–7.53 (4H, m, Ph), 9.19 (2H, s, naphth.); Anal. Calcd for $C_{35}H_{21}NO_2$: C, 86.22; H, 4.34; N, 2.87; Found: C, 86.34; H, 4.38; N, 2.84; HRMS–EI (*m/z*): $[M]^{+\cdot}$ calcd for $C_{35}H_{21}NO_2$, 487.1572; found, 487.1578.

Aldehyde 84. Anhydride **83**[111] (1.8 g, 5.3 mmol) and *p*-aminobenzaldehyde polymer (770 mg 6.36 mmol) were suspended in AcOH (14 mL) and reaction was stirred at reflux overnight. Orange color of aminobenzaldehyde disappeared and reaction was cooled to rt. Yellow solid was filtered off, washed with small amount of AcOH and dried under vacuum, giving 1.54 g (66%) of aldehyde **84**. R_f 0.4 (DCM); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 6.20 (2H, br s, NH_2), 7.00–7.05

(2H, m, Ph), 7.09–7.14 (2H, m, Ph), 7.17–7.24 (3H, m, Ph), 7.24–7.31 (3H, m, Ph), 7.65 (2H, m, C_6H_4), 7.97 (2H, m, C_6H_4), 10.03 (1H, s, CHO); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, δ): 104.0, 110.4, 114.9, 126.3, 127.7, 128.2, 128.9, 129.1, 129.4, 129.7, 130.2, 130.3, 131.6, 133.4, 135.1, 135.8, 136.6, 146.6, 154.4, 165.0, 167.1, 191.1; Anal. Calcd for $C_{28}H_{17}N_3O_3$: C, 75.84; H, 3.86; N, 9.48; Found: C, 75.94; H, 3.88; N, 9.44; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{28}H_{17}N_3O_3$, 443.1270; found, 443.1257.

Corrole 85. Aldehyde **84** (1.54 g, 3.47 mmol) and 5-(pentafluorophenyl)-dipyrrane (2.17 g, 6.95 mmol) were dissolved in 50 mL of DCM and 0.57 mL of TFA stock solution (see page 136) was added. Reaction was stirred at rt for 20 min and then quenched by the addition of triethylamine (0.1 mL). Reaction mixture was diluted with DCM to 450 mL and DDQ (2.05 g, 9 mmol; dissolved in minimal amount of toluene) was added. After 2 h of stirring at rt, reaction mixture was passed through silica pad, and then chromatographed (DCM/hexanes 1:1). The product was contaminated with additional fluorescent compounds which were successfully removed by the chromatography on SEC (eluted with toluene). Product-containing fractions were collected and evaporated. After crystallization, corrole **85** was obtained as dark fine powder (211 mg, 6%). R_f 0.4 (DCM/hexanes 1:1); ^{1}H NMR (500 MHz, THF-d_8, δ): (−4)–(−1.5) (3H, br s, NH), 6.90 (2H, br s, NH_2), 7.02–7.36 (10H, m, Ph), 7.93 (2H, d, J = Hz, C_6H_4), 8.33 (2H, d, J = Hz, C_6H_4), 8.63 (2H, br s, β-H), 8.71 (2H, m, β-H), 8.83 (2H, br s, β-H), 9.14 (2H, br s, β-H); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{58}H_{28}F_{10}N_7O_2$, 1044.2139; found, 1044.2171; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 411 (66.7), 562 (8.9), 613 (5.6).

4-Amino-1,3-dioxo-6,7-diphenyl-2-*p*-tolyl-2,3-dihydro-1*H*-isoindole-5-carbonitrile (86). Anhydride **83** (511 mg, 1.5 mmol) and *p*-toluidine (193 mg, 1.8 mmol) were heated under reflux in 5 mL of AcOH overnight. After cooling, solvent was evaporated off, the residue was dissolved in chloroform, washed with $NaHCO_3$, water and brine. Organic layer was separated and dried over $MgSO_4$. Flash column chromatography (DCM/hexanes 1:3 $\longrightarrow$ 2:1) and crystallization (chloroform/hexanes) afforded 350 mg (54%) of **86** as yellow crystals. R_f 0.3 (DCM/hexanes 1:2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 2.37 (3H, s, CH_3), 6.14 (2H, br s, NH_2), 7.01 (2H, m, C_6H_4), 7.03 (2H, m, C_6H_4), 7.11 (3H, m, Ph), 7.15 (7H, m, Ph); ^{13}C NMR (125 MHz, $CDCl_3$,

TMS, δ): 21.2, 103.7, 111.0, 115.1, 126.3, 127.6, 127.7, 128.2, 128.5, 128.8, 129.4, 129.5, 129.6, 130.4, 132.0, 133.6, 136.1, 138.2, 146.4, 153.9, 165.7, 167.8; Anal. Calcd for $C_{28}H_{19}N_3O_2$: C, 78.31; H, 4.46; N, 9.78; Found: C, 78.37; H, 4.44; N, 9.83; HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{28}H_{19}N_3O_2Na$, 452.1370; found, 452.1392.

7-Hydroxy-3-phenylethynyl-chromen-2-one (92).
A flame-dried Schlenk flask was loaded with bromocoumarin **91** (0.96 g, 4 mmol), $Pd(PPh_3)_3Cl_2$ (140 mg, 0.2 mmol) and copper(I) iodide (19 mg, 0.1 mmol). Air was evacuated and the flask was flushed with argon. Dry dioxane (8 mL), Hünig's base (1.4 mL) and phenylacetylene (0.66 mL, 6 mmol) were added *via* syringe maintaining inert atmosphere over the reaction mixture. The reaction was stirred at 90 °C overnight. After cooling to rt, reaction mixture was diluted with THF, 1M HCl solution and brine were added. Organic layer was separated, dried over Na_2SO_4 and evaporated with Celite. Gravity column chromatography (AcOEt/hexanes 2:3) afforded title compound as a yellow solid (200 mg, 19%). R_f 0.5 (AcOEt/hexanes 1:1); ^{1}H NMR (500 MHz, THF-d_8, TMS, δ): 6.69 (1H, d, $J = 2.1$ Hz, $H8$), 6.75 (1H, dd, $^3J = 8.6$ Hz, $^4J = 2.4$ Hz, $H6$), 7.35 (3H, m, Ph), 7.40 (1H, d, $J = 8.4$ Hz, $H5$), 7.51 (2H, m, Ph), 7.97 (1H, s, $H4$), 9.80 (1H, br s, OH); ^{13}C NMR (125 MHz, THF-d_8, TMS, δ): 85.3, 94.1, 103.2, 109.0, 112.7, 114.2, 124.0, 129.2, 129.4, 130.2, 132.4, 146.0, 156.7, 159.2, 163.2; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{17}H_{10}O_3$, 262.0630; found, 262.0636.

Corrole 96.
7-Diethylamino-4-methylcoumarin (139 mg, 0.4 mmol) and 5-(pentafluorophenyl)-dipyrrane (250 mg, 0.8 mmol) were dissolved in DCM (24 mL) and TFA (96 μL, 1.2 mmol) was slowly added. After stirring at rt for 1 h, Et_3N (166 μL, 1.2 mmol) was added and the reaction mixture was diluted by adding of 600 mL of DCM. Subsequently, DDQ (236 mg, 1.04 mmol) in THF (1.5 mL) was added with vigorous stirring. After 15 min, the reaction mixture was concentrated to 50 mL and filtered through a short (5 cm) silica pad (DCM, then DCM/acetone 95:5). The fluorescent band was collected, evaporated and chromatographed again (DCVC, DCM ⟶ DCM/acetone 95:5). Crystallization from chloroform/hexanes gave 63 mg (17%) of corrole **96**. R_f 0.64 (DCM/acetone 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): (–4)–(–1.5) (3H, br s, NH), 1.25 (6H, t, $J = 7.1$ Hz, CH_2CH_3),

3.45 (4H, q, $J = 7.1$ Hz, CH_2CH_3), 6.38 (1H, s, CH), 6.57 (1H, d, $J = 2.6$ Hz, Ar), 6.66 (1H, dd, $^3J = 9.0$ Hz, $^4J = 2.6$ Hz, Ar), 7.60 (2H, br s, (CH=CH)), 7.71 (1H, d, $J = 9.0$ Hz, Ar), 7.97, 8.24 (2×2H, d, $J = 7.9$ Hz, C_6H_4, AA'BB'), 8.58 (2H, br d, $J = 2.6$ Hz, β-H), 8.74 (4H, br s, β-H), 9.12 (2H, d, $J = 4.1$ Hz, β-H); Anal. Calcd for $C_{52}H_{31}F_{10}N_5O_2$: C, 65.89; H, 3.30; N, 7.39; Found: C, 65.98; H, 3.13; N, 7.29; HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{52}H_{32}F_{10}N_5O_2$, 948.2391; found, 948.2421; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 305 (37), 413 (417), 563 (22), 612 (13).

Coumarin 98. A mixture of 7-diethylamino-4-methylcoumarin (925 mg, 4 mmol) and *t*-BuOK (449 mg, 4 mmol) in DMSO (10 mL) was stirred for 10 min. Aldehyde **97** (1.11 g, 5 mmol) was added and the resulting mixture was stirred at rt for 5 h. Subsequently, AcOH (1.5 mL) was added, followed by water (90 mL). A yellow-red precipitate appeared, which was filtered off, washed with water and air dried. Chromatography on silica (DCM $\longrightarrow$ DCM/acetone 95:5) followed by crystallization from EtOH afforded 461 mg (27%) of **98** (contaminated with some unidentified species) as red crystals; mp 180 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 1.15 (6H, t, $J = 7.1$ Hz, CH_2CH_3), 3.46 (4H, q, $J = 7.1$ Hz, CH_2CH_3), 6.39 (1H, s, CH), 6.56 (1H, d, $J = 2.6$ Hz, Ar), 6.72 (1H, dd, $^3J = 9.0$ Hz, $^4J = 2.6$ Hz, Ar), 7.65 (1H, d, $J = 16$ Hz, CH=CH), 7.72 (1H, d, $J = 16$ Hz, CH=CH), 7.87 (1H, d, $J = 9.0$ Hz, Ar), 7.93–8.03 (8H, m, biphen.), 10.07 (1H, s, CHO); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ):12.8, 44.4, 97.6, 102.4, 107.3, 109.0, 121.8, 126.8, 127.7, 127.9, 128.4, 129.1, 130.6, 135.7, 136.7, 139.6, 145.5, 150.4, 150.9, 156.6, 161.6, 193.2; Anal. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31; Found: C, 79.22; H, 5.73; N, 3.28; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{28}H_{25}NO_3$, 423.1834; found, 423.1853; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 341 (42); IR (KBr): ν, cm^{-1} 813, 1138, 1412, 1520, 1604, 1696.

Corrole 99. Coumarin **93** (339 mg, 0.8 mmol) and 5-(pentafluorophenyl)-dipyrrane (500 mg, 1.6 mmol) were dissolved in DCM (48 mL) and TFA (192 μL, 2.4 mmol) was slowly added. After stirring at rt for 1 h, Et_3N (332 μL, 2.4 mmol) was added. DDQ (472 mg, 2.08 mmol) was dissolved in toluene-DCM (1:2, 48 mL) and both solutions were added simultaneously *via* syringes to vigorously stirred DCM (50 mL). After 15 min, the reaction mixture was concentrated to $^1/_4$ of the initial volume and filtered through a short (10 cm) silica pad (DCM $\longrightarrow$ DCM/acetone 99:1). The fluorescent band was collected, evap-

orated and loaded on SEC (THF). Fractions containing the desired product were evaporated to afford 10 mg (1.2%) of corrole **99**. R_f 0.6 (DCM/acetone 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): (–4)–(–1.5) (3H, br s, NH), 1.25 (6H, t, $J = 7.2$ Hz, CH_2CH_3), 3.45 (4H, q, $J = 7.2$ Hz, CH_2CH_3), 6.32 (1H, s, CH), 6.57 (1H, d, $J = 2.6$ Hz, Ar), 6.65 (1H, dd, $^3J = 9.0$ Hz, $^4J = 2.6$ Hz, Ar), 7.43 (2H, br s, CH=CH), 7.65 (1H, d, $J = 9.0$ Hz, Ar), 7.79, 7.97 (2×2H, d, $J = 8.4$ Hz, C_6H_4, AA'BB'), 8.04, 8.29 (2×2H, d, $J = 8.0$ Hz, C_6H_4, AA'BB'), 8.59 (2H, d, $J = 4.2$ Hz, β-H), 8.74 (2H, d, $J = 4.6$ Hz, β-H), 8.80 (2H, d, $J = 4.6$ Hz, β-H), 9.13 (2H, d, $J = 4.2$ Hz, β-H); MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{58}H_{35}F_{10}N_5O_2$, 1023.3; found, 1023.2; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 347 (38), 413 (112), 562 (16), 613 (9).

4-[(4-Trifluoromethylphenyl)ethenyl]-7-hydroxy-2-oxo-2*H*-chromene (102). A mixture of 7-hydroxy-4-methylcoumarin (3.52 g, 20 mmol) and *t*-BuOK (4.49 g, 40 mmol) in DMSO (80 mL) was stirred for 10 min. *p*-(Trifluoromethyl)benzaldehyde (4.1 mL, 30 mmol) was added and the resulting mixture was stirred at rt for 5 h. Subsequently, AcOH (10 mL) was added, followed by water (400 mL). A yellow-red precipitate appeared, which was filtered off, washed with water and air dried. Crystallization from EtOH afforded 2.6 g (39%) of **102** as yellowish crystals. Mp 259–61 °C; ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 6.57 (1H, s, CH), 6.74 (1H, d, $J = 2.3$ Hz, Ar), 6.82 (1H, dd, $^3J = 8.7$ Hz, $^4J = 2.5$ Hz, Ar), 7.66 (1H, d, $J = 16$ Hz, CH=CH), 7.76–7.80 (3H, m, CH=CH + C_6H_4), 8.00 (2H, d, $J = 7.8$ Hz, C_6H_4), 8.02 (1H, d, $J = 9.0$ Hz, Ar), 10.59 (1H, s, OH); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ):103.0, 106.2, 111.0, 113.4, 123.9, 126.0 (q, $J = 2.7$ Hz), 127.2, 128.9, 129.4 (q, $J = 38$ Hz), 136.3, 140.30, 14.31, 150.2, 155.8, 161.1, 161.8 Anal. Calcd for $C_{18}H_{11}O_3F_3$: C, 65.06; H, 3.34; Found: C, 64.83; H, 3.16; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{18}H_{11}O_3F_3$, 332.0660; found, 332.0667; UV-vis (CH_3CN): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 308 (22); IR (KBr): ν, cm^{-1} 842, 1066, 1321, 1386, 1677, 3103.

Aldehyde 104. The mixture of coumarin **102** (664 mg, 2 mmol), pentafluorobenzaldehyde (248 μL, 2 mmol) and CsF (608 mg, 4 mmol) in DMF (10 mL) was stirred at 65 °C for 1 h. Subsequently, water was added and the resulting mixture was extracted with DCM. The organic solvent was removed under reduced pressure and the residue was crystallized from EtOH affording 800 mg (79%) of title compound as off-white solid. Mp 236–9 °C; ^{1}H NMR (500 MHz, DMSO-d_6, TMS,

δ): 6.82 (1H, s, CH), 7.32 (1H, dd, $^3J = 9.0$ Hz, $^4J = 2.8$ Hz, Ar), 7.37 (1H, d, $J = 2.8$ Hz, Ar), 7.75 (1H, d, $J = 16$ Hz, CH=CH), 7.82, 8.05 (2×2H, d, $J = 8.2$ Hz, C_6H_4, AA'BB'), 7.87 (1H, d, $J = 16$ Hz, CH=CH), 8.31 (1H, d, $J = 9.0$ Hz, Ar), 10.24 (1H, s, CHO); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ):104.3, 109.3, 112.7 (m), 113.0, 1115.4, 123.4, 123.5, 126.1 (q, $J = 3.9$ Hz), 127.9, 128.0, 129.0, 129.7 (q, $J = 38$ Hz), 137.0 (m), 140.2 (m), 146.6 (m), 148.7 (m), 149.6, 155.3, 159.0, 160.4, 183.9; Anal. Calcd for $C_{25}H_{11}O_4F_7$: C, 59.07; H, 2.18; Found: C, 59.08; H, 1.96; HRMS–EI (*m/z*): $[M]^{+\cdot}$ calcd for $C_{25}H_{11}O_4F_7$, 508.0546; found, 508.0539; UV-vis (DMSO): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 315 (25); IR (KBr): ν, cm^{-1} 841, 1114, 1327, 1489, 1613, 1698.

Corrole 105. Aldehyde **104** (306 mg, 0.6 mmol) and 5-(pentafluorophenyl)-dipyrrane (375 mg, 1.2 mmol) were suspended in DCM (18 mL) and TFA (18 μL, 0.23 mmol) was slowly added. After stirring at rt for 1 h (aldehyde slowly dissolved), Et_3N (33 μL, 0.23 mmol) was added. DDQ (354 mg, 1.56 mmol) was dissolved in toluene/DCM (1:2, 18 mL) and both solutions were added simultaneously *via* syringes to vigorously stirred DCM (40 mL). After 15 min, the reaction mixture was concentrated to $^1/_4$ of the initial volume and filtered through silica pad. The fluorescent band was collected, evaporated and loaded on SEC (THF). Fractions containing the desired product were evaporated to afford 33 mg (5%) of corrole **105**. R_f 0.3 (DCM/hexane 3:1); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 6.59 (1H, s, CH), 7.24 (1H, d, $J = 2.0$ Hz, Ar), 7.33 (1H, dd, $^3J = 9.0$ Hz, $^4J = 2.0$ Hz, Ar), 7.38 (1H, d, $J = 16$ Hz, CH=CH), 7.46 (1H, d, $J = 16$ Hz, CH=CH), 7.72 (4H, br s, C_6H_4), 7.92 (1H, d, $J = 9.0$ Hz, Ar), 8.04, 8.29 (2×2H, d, $J = 8.0$ Hz, C_6H_4, AA'BB'), 8.54 (2H, br s, β-H), 8.70 (2H, d, $J = 4.5$ Hz, β-H), 8.82 (2H, d, $J = 4.5$ Hz, β-H), 9.08 (2H, br s, β-H); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{55}H_{22}F_{17}N_4O_3$, 1109.1415; found, 1109.1372; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 308 (42), 408 (123), 562 (20), 604 (11).

Coumarin 106. Coumarin **100** (1.156 g, 5 mmol) was dissolved in DMSO (7 mL) and after addition of *t*-BuOK (561 mg, 5 mmol) the mixture was stirred at rt for 10 min. *p*-Trifluoromethylbenzaldehyde (1.02 mL, 7.5 mmol) was added and stirring was continued for 5 h. After this time 3 mL of acetic acid was added, followed by water (100 mL). Precipitate was filtered off and air-dried. Purification by crystallization (ethanol) as well as by flash chromatography (DCM) failed and

I was able to obtain pure sample after very slow chromatography (5% methanol in DCM). Crystallization from ethanol afforded 752 mg (39%) of title product as orange plates. R_f 0.3 (DCM); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 1.23 (6H, t, $J = 7.2$ Hz, CH_3), 3.43 (4H, q, $J = 7.2$ Hz, CH_2), 6.25 (1H, s, coum.-H3), 6.55 (1H, d, $J = 2.5$ Hz, coum.-H8), 6.62 (1H, dd, $^3J = 8.9$ Hz, $^4J = 2.4$ Hz, coum.-H6), 7.28 (1H, d, $J = 15.4$ Hz, *trans*-CH=CH+solv.), 7.38 (1H, d, $J = 16.1$ Hz, *trans*-CH=CH), 7.55 (1H, d, $J = 9.0$ Hz, coum.-H5), 7.67 (4H, s, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 12.4, 44.8, 98.1, 104.5, 107.5, 108.6, 123.9 (q, $J = 270$ Hz), 124.0, 125.3, 125.9 (m), 127.5, 130.8 (q, $J = 33$ Hz), 134.9, 139.3, 149.8, 150.7, 156.5, 162.3; Anal. Calcd for $C_{22}H_{20}F_3NO_2 \cdot 0.25C_2H_5OH$: C, 67.42; H, 5.25; N, 3.57; Found: C, 67.61; H, 5.07; N, 3.85; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{22}H_{20}F_3NO_2$, 387.1446; found, 387.1454; UV-vis (THF): λ_{max} 410 nm.

Coumarin 108. Coumarin **102** (332 mg, 1 mmol) and cesium fluoride (304 mg, 2 mmol) were suspended in dry DMF (2 mL). Pentafluorobenzonitrile (123 μL, 1 mmol) was added and reaction was stirred at 65 °C for 1 h (under argon). Reaction mixture was diluted with water (20 mL) and extracted with DCM (3×10 mL). Combined organic layers were dried over $MgSO_4$, concentrated and passed through silica pad. Crystallization from ethanol afforded 406 mg (80%) of coumarin **108** as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 6.84 (1H, s, coum.-*H*3), 7.35 (1H, dd, $^3J = 8.8$ Hz, $^4J = 2.6$ Hz, coum.-*H*6), 7.38 (1H, d, $J = 2.6$ Hz, coum.-*H*8), 7.76 (1H, d, $J = 16.1$ Hz, *trans*-CH=CH), 7.82 (2H, d, $J = 8.3$ Hz, C_6H_4), 7.87 (1H, d, $J = 16.1$ Hz, *trans*-CH=CH), 8.04 (2H, d, $J = 8.2$ Hz, C_6H_4), 8.32 (1H, d, $J = 8.9$ Hz, coum.-*H*5); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 104.2, 108.4, 109.3, 113.0, 115.5, 123.4, 126.1, 128.1, 129.0, 129.5, 129.7, 137.0, 137.6, 140.2, 140.6, 142.6, 147.4, 149.6, 155.3, 158.9, 160.4; Anal. Calcd for $C_{25}H_{10}F_7NO_3$: C, 59.42; H, 1.99; N, 2.77; Found: C, 59.39; H, 2.19; N, 2.88; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{10}H_7NO_4$, 505.0549; found, 505.0557.

7-Hydroxy-2-oxo-2H-chromene-3-carboxylic acid amide (110). 3-Ethoxycarbonyl-7-hydroxycoumarin (**109**,[140] 2.58 g, 11 mmol) and ammonium acetate (4.07 g, 13.2 mmol) were heated in a flask, equipped with air condenser at 140 °C for 1 h (reaction progress was followed by TLC). The reaction mixture thickened under cooling and it was triturated with small amount of boiling methanol

precipitate was filtered off after cooling. The solid was washed with methanol and dried at 140 °C for 2 h, giving 1.58 g (70%) of title compound. R_f 0.5 (AcOEt); mp 309–10 °C; ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 6.79 (1H, d, $J = 2.2$ Hz, $H8$), 6.88 (1H, dd, $^3J = 8.6$ Hz, $^4J = 2.3$ Hz, $H6$), 7.76 (1H, br s, NH), 7.80 (1H, d, $J = 8.6$ Hz, $H5$), 8.03 (1H, br s, NH), 8.79 (1H, s, $H4$), 11.08 (1H, br s, OH); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 102.2, 111.5, 114.3, 114.8, 132.4, 148.8, 156.9, 161.4, 163.4, 164.2; Anal. Calcd for $C_{10}H_7NO_4$: C, 58.54; H, 3.44; N, 6.83; Found: C, 58.59; H, 3.55; N, 6.82; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{10}H_7NO_4$, 205.0375; found, 205.0379.

2,3,5,6-Tetrafluoro-4-((6-oxo-6*H*-benzo[*c*]chromen-3-yl)oxy)benzaldehyde (114). 3-Hydroxy-6*H*-benzo[*c*]chromen-6-one (**113**,[143] 1.06 g, 5 mmol) was dissolved in DMF (10 mL). Then cesium fluoride (1.52 g, 10 mmol) was added, followed by pentafluorobenzaldehyde (0.62 mL, 5 mmol). A white precipitate was formed immediately after the aldehyde addition. The reaction was stirred for 2 h, diluted with water and stirred for further 30 min. The obtained precipitate was filtered off, washed thoroughly with water and air-dried. Crystallisation from glacial acetic acid yielded title compound (1.67 g, 86%) as an off-white solid. R_f 0.6 (chloroform); mp 227–8 °C; ^{1}H NMR (500 MHz, DMSO-d_6, TMS, δ): 7.32 (1H, dd, $^3J = 8.8$ Hz, $^4J = 2.6$ Hz, Ar), 7.37 (1H, d, $J = 2.6$ Hz, Ar), 7.69 (1H, m, Ar), 7.97 (1H, m, Ar), 8.25 (1H, m, Ar), 8.43 (2H, m, Ar), 10.24 (1H, s, CHO); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 104.9, 112.4, 113.2, 114.9, 120.4, 123.1, 126.1, 129.2, 130.2, 134.4, 135.9, 137.1, 141.4 (dm, $J = 235$ Hz), 147.7 (dm, $J = 250$ Hz), 152.4, 157.9, 160.5, 183.9; Anal. Calcd for $C_{20}H_8F_4O_4$: C, 61.87; H, 2.08; F, 19.57; Found: C, 61.98; H, 2.28; F, 19.57; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{20}H_8F_4O_4$, 388.0359; found, 388.0363; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 263 (19), 273 (22), 301 (18).

2,3,5,6-Tetrafluoro-4-(6-oxo-6*H*-benzo[*c*]chromen-3-yloxy)benzonitrile (115). To the solution of **113** (637 mg, 3 mmol) and pentafluorobenzonitrile (0.4 mL, 3.3 mmol) in 6 mL of DMF cesium fluoride (957 mg, 6.3 mmol) was added. Reaction was stirred at rt for 4 h, then diluted with water (50 mL) and stirred for further 30 min. Precipitate was filtered off, washed with water and air-dried. The yield of crude product was 1.13 g (98%). Analytically pure sample was obtained by recrystallization from ethyl acetate. R_f 0.5 (AcOEt/hexanes 3:2);

mp 205–6 °C; ^{1}H NMR (600 MHz, DMSO-d_6, TMS, δ): 7.33 (1H, dd, ^3J = 8.8 Hz, ^4J = 2.7 Hz, Ar), 7.37 (1H, d, J = 2.7 Hz, Ar), 7.69 (1H, m, Ar), 7.97 (1H, m, Ar), 8.24 (1H, m, Ar), 8.44 (2H, m, Ar); ^{13}C NMR (150 MHz, DMSO-d_6, TMS, δ): 104.2, 112.7, 114.5, 119.9, 122.5, 125.6, 129.1, 129.7, 133.8, 135.4, 151.8, 157.2, 159.9; Anal. Calcd for $C_{20}H_7F_4NO_3$: C, 62.35; H, 1.83; N, 3.64; F, 19.72; Found: C, 62.48; H, 1.96; N, 3.56; F, 19.71; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{20}H_7F_4NO_3$, 385.0362; found, 385.0350.

Corrole 116. Aldehyde **114** (970 mg, 2.5 mmol) and 5-(pentafluorophenyl)-dipyrrane (1.56 g, 5 mmol) were suspended in dichloromethane (37 mL). Then the pre-prepared solution of TFA (410 μL; see page 136) was added while stirring. The reaction was stirred at rt for 40 min (monitored by TLC). Subsequently, triethylamine (70 μL) was added to quench the reaction. The resulting solution was diluted to 150 mL with DCM and oxidized with DDQ (1.48 g, 6.5 mmol; dissolved in a minimal amount of toluene). After 2 h, the reaction mixture was filtered through a silica pad, corrole-containing fractions were collected and evaporated with Celite and then chromatographed on a 15 cm column, eluting with DCM/hexanes (hexanes ⟶ DCM/hexanes 1:1; when the red fluorescent product was close to the bottom of a column, 0.2% of methanol was added to the eluent). Crystalline sample was obtained by boiling the product in a small amount of dichloromethane and filtering off precipitate after cooling the mixture (150 mg, 6%). R_f 0.6 (DCM/hexanes 2:1); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 7.28 (1H, s, coum.), 7.35 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, coum.), 7.62 (1H, m, coum.), 7.88 (1H, m, coum.), 8.13 (1H, d, J = 8.4 Hz, coum.), 8.20 (1H, d, J = 9.2 Hz, coum.), 8.43 (1H, m, coum.), 8.59 (2H, m, β-H), 8.69 (2H, d, J = 4.4 Hz, β-H) 8.82 (2H, d, J = 4.4 Hz, β-H) 9.12 (2H, d, J = 4.4 Hz, β-H); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{50}H_{19}F_{14}N_4O_3$, 989.1228; found, 989.1226; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 274 (37), 301 (31), 408 (145), 562 (23), 604 (13).

7-Hydroxy-9-oxa-4-aza-phenanthren-10-one (118). The solution of 2-bromonicotinic acid (202 mg, 1 mmol), resorcinol (198 mg, 1.8 mmol) and NaOH (80 mg, 2 mmol) in 2 mL of water was heated to 60–70 °C and 70 μL of 10% $CuSO_{4(aq.)}$ solution was added. Precipitate was not formed as it was in the case of model compound **113**[143] and the solution was heated for further 15 min. Af-

ter cooling to rt reaction mixture became turbid and it was extracted with DCM (5×20 mL). After solvent evaporation, the remaining amorphous residue (16 mg, 8%), was sparingly soluble in common organic solvents. HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{12}H_7NO_3$, 213.0426; found, 213.0433.

Biscoumarin 123. The mixture of coumarin **109** (3.47 g, 14.8 mmol) and 3-diethylaminophenol (2.45 g, 14.8 mmol) was heated in a closed vessel at 140 °C for 6 h. After cooling, tarry mass was triturated with ether to wash out unreacted material and other contaminants. Raw product was boiled in small amount of 2-propanol, cooled and filtered, giving 1.43 g (55%) of biscoumarin **123** as dark orange crystals. R_f 0.5 (DCM/acetone 7:3); mp 281–3 °C; ^{1}H NMR (600 MHz, DMSO-d_6, TMS, δ): 1.17 (6H, t, $J = 6.9$ Hz, CH_3), 3.50 (4H, q, $J = 7.0$ Hz, CH_2), 6.55 (1H, d, $J = 3.0$ Hz, Ar), 6.72 (1H, d, $J = 3.0$ Hz, Ar), 6.80 (1H, dd, $^3J = 9.6$ Hz, $^4J = 2.4$ Hz, Ar), 6.89 (1H, dd, $^3J = 9.3$ Hz, $^4J = 2.7$ Hz, Ar), 8.07 (1H, d, $J = 9.6$ Hz, Ar), 8.15 (1H, d, $J = 9.0$ Hz, Ar), 11.07 (1H, br s, OH); ^{13}C NMR (125 MHz, DMSO-d_6, TMS, δ): 12.8, 44.7, 97.0, 97.2, 103.2, 103.7, 108.0, 110.2, 114.0, 130.9, 131.4, 152.3, 152.8, 156.4, 156.7, 157.0, 157.9, 163.8; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{20}H_{27}NO_5$, 351.1107; found, 351.1096; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 283 (17), 371 (17), 444 (32); λ_{em}, 507 nm.

Synthesis of biscoumarin 126. Hydroxybiscoumarin **123** (351 mg, 1 mmol) and pentafluorobenzonitrile (251 mg, 1.3 mmol) were suspended in DMF (3 mL). Cesium fluoride (350 mg, 2.3 mmol) was added and the mixture was stirred at rt for 4 h (during this time both substrates have dissolved). Subsequently, 7 mL of water was added and reaction was stirred for the next 30 min. Reaction mixture was extracted with DCM and combined organic layers were dried over $MgSO_4$, evaporated and chromatographed, giving 320 mg (61%) of title compound as yellow crystalline solid. R_f 0.4 (DCM); mp 305–6 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 1.28 (6H, t, $J = 7.2$ Hz, CH_3), 3.50 (4H, q, $J = 7.2$ Hz, CH_2), 6.54 (1H, d, $J = 2.7$ Hz, Ar), 6.71 (1H, dd, $^3J = 9.3$ Hz, $^4J = 2.5$ Hz, Ar), 6.95 (1H, d, $J = 2.6$ Hz, Ar), 7.04 (1H, dd, $^3J = 9.0$ Hz, $^4J = 2.7$ Hz, Ar), 8.00 (1H, dd, $J = 9.4$ Hz, Ar), 8.26 (1H, dd, $J = 9.1$ Hz, Ar); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 12.5, 45.2, 97.9, 99.2, 103.9, 104.8, 106.8, 109.9, 112.2, 113.0, 129.8, 130.9, 151.5, 152.9, 156.0, 156.5, 156.8, 158.3, 159.7; Anal. Calcd for $C_{27}H_{16}F_4N_2O_5 \cdot 0.5H_2O$: C, 60.79; H, 3.21; N, 5.25; Found: C, 61.08; H, 3.17; N, 5.24; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for

$C_{27}H_{16}F_4N_2O_5$, 524.0995; found, 524.0978; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 290 (28.6), 344 (17.0), 462 (35.9); λ_{em}, 528 nm.

1-(Acridin-9-yl)-5-(2,6-dichlorophenyl)dipyrrane (132). Acridine (358 mg, 2 mmol) and 5-(2,6-dichlorophenyl)dipyrrane[97] (291 mg, 1 mmol) were dissolved in toluene (20 mL). Benzoyl chloride (128 μL, 1.1 mmol) was added while stirring. The mixture was stirred for 24 h at 75 °C. Toluene was removed under reduced pressure and residue was treated for 6 h with diluted aqueous ammonia in the presence of a few milliliters of DCM. The mixture was extracted with DCM and the organic layers were collected and dried over Na_2SO_4. Solvent was evaporated and the residue was chromatographed (gravity column, silica gel, toluene/acetone 4:1) to yield the product contaminated with traces of acridine, which was removed by diffusion crystallization, yielding 163 mg (35%) of **132**. R_f 0.4 (silica, DCM/MeOH 98:2); mp 240 °C (dec); ^{1}H NMR (400 MHz, DMF-d_7, TMS, δ): 6.05 (2H, t, $J = 2.4$ Hz, pyrr.), 6.19 (1H, m, pyrr.), 6.49 (1H, dd, $^3J = 3.4$ Hz, $^4J = 2.5$ Hz, pyrr.), 6.53 (1H, br s, *meso*-CH), 6.81 (1H, dd, $^3J = 4.7$ Hz, $^4J = 2.4$ Hz, pyrr.), 7.34 (1H, dd, $^3J = 8.6$ Hz, $^4J = 7.5$ Hz, C_6H_3), 7.50 (2H, d, $J = 8.0$ Hz, C_6H_3), 7.54 (2H, m, acr.), 7.79 (2H, m, acr.), 8.15 (2H, dm, acr.), 8.26 (2H, dm, acr.), 10.79 (1H, br s, NH), 11.36 (1H, br s, NH); ^{13}C NMR (100 MHz, DMF-d_7, TMS, δ): 41.4, 96.6, 107.7, 107.9, 109.2, 113.3, 117.9, 124.5, 126.1, 128.1, 129.7, 129.9, 130.1, 130.3, 130.5, 134.9, 136.6, 138.6, 140.1, 149.6; Anal. Calcd for $C_{28}H_{19}Cl_2N_3$: C, 71.80; H, 4.09; N, 8.97; Found: C, 71.94; H, 4.08; N, 8.83; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{28}H_{19}Cl_2N_3$, 467.0956; found, 467.0971; UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 415 (8.1), 362 (7.4), 345 (5.5).

1-(Acridin-9-yl)-5-(4-cyanophenyl)dipyrrane (133). Acridine (358 mg, 2 mmol) and 5-(4-cyanophenyl)dipyrrane[167] (247 mg, 1 mmol) were dissolved in toluene (20 mL). Benzoyl chloride (128 μL, 1.1 mmol) was added while stirring. The mixture was stirred for 24 h at 75 °C. Toluene was removed under reduced pressure and the residue was washed for 6 h with diluted aqueous ammonia in the presence of a few milliliters of DCM. The mixture was extracted with DCM and the organic layers were collected and dried over Na_2SO_4. Solvent was evaporated and the residue was submitted to silica-pad filtration. The residue was then purified by DCVC (toluene/acetone 4:1) and crystallized from hexanes/DCM to yield yellow powder (291 mg, 69%). R_f 0.35 (silica, DCM/MeOH 98:2); mp 195 °C (dec);

^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 5.85 (1H, s, pyrrole), 6.19 (1H, m, pyrrole), 6.28 (2H, m, pyrrole), 6.42 (1H, m, *meso*-CH), 6.83 (1H, m, pyrrole), 7.08 (2H, m, acr.), 7.35 (2H, m, acr.), 7.49 (2H, d, $J = 8.8$ Hz, C_6H_4), 7.55 (2H, d, $J = 8.1$ Hz, acr.), 7.69 (2H, d, $J = 8.6$ Hz, C_6H_4), 7.73 (2H, m, acr.), 9.20 (1H, br s, NH), 9.82 (1H, br s, NH); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 44.3, 108.4, 108.7, 109.4, 111.0, 113.1, 118.4, 118.8, 124.5, 124.9, 125.4, 126.7, 128.0, 129.5, 130.1, 130.6, 132.4, 148.1; HRMS–FD (*m/z*): $[M]^{+\cdot}$ calcd for $C_{29}H_{20}N_4$, 424.1688; found, 424.1705; UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 400 (8.0), 362 (8.9), 347 (5.4).

1-(Acridin-9-yl)-5-(2,6-dichlorophenyl)dipyrrin (134). Dipyrrane **132** (467 mg, 1 mmol) was dissolved in a minimal volume of THF and diluted with toluene to 25 mL. Concentrated solution of DDQ (205 mg, 0.9 mmol) in THF was added while stirring. The mixture was stirred overnight at rt. The resulting mixture was concentrated and the precipitate was filtered off and washed with toluene. The solid was dissolved in DCM, evaporated with silica and chromatographed (DCM ⟶ DCM/MeOH 95:5). The product was recrystallized from THF/hexanes to yield orange crystalline powder (214 mg, 46%); R_f 0.75 (silica, DCM/MeOH 98:2); mp 240–2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 6.30 (1H, dd, $^3J = 4.0$ Hz, $^4J = 2.0$ Hz, pyrrole), 6.34 (1H, dd, $^3J = 4.0$ Hz, $^4J = 1.3$ Hz, pyrrole), 6.81 (1H, d, $J = 4.4$ Hz, pyrrole), 6.84 (1H, d, $J = 4.4$ Hz, pyrrole), 7.27 (1H, m, pyrrole), 7.42 (1H, dd, $^3J = 8.8$ Hz, $^4J = 7.2$ Hz, C_6H_3), 7.51–7.58 (4H, m, C_6H_3+acr.), 7.82 (2H, m, acr.), 8.27 (2H, m, acr.), 8.32 (2H, d, $J = 8.6$ Hz, acr.); ^{13}C NMR (50 MHz, $CDCl_3$, TMS, δ): 96.7, 114.0, 122.9, 124.6, 126.2, 126.7, 126.9, 128.0, 129.4, 130.3, 132.0, 133.9, 134.0, 134.7, 135.7, 140.8, 146.9, 148.5, 162.3, 169.5; HRMS–EI (*m/z*): $[M]^{+\cdot}$ calcd for $C_{28}H_{17}Cl_2N_3$, 465.0800; found, 465.0816; UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 472 (35.0), 366 (15.6).

1-(Acridin-9-yl)-5-(4-cyanophenyl)dipyrrin (135). Dipyrrane **133** (380 mg, 0.9 mmol) was dissolved in a minimal volume of THF and diluted with toluene to 25 mL. A concentrated solution of DDQ (205 mg, 0.9 mmol) in THF was added while stirring. The mixture was stirred overnight at rt. The resulting mixture was concentrated and the precipitate was filtered off and washed with toluene. The solid was dissolved in DCM, evaporated with silica and chromatographed (DCM ⟶ DCM/MeOH 98:2). The product was recrystallized from DCM/hexanes to yield title compound as orange crystalline powder (195 mg,

51%). R_f 0.5 (silica, DCM/MeOH 98:2); mp > 240 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 6.33 (1H, dd, $^3J = 4.0$ Hz, $^4J = 2.2$ Hz, pyrrole), 6.43 (1H, dd, $^3J = 4.0$ Hz, $^4J = 1.3$ Hz, pyrrole), 6.86 (1H, d, $J = 4.4$ Hz, pyrrole), 6.93 (1H, d, $J = 4.4$ Hz, pyrrole), 7.29 (1H, m, pyrrole), 7.53 (2H, m, acr.), 7.75–7.87 (6H, m, C_6H_4+acr.), 8.21 (2H, m, acr.), 8.31 (2H, d, $J = 8.8$ Hz, acr.); ^{13}C NMR (50 MHz, THF-d_8, TMS, δ): 97.074, 113.8, 114.2, 118.8, 125.1, 125.4, 126.8, 127.4, 127.5, 130.4, 131.1, 132.4, 132.5, 134.3, 134.6, 141.2, 141.6, 142.7, 148.4, 150.0, 163.8; HRMS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{29}H_{18}N_4$, 422.1531; found, 422.1513; UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 475 (32.2), 363 (13.9).

9-(1*H*-Pyrrol-2-yl)-9,10-dihydro-acridine 138.
Acridine (1.79 g, 10 mmol) was dissolved in freshly distilled pyrrole (70 mL) and the mixture was degased with argon for 15 min. The flask was equipped with condenser and balloon filled with argon, securing joints with teflon O-rings, and the mixture was refluxed under argon for 24 h. After cooling to rt, pyrrole was evaporated under vacuum and the residue was chromatographed. First, reduced form (compound **138**) was collected (EtOAc/hexanes 1:1) and after increasing eluent polarity (2% MeOH in DCM) – oxidized one (9-(1*H*-pyrrol-2-yl)acridine).

Reduced form (**138**): 2.09 g (85%). R_f 0.5 (EtOAc/hexanes 2:3); mp 155–155.5 °C (lit.[164] 152-3 °C); HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{17}H_{14}N_2$, 246.1157; found, 246.1163.

Oxidized form (**130**): 245 mg (10%). R_f 0.5 (DCM/MeOH 95:5); mp 233–5 °C (lit.[164] 229-30 °C); ^{1}H NMR (400 MHz, DMSO-d_6, TMS, δ): 6.44 (1H, m, pyrr.), 6.53 (1H, m, pyrr.), 7.20 (1H, m, pyrr.), 7.59 (2H, m, acr.), 7.85 (2H, m, acr.), 8.06 (2H, d, $J = 8.7$ Hz, acr.), 8.19 (2H, d, $J = 8.7$ Hz, acr.), 11.64 (1H, br s, NH); ^{13}C NMR (50 MHz, DMSO-d_6, TMS, δ): 109.6, 113.1, 121.2, 124.6, 125.8, 126.7, 127.7, 130.0, 130.9, 139.9, 149.2; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{17}H_{12}N_2$, 244.1001; found, 244.0995.

5-Acridin-9-yl-1*H*-pyrrole-2-carbaldehyde 137. Vilsmeier complex was prepared by dropwise addition of 217 μL of $POCl_3$ to DMF (3 mL) while maintaining the temperature below 5 °C. The complex was stirred at 0 °C for 20 min and then the solution of **130** in DMF 2 mL was added. The reaction was allowed to warm up to rt and was stirred for further 1 h. Then the temperature was raised to 80 °C, reaction was stirred for 4 h and after cooling to rt was poured on crushed ice

(10 g). Later, the mixture was neutralized by Na_2CO_3 and heated briefly at reflux. Precipitate was collected by filtration and air-dried. Dissolving in ethanol and boiling with activated carbon allowed to remove majority of colorful impurities. The yield of crude product was 430 mg (68%). Crystallization from ethanol afforded dark orange crystals. HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{18}H_{12}N_2O$, 272.0950; found, 272.0938.

4-(5-Acridin-9-yl-1*H*-pyrrol-2-yl)-benzaldehyde (142). A flame-dried Schlenk flask was charged with crude **138** (3.53 g, 14.3 mmol), *p*-bromobenzaldehyde (3.19 g, 17.2 mmol), palladium(II) acetate (322 mg, 1.44 mmol) and potassium acetate (2.8 g, 28.7 mmol). Air was evacuated and flask was purged with argon. DMA (40 mL) was added maintaining inert atmosphere and the reaction was stirred at 130 °C for 17 h. After cooling, reaction mixture was passed through silica pad, diluted with water and extracted (DCM). Combined organic fractions were dried over Na_2SO_4, and evaporated. The residue was chromatographed on alumina: first with DCM to wash out side-product with blue fluorescence and then main product was collected (while eluting with AcOEt/hexanes 3:2 $\longrightarrow$ pure AcOEt). Product-containing fractions were collected, solvent was evaporated off and residue (2.45 g, 49 %) was recrystallized from dioxane. R_f 0.6 (alumina, AcOEt/hexanes+drop of Et_3N); ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.66 (1H, m, pyrrole), 7.18 (1H, m, pyrrole), 7.63 (2H, m, acr.), 7.84–7.91 (2H, m, acr.), 7.92 (2H, d, $J = 8.4$ Hz, C_6H_4), 8.01 (2H, d, $J = 8.3$ Hz, C_6H_4), 8.08 (2H, d, $J = 8.7$ Hz, acr.), 8.22 (2H, d, $J = 8.7$ Hz, acr.), 9.96 (1H, s, CHO), 12.27 (1H, br s, NH); ^{13}C NMR (50 MHz, THF-d_8, TMS, δ): 110.7, 115.4, 124.6, 125.9, 127.1, 127.5, 128.4, 130.1, 131.1, 131.1, 133.2, 134.3, 138.6, 138.9, 149.1, 192.8; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{24}H_{16}N_2O$, 348.1263; found, 248.1269.

Corrole 143. Aldehyde **142** (331 mg, 0.95 mmol) and 5-(pentafluorophenyl)-dipyrrane (593 mg, 1.9 mmol) were suspended in 14 mL of DCM. TFA stock solution (0.98 mL; see page 136) was added and reaction was stirred at rt for 1 h (aldehyde was totally consumed). Subsequently, the reaction was quenched by triethylamine addition (170 μL). Reaction mixture was diluted with DCM to 300 mL and oxidized by addition of DDQ (560 mg, 2.47 mmol) dissolved in 100 mL of DCM. After 2 h the mixture was passed through silica pad, evaporated with Celite and chromatographed (2% methanol in toluene). After the first column there were still

impurities with similar R_f, which were separated on SEC (eluted with THF). Crystallization from chloroform/hexanes afforded 44 mg (5%) of desired corrole. R_f 0.5 (5% MeOH in DCM); ^{1}H NMR (400 MHz, DMSO-d_6, δ): (−4)–(−1.5) (3H, br s, NH), 6.78 (1H, s, pyrrole), 7.25 (1H, br s, pyrrole), 7.72 (2H, m, acr.), 7.95 (2H, m, acr.), 8.08-8.43 (8H, m, C_6H_4+acr.+β-H), 8.70 (4H, br s, C_6H_4+β-H), 8.97 (2H, br s, β-H), 9.22 (2H, br s, β-H), 12.36 (1H, s, *exo*-pyrr.-NH); HRMS–FD (*m/z*): $[M]^{+\cdot}$ calcd for $C_{54}H_{26}F_{10}N_6$, 948.2059; found, 948.2083; UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 415 (117.7), 563 (18.9), 615 (11.1).

Aldehyde 152. Phenol **151**[175] (567 mg, 2.15 mmol) and pentafluorobenzaldehyde (547 mg, 2.8 mmol) were dissolved in dry DMF (5 mL). Cesium fluoride (750 mg, 4.9 mmol) was added and the reaction was stirred at rt for 3 h (TLC). The reaction mixture was diluted with water and precipitate was filtered off, washed with small amount of cold ethanol and air-dried, affording 585 mg (62%) of title compound as a yellow crystalline solid. R_f 0.45 (DCM/hexanes 3:1); mp 232–3 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 7.23 (1H, dd, $^3J = 8.8$ Hz, $^4J = 2.2$ Hz, Ar), 7.33 (1H, d, $J = 2.1$ Hz, Ar), 7.81 (2H, m, Ar), 8.25 (2H, m, Ar), 8.31 (1H, d, $J = 8.8$ Hz, Ar), 10.33 (1H, s, CHO); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 100.8, 112.0, 115.6, 119.5, 124.0, 125.2, 126.9, 127.0, 132.3, 133.1, 134.1, 134.3, 138.3, 140.2, 142.2, 146.6, 148.7, 154.2, 156.9, 157.7, 174.9, 181.2, 181.7; Anal. Calcd for $C_{23}H_8F_4O_5$: C, 62.74; H, 1.83; F, 17.26; Found: C, 62.54; H, 1.89; F, 17.23; HRMS–EI (*m/z*): $[M]^{+\cdot}$ calcd for $C_{23}H_8F_4O_5$, 440.0308; found, 440.0294.

Corrole 153. Aldehyde **152** (440 mg, 1 mmol) and 5-(pentafluorophenyl)-dipyrrane (624 mg, 2 mmol) were suspended in 15 mL DCM. Preprepared TFA stock solution (165 μL; see page 136) was added and the reaction was stirred at rt for 20 min. Subsequently, the reaction was quenched with triethylamine (30 μL) and diluted to 150 mL with DCM. DDQ (590 mg, 2.6 mmol; dissolved in minimal amount of toluene) was added and the reaction was stirred for the next 2 h. The reaction mixture was passed through silica pad and product-containing fractions were collected. After evaporation with Celite, crude product was submitted to column chromatography (toluene) giving, after crystallization from DCM/hexanes, 59 mg (6%) of title compound. R_f 0.7 (toluene); ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 7.55 (1H, dd, $^3J = 8.5$ Hz, $^4J = 2.3$ Hz, Ar), 7.58 (1H, d, $J = 2.2$ Hz, Ar), 7.81 (2H, m, Ar), 8.26 (2H, m, Ar), 8.43 (1H, d, $J = 8.6$ Hz,

Ar), 8.57 (2H, d, $J = 1.0$ Hz, β-H), 8.69 (2H, d, $J = 4.7$ Hz, β-H), 8.83 (2H, d, $J = 4.8$ Hz, β-H), 9.10 (2H, d, $J = 4.2$ Hz, β-H); MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{53}H_{18}F_{14}N_4O_4$, 1040.1; found, 1040.1; UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 408 (144.8), 562 (22.5), 604 (12.1).

DPP derivative 158. Sodium metal (4 g, 173.5 mmol) was dissolved in 87 mL of *t*-amyl alcohol at 90 °C over 1 h with addition of catalytic amount of $FeCl_3$. Heating was removed and the solution was allowed to cool down to about 50 °C, benzonitriles **155** and **156** (43.4 mmol of each) were added and mixture was heated again to 90 °C. Diisopropyl succinate (7 g, 34.7 mmol) was dissolved in 35 mL of *t*-amyl alcohol and added dropwise to the reaction mixture over 30 min. Subsequently, the reaction mixture was kept at this temperature for the next 20 h. After this time heating was removed and the mixture was allowed to cool down to *ca.* 50 °C, glacial acetic acid (35 mL) was slowly added, the mixture was refluxed for a 5 min and filtered through a sinter glass filter (G4). The filter cake was washed several times with hot methanol and water and then air-dried.

The orange solid, obtained in previous step (3.2 g) and K_2CO_3 (12.3 g 89 mmol) were suspended in DMF (140 mL) and heated to 120 °C. The solution of benzyl bromide (9.8 mL, 81 mmol) in 65 mL of DMF was added at this temperature dropwise over 40 min and then stirred for further 30 min. After cooling to rt, 400 mL of water was added while stirring. Precipitate was collected by filtration, washed with water and dried. There were 3 spots on TLC and least polar was easily separated by flash column chromatography (DCM/hexanes 1:1 $\longrightarrow$ pure DCM). However, next two compounds passed the column in one fraction. It was possible to separate the mixture on DCVC (DCM/hexanes 3:1 + 0.5% MeOH) and 1.29 g of acetal **158** was collected. ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 0.80 (3H, s, CH_3), 1.27 (3H, s, CH_3), 3.65 (2H, d, $J = 10.9$ Hz, diox.-CH_2), 3.77 (2H, d, $J = 11.2$ Hz, diox.-CH_2), 4.95 (2H, s, Bn-CH_2), 4.98 (2H, s, Bn-CH_2), 5.41 (1H, s, diox.-CH), 7.15–7.34 (10H, m, Ar), 7.41–750 (3H, m, Ar), 7.58 (2H, d, $J = 8.3$ Hz, C_6H_4), 7.74 (2H, m, Ar), 7.78 (2H, d, $J = 8.4$ Hz, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 21.9, 23.0, 30.3, 45.5, 45.6, 77.6, 100.8, 109.7, 109.8, 126.7, 126.7, 127.3, 127.9, 128.2, 128.7, 128.8, 128.8, 129.0, 129.1, 131.4, 137.5, 141.6, 148.6, 149.1, 162.7, 162.8; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{38}H_{34}O_4N_2$, 582.2519; found, 582.2527; UV-vis (THF): λ_{max}, nm 292, 366, 471.

DPP derivative 159. In order to deprotect aldehyde group in **158**, acetal was stirred overnight in the mixture of DCM/TFA/H_2O (40:10:1). Reaction mixture was neutralized slowly with $NaHCO_{3(sat)}$, extracted with DCM and organic fractions were dried over $MgSO_4$. Solution was evaporated with Celite and purification on a short column afforded aldehyde **159** (1.1 g, 13% after three steps). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 4.99 (4H, s, CH_2), 7.16–7.32 (10H, m, $C_6H_5CH_2$), 7.46 (3H, m, Ph), 7.77 (2H, m, Ph), 7.92 (4H, m, AA'BB'), 10.04 (1H, s, CHO); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 45.7, 109.6, 111.2, 126.7, 127.5, 127.6, 128.8, 128.9, 129.0, 129.1, 129.5, 129.9, 131.8, 133.3, 137.1, 137.2, 137.5, 146.6, 150.6, 162.5, 162.7, 191.2; Anal. Calcd for $C_{33}H_{24}N_2O_3$: C, 79.82; H, 4.87; N, 5.64; Found: C, 79.58; H, 4.76; N, 5.54; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{33}H_{24}N_2O_3$, 496.1787; found, 496.1779.

Corrole 160. Aldehyde **159** (993 mg, 2 mmol) and 5-(pentafluorophenyl)dipyrrane (1.25 g, 4 mmol) were suspended in 30 mL of DCM and TFA stock solution was added (330 μL; see page 136). The reaction was stirred for 40 min (monitored by TLC) and then quenched by triethylamine addition (60 μL). The reaction mixture was diluted to 350 mL with chloroform and DDQ (1.18 g, 5.2 mmol; dissolved in minimal amount of toluene) was added during vigorous stirring. After 2 h reaction mixture was passed through silica pad, concentrated and chromatographed (DCM/hexanes 1:1 ⟶ 3:1 + 0.5% MeOH). Two red-fluorescent spots were collected with similar R_f (corrole and porphyrin) and desired corrole was separated by SEC (eluted with THF). Crystallization from DCM/MeOH afforded 54 mg (2%) of corrole **160** (still contaminated according to NMR). MS–EI (m/z): $[M+H]^+$ calcd for $C_{63}H_{34}F_{10}N_6O_2$, 1097.3; found, 1097.3.

5-[2,3,5,6-Tetrafluoro-4-(4-iodophenoxy)-phenyl]dipyrrane (164). Aldehyde **161** (792 mg, 2 mmol) was dissolved in 14 mL of freshly distilled and degassed pyrrole. Indium(III) chloride (44 mg, 0.2 mmol) was added and reaction was stirred at rt for 1.5 h. The reaction was quenched by the addition of powdered NaOH (160 mg, 4 mmol) and was stirred for further 1 h. Reaction was filtered through Celite and excess of pyrrole was removed on rotary evaporator. The oily residue was chromatographed (DCM/hexanes 1:3 ⟶ 1:1) affording the title compound (680 mg 66%). ^{1}H NMR (200 MHz, $CDCl_3$, TMS, δ): 5.93 (1H, s, *meso*-CH), 6.07 (2H, s, pyrr.), 6.18 (2H, m, pyrr.), 6.74 (4H, m, pyrr.+C_6H_4), 7.61

(2H, m, C_6H_4), 8.13 (2H, br s, NH); ^{13}C NMR (50 MHz, $CDCl_3$, TMS, δ): 33.0, 86.6, 107.7, 108.6, 117.8, 118.1, 128.2, 138.7; HRMS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{21}H_{13}N_2O$, 512.0009; found, 512.0005.

Bis-(4-ethoxyphenyl)-(4-methoxyphenyl)amine (166). A flame-dried Schlenk flask was charged with *p*-anisidine (370 mg, 3 mmol), $Pd_2(dba)_3$ (82 mg, 0.09 mmol), *t*-BuONa (720 mg, 7.5 mmol), dry dioxane (4.5 mL), 1-bromo-4-ethoxybenzene (1.81 g, 9 mmol) and P(*t*-Bu)$_3$ (1.44 mL, 0.36 mmol; 0.25 M solution in dioxane) under an inert atmosphere. Reaction mixture was stirred at 100 °C overnight. Upon cooling, the reaction mixture was diluted with diethyl ether (30 mL), washed with brine (3×30 mL), and then dried over Na_2SO_4. Oily residue after solvent evaporation was purified by chromatography (AcOEt/hexanes 1:9) affording desired triarylamine (1.08 g, 98%). ^{1}H NMR (200 MHz, $CDCl_3$, TMS, δ): 1.39 (6H, m, CH_2CH_3), 3.77 (3H, s, OCH_3), 3.98 (4H, q, $J = 7.0$ Hz, CH_2CH_3), 6.70–6.82 (6H, m, Ar), 6.90–7.02 (6H, m, Ar); ^{13}C NMR (50 MHz, $CDCl_3$, TMS, δ): 15.0, 55.5, 63.7, 114.4, 115.1, 124.7, 124.8, 141.9, 142.0, 154.2, 154.8. HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{23}H_{25}NO_3$, 363.1834; found, 363.1841.

4-[Bis-(4-ethoxyphenyl)amino]phenol (167).

Method A. Triarylamine **166** (1.127 g, 3.1 mmol) and (n-Bu)$_4$NI (1.4 g, 3.72 mmol) were stirred in dry DCM (15 mL) at −78 °C under argon atmosphere. A solution of BCl_3 (3.72 mL, 1 M in DCM, 3.72 mmol) was added over 2 min. After 5 min, the reaction solution was allowed to warm to 20 °C and was stirred for 1 h. The reaction mixture was quenched with ice and H_2O, diluted with $NaHCO_{3(aq,sat)}$ and extracted with DCM. The combined organic layers were dried over Na_2SO_3, solvent was removed and the residue was purified by flash chromatography (EtOAc/hexanes 1:4) affording 334 mg (31%) of **167**.

Method B. An oven dried Schlenk flask was charged with *p*-aminophenol (3.27 g, 30 mmol), $Pd_2(dba)_3$ (275 mg, 0.3 mmol), *t*-BuONa (10 g, 0.1 mol), dry dioxane (45 mL), 1-bromo-4-ethoxybenzene (15.08 g, 75 mmol) and P(*t*-Bu)$_3$ (4.8 mL, 0.25 M solution in dioxane, 1.2 mmol) under an inert atmosphere. The reaction mixture was stirred at 90 °C overnight. Upon cooling, the reaction mixture was diluted with diethyl ether (200 mL), washed with brine (3×50 mL), and then dried over Na_2SO_4. Oily residue after solvent evaporation was purified by chromatography (AcOEt/hexanes 1:4) affording desired triarylamine (10.4 g, 99%).

Colorless oil (becomes blueish on standing). R_f 0.5 (EtOAc/hexanes 1:4); ^{1}H NMR (400 MHz, DMSO-d_6, TMS, δ): 1.29 (6H, t, $J = 6.8$ Hz, CH_2CH_3), 3.94 (4H, q, $J = 7.2$ Hz, CH_2CH_3), 6.67 (2H, d, $J = 8.8$ Hz, Ar), 6.78 (10H, m, Ar), 9.19 (1H, br s, OH); HRMS–ESI (m/z): $[M]^{+\cdot}$ calcd for $C_{22}H_{23}NO_3$, 349.1672; found, 349.1675.

Aldehyde 168. Phenol **167** (4.2 g, 12 mmol) and cesium fluoride (3.65 g, 24 mmol) were suspended in dry DMF (20 mL). Pentafluorobenzaldehyde (2.35 g, 12 mmol) was added and reaction was stirred at rt for 3 h (under argon). Reaction mixture was diluted with water and extracted (DCM). Combined organic layers were dried over $MgSO_4$, concentrated and passed through silica pad. Crystallization from chloroform/hexanes afforded 4.31 g (68%) of aldehyde **168** as off-white solid. R_f 0.45 (EtOAc/hexanes 1:4); mp 156–7 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 1.40 (6H, t, $J = 7.0$ Hz, CH_3), 4.00 (4H, q, $J = 6.9$ Hz, ac.-CH_2), 6.78–7.03 (12H, m, Ar), 10.28 (1H, s, CHO); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 14.9, 63.7, 110.8 (t, $J = 40$ Hz), 115.3, 117.1, 122.2, 126.1, 140.0, 140.9, 141.2 (dm, $J = 255$ Hz), 145.9, 147.6 (dm, $J = 260$ Hz), 150.6, 155.2, 182.0; Anal. Calcd for $C_{29}H_{23}F_4NO_4 \cdot 0.25H_2O$: C, 65.72; H, 4.47; N, 2.64; Found: C, 65.93; H, 4.45; N, 2.65; HRMS–ESI (m/z): $[M]^{+\cdot}$ calcd for $C_{29}H_{23}F_4NO_4$, 525.1558; found, 525.1554.

Dipyrrane 169. The a solution of aldehyde **168** (4.82 g, 9.18 mmol) in freshly distilled pyrrole (64 mL) was degassed with argon for 15 min. $InCl_3$ (203 mg, 0.92 mmol) was added and reaction was stirred at rt, under argon atmosphere, for 1.5 h. Next, powdered NaOH (734 mg, 18.4 mmol) was added and the reaction was stirred for further 1 h. The reaction mixture was filtered through Celite, pyrrole was distilled off under reduced pressure and oily residue was purified by flash chromatography on short column (EtOAc/hexanes 1:3 $\longrightarrow$ 1:1) affording 5.48 g of **169** (93%). All attempts to crystallize this dipyrrane failed and it was stored in the form of dried foam. ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 1.39 (6H, t, $J = 7.0$ Hz, CH_3), 3.99 (4H, q, $J = 7.0$ Hz, CH_2), 5.92 (1H, s, *meso*-CH), 6.05 (2H, br s, pyrr.-CH), 6.16 (2H, dd, $^3J = 5.6$ Hz, $^4J = 2.7$ Hz, pyrr.-CH), 6.73 (2H, m, pyrr.-CH), 6.76–6.84 (6H, m, Ar), 6.90 (2H, m, Ar), 6.98 (4H, m, Ar), 8.15 (2H, br s, NH); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 14.9, 33.2, 63.7, 107.6, 108.7, 115.3, 116.2 (m), 116.7, 118.0, 122.8, 125.8, 128.5, 133.8 (m), 141.2, 141.8 (dm, $J = 251$ Hz), 145.1, 145.2 (dm, $J = 246$ Hz), 151.5, 154.9; HRMS–FD (m/z): $[M]^{+\cdot}$

calcd for $C_{37}H_{31}F_4N_3O_3$, 641.2302; found, 641.2307.

Triad 175. Aldehyde **174** (104 mg, 0.15 mmol) and dipyrrane **169** were dissolved in 9 mL of DCM and TFA stock solution was added (100 μL; see page 136). Reaction was stirred at rt for 20 min (TLC) and then neutralized with triethylamine (17μL). Reaction was diluted to 150 mL and freshly prepared toluene solution of DDQ (90 mg, 0.4 mmol) was added while stirring vigorously. After 2 h reaction was passed through silica pad and chromatographed (toluene). Product-containing fractions were evaporated and dried under vacuum to give 4 mg (1%) of **175**. MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{21}H_{13}N_2O$, 1948.7; found, 1948.3.

PDI derivative 177. The mixture of perylenetetracarboxylic dianhydride (981 mg, 2.5 mmol), 1-hexylheptylamine (598 mg, 3 mmol) and aminoacetaldehyde ethyl acetal (400 mg, 3 mmol) were heated in a melt imidazole (20 g) at 160 °C for 24 h. Ethanol (10 mL) was added to the reaction mixture after cooling to 80 °C and the precipitate formed was allowed to stay overnight for aggregation. Resulting mixture was filtered through sinter glass filter (G4) and solid was washed with water. After drying under vacuum, crude product was chromatographed (chloroform) to give acetal **177** (155 mg, 9%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 0.83 (6H, t, $J = 6.9$ Hz, CH_3), 1.18 (6H, t, $J = 7.1$ Hz, ac.-CH_3), 1.21–1.38 (16H, m, Alk), 1.88 (2H, m, CH_2), 2.25 (2H, m, CH_2), 3.61 (2H, m, CH_2), 3.79 (2H, m, CH_2), 4.41 (2H, m, N$-CH_2$), 5.06 (1H, m, ac.-CH), 5.19 (1H, m, N$-$CH), 8.53–8.65 (8H, m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 14.0, 15.3, 22.6, 26.9, 29.2, 31.7, 32.4, 41.8, 54.8, 61.8, 98.8, 122.9, 123.0, 123.1, 126.3, 126.4, 129.4, 129.5, 131.5, 134.3, 134.7, 163.4; HRMS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{43}H_{48}N_2O_6$, 688.3512; found, 688.3496.

Acetal **177** was deprotected to corresponding aldehyde (**178**) following Langhals' method.[201]

Triad 179. Aldehyde **178** (123 mg, 0.2 mmol) and dipyrrane **169** (257 mg, 0.4 mmol) were suspended in 6 mL of DCM and the mixture was cooled to 0 °C. TFA stock solution (66 μL; see page 136) was added and reaction was allowed to warm up to rt while stirring. There were no signs of reaction (TLC) and next portions of TFA solution were added with the interval of 30 min (4 portions, total amount 264 μL) while monitoring the reaction progress by TLC. Conversion was low and reaction was left overnight. After neutralization with trietylamine (45 μL)

reaction was diluted to 150 mL with DCM and DDQ (118 mg, 0.52 mmol; dissolved in minimum amount of toluene) was added. After 1 h the reaction mixture was passed through silica pad, evaporated with Celite and chromatographed (toluene). Product-containing fractions were collected, solvent was removed and residue was dried under vacuum giving 35 mg of **179** (9%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 0.82 (6H, t, $J = 7.1$ Hz, CH_3), 0.91–1.39 (16H, m, Alk), 1.42 (12H, t, $J = 6.7$ Hz, CH_3), 2.17 (4H, m, CH_2), 3.90–4.07 (12H, m, CH_2), 6.72–7.19 (32H, m, Ar), 8.44 (2H, br s, β-H), 8.90 (4H, m, β-H), 9.73 (2H, br s, β-H) MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{113}H_{92}F_8N_8O_{10}$, 1872.7; found, 1872.6 UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 302 (115.9), 419 (209.6), 461 (42.6), 492 (92.8), 530 (142.8), 561 (34.2), 612 (16.8)

PDI derivative 185. The mixture of anhydride **181** (756 mg, 1.32 mmol), acetal **183** (410 mg, 1.98 mmol) and catalytic amount of $Zn(OAc)_2$ were heated in a melted imidazole (7.2 g) at 160 °C for 4 h. Water (5 mL) was added to the reaction mixture after cooling to 80 °C, followed by 2 N HCl, and precipitate formed was allowed to stay overnight for aggregation. Resulting mixture was filtered through sinter glass filter (G4) and solid was washed with water. After drying under vacuum at 70 °C crude product was chromatographed (SiO_2, chloroform) to give acetal **184** (790 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 0.84 (12H, m, CH_3), 1.20–1.50 (16H, m, Alk), 1.88 (2H, m, Alk), 2.25 (2H, m, Alk), 3.70 (2H, d, $J = 10.8$ Hz, ac.-CH_2), 3.82 (2H, d, $J = 11.2$ Hz, ac.-CH_2), 5.19 (1H, m, N-CH), 5.50 (1H, s, ac.-N-CH), 7.37 (2H, m, C_6H_4), 7.72 (2H, m, C_6H_4), 8.57–8.80 (8H, m, Ar).

Deprotection of acetal to aldehyde **185** was performed by stirring its solution in DCM/TFA/H_2O mixture (40:10:1) overnight. The yield after two steps was (687 mg, 77%). R_f 0.45 (2% MeOH in DCM, identical for aldehyde and acetal). ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 0.83 (6H, t, $J = 7.1$ Hz, CH_3), 1.20–1.45 (16H, m, Alk), 1.88 (2H, m, Alk), 2.25 (2H, m, Alk), 5.19 (1H, m, N-CH), 7.57 (2H, d, $J = 8.2$ Hz, C_6H_4), 8.11 (2H, d, $J = 8.6$ Hz, C_6H_4) 8.60–8.80 (8H, m, Ar), 10.14 (1H, s, CHO) ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 14.0, 22.6, 26.9, 29.2, 31.7, 32.4, 54.9, 122.9, 123.1, 123.5, 126.4, 126.7, 129.5, 129.8, 129.9, 130.7, 132.0, 134.1, 135.5, 136.4, 140.5, 163.3, 191.3 HRMS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{44}H_{40}N_2O_5$, 676.2937; found, 676.2928

Corrole 186. Aldehyde **185** (366 mg, 0.54 mmol) and dipyrrane **169** (694 mg,

1.08 mmol) were dissolved in DCM (8 mL) and TFA stock solution (90 μL; see page 136) was added. There were no signs of reaction after 20 min and additional portion of TFA (90 μL) was added. After 1 h reaction was quenched with triethylamine (30μL), and diluted to 100 mL with DCM. Solution of DDQ (319 mg, 1.4 mmol) in toluene was added and the reaction solution was filtered through silica pad. Product-containing fractions were collected and evaporated on Celite. Chromatography (SiO_2, toluene) afforded 86 mg of **186** (13%). Crystalline sample was obtained by reprecipitation with MeOH from DCM solution. R_f 0.6 (toluene); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 0.87 (6H, m, CH_3), 1.20–1.45 (26H, m, Alk), 1.82 (2H, m, Alk), 1.95 (2H, m, Alk), 2.33 (2H, m, Alk), 4.04 (8H, m, O$-CH_2$), 5.24 (1H, m, N-CH), 6.80–7.20 (24H, m, Ar) 7.72 (2H, d, $J = 7.8$ Hz, C_6H_4), 8.10–8.65 (12H, m, C_6H_4+Ar+β-H), 8.80 (2H, d, $J = 4.6$ Hz, β-H), 8.86 (2H, d, $J = 4.8$ Hz, β-H), 8.99 (2H, d, $J = 4.1$ Hz, β-H); MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{118}H_{94}N_8O_{10}$, 1934.7; found, 1934.5; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 302 (71.2), 414 (139.2), 457 (30.3), 490 (66.3), 527 (108.5), 564 (23.7), 613 (13.6).

Amine 187. Phenol **167** (350 mg, 1 mmol) and pentafluorobenzonitrile (251 mg, 1.3 mmol) were dissolved in 2 mL of dry DMF. CsF was added and reaction was stirred at rt for 4 h. Reaction was diluted with water and stirred for further 30 min and then extracted with DCM. Organic layer was dried over $MgSO_4$ and chromatographed (toluene). Crystallization from chloroform/MeOH afforded 523 mg of **187** (87%). R_f 0.4 (DCM/hexanes 3:2); mp 139–140 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS, δ): 1.40 (6H, t, $J = 7.0$ Hz, CH_3), 4.01 (4H, m, CH_2), 6.70–7.10 (12H, m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ): 14.9, 63.7, 107.3, 115.3, 117.1, 122.0, 126.3, 140.4, 142.3, 147.0, 149.1, 150.3, 155.3; Anal. Calcd for $C_{29}H_{22}F_4N_2O_3$: C, 66.66; H, 4.24; N, 5.36; F, 14.54; Found: C, 66.76; H, 4.34; N, 5.34; F, 14.45; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{29}H_{22}F_4N_2O_3$, 522.1567; found, 522.1560; UV-vis (THF): λ_{max} 297 nm ($\varepsilon = 2.5 \times 10^4$).

Amine 189. Phenol **167** (1.82 g, 5.2 mmol), *tert*-butyl chloroacetate (1.17 g, 7.8 mmol) and Cs_2CO_3 (2.54 g, 7.8 mmol) were heated in 15 mL of dry DMF at 70 °C for 2 h. Reaction was diluted with water and extracted with DCM. Organic layer was dried over $MgSO_4$ and chromatographed (EtOAc/hexanes 1:9). Crystallization from chloroform/hexanes afforded 2.36 g of **189** (98%). R_f 0.5 (EtOAc/hexanes 1:3); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 1.40 (6H, t,

$J = 6.8$ Hz, CH_2CH_3), 1.49 (9H, s, CH_3), 3.98 (4H, q, $J = 6.8$ Hz, CH_2CH_3), 4.46 (2H, s, CH_2), 6.76 (6H, m, Ar), 6.93 (6H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, δ): 14.9, 27.9, 63.6, 66.2, 82.2, 115.1, 115.3, 124.1, 125.1, 141.7, 142.9, 153.0, 154.4, 168.3; HRMS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{28}H_{33}NO_5$, 463.2359; found, 463.2344.

Corrole 190. *p*-Tolualdehyde (144 mg, 1.2 mmol) and dipyrrane **169** (1.54 g, 2.4 mmol) were dissolved in 18 mL DCM and TFA stock solution was added (200 μL; see page 136). The reaction was stirred at rt for 20 min (monitored by TLC). It was then quenched with triethylamine (35 μL), diluted to 200 mL with DCM and DDQ (708 mg, 3.12 mmol; dissolved in minimal amount of toluene) was added while stirring vigorously. After 2 h reaction mixture was passed through silica pad and concentrated. Flash column chromatography (toluene) afforded 251 mg of corrole **190** (15%). It was difficult to crystallize the product in typical solvent, but it precipitates smoothly while evaporating the solution in DCM/hexanes 1:1. R_f 0.5 (toluene); ^{1}H NMR (600 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 1.42 (12H, t, $J = 7.2$ Hz, CH_2CH_3), 2.69 (3H, s, tol.-CH_3), 4.02 (8H, q, $J = 7.0$ Hz, CH_2CH_3), 6.84 (8H, m, Ar), 7.07 (12H, m, Ar), 7.12 (4H, m, Ar), 7.57 (2H, d, $J = 7.3$ Hz, tol.), 7.87 (2H, d, $J = 7.3$ Hz, tol.), 8.60 (2H, br s, β-H), 8.73 (4H, m, β-H), 9.95 (2H, m, β-H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS, δ): 14.9, 26.9, 63.7, 113.3, 115.3, 116.9, 117.4, 122.8, 125.5, 125.9, 127.7, 128.1, 134.6, 135.0, 137.5, 138.4, 140.9, 141.2, 142.7, 145.3, 145.4, 147.1, 151.7, 155.0; MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{82}H_{62}F_8N_6O_6$, 1378.5; found, 1378.5; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 301 (64.0), 414 (142.7) 563 (21.3), 615 (12.4).

Corrole 191. Aldehyde **185** (220 mg, 0.33 mmol) and 5-(pentafluorophenyl)-dipyrrane (203 mg, 0.65 mmol) were dissolved in DCM (5 mL) and TFA stock solution (55 μL; see page 136) was added. After 20 min reaction was quenched with triethylamine (10μL), and was diluted to 50 mL with DCM. Solution of DDQ (195 mg, 0.83 mmol) in toluene was added and the reaction mixture was filtered through silica pad. Product-containing fractions were collected and evaporated on Celite. Purification by DCVC (DCM/hexanes 4:1) afforded 29 mg of **191** (7%). R_f 0.6 (DCM/hexanes 3:2); ^{1}H NMR (500 MHz, THF-d_8, TMS, δ): −1.71 (3H, br s, NH), 0.85 (6H, m, CH_3), 1.20–1.50 (16H, m, Alk), 1.93 (2H, m, Alk), 2.39 (2H, m, Alk), 5.25 (1H, m, Alk), 7.89 (2H, m, C_6H_4), 8.40 (2H, m, C_6H_4), 8.59 (10H,

m, β-H+Ar), 8.81 (4H, br s, β-H), 9.09 (2H, s, β-H); MS–FD (m/z): $[M]^{+\cdot}$ calcd for $C_{74}H_{50}F_{10}N_6O_4$, 1276.4; found, 1276.3; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 410 (163.1), 458 (35.2), 490 (83.4), 527 (138.7), 561 (28.0), 611 (16.0).

Triad 196. A flame-dried Schlenk flask with stirr bar was charged with corrole **50** (75.5 mg, 77 μmol), porphyrin complex **195** (64 mg, 77 μmol), palladium(II) acetate (0.9 mg, 3.9 μmol), triphenylphosphine (4 mg, 15 μmol) and Cs_2CO_3 (28 mg, 85 μmol). Air was evacuated and flask was purged with argon. Dry DMSO (0.5 mL) was added and reaction was stirred at 80 °C overnight. After cooling to rt, reaction mixture was diluted with DCM, washed thoroughly with water and brine. Organic layer was separated, dried over Na_2SO_4. After solvent evaporation, the residue was chromatographed on a long column (toluene) and then product-containing fractions were submitted for purification on SEC (toluene). Solvent was removed and residue was dried under vacuum yielding 73 mg (55%) of desired corrole. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): (−4)–(−1.5) (3H, br s, NH), 1.26 (9H, s, CH_3), 1.85 (12H, s, CH_3), 2.63 (6H, s, CH_3), 7.28 (6H, br s, Ar), 7.78 (1H, d, $J = 8.8$ Hz, Ar), 7.99 (2H, m, Ar), 8.07 (2H, d, $J = 8.0$ Hz, Ar), 8.17 (1H, d, $J = 8.0$ Hz, Ar), 8.25 (1H, s, Ar), 8.32 (3H, m, Ar), 8.58 (2H, br d, $J = 3.6$ Hz, β-H), 8.72 (4H, s, Ar), 8.75–8.85 (6H, m, Ar), 8.88 (2H, d, $J = 4.8$ Hz, β-H), 9.00 (3H, m, Ar), 9.13 (2H, d, $J = 4.4$ Hz, β-H); MS–EI (m/z): $[M]^{+\cdot}$ calcd for $C_{104}H_{65}F_{10}N_9O_2Zn$, 1725.4; found, 1725.5; UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 245 (39.6),298 (21.1), 421 (356.7), 551 (23.8), 611 (6.9).

6 Summary and conclusions

Taking into consideration the results presented in this work, I can affirm that all main objectives of my research were achieved.

In the first stage of my research, I have synthesized covalently linked bichromophoric systems composed of corrole moiety and aromatic compounds from various families such as aromatic imides, coumarins, diketopyrrolopyrroles and acridines. These chromophores were carefully chosen to act in such dyads, either as energy-donor or as electron-acceptor when combined with *meso*-substituted free base corroles. I solved numerous problems associated with both synthesis of these building blocks possessing suitable functional groups, as well as with the lack of synthetic compatibility of these substrates with corrole synthesis.

I focused on aromatic functional dyes which although known in general literature were never utilized in the design of models of electron-transfer and energy-transfer. This approach resulted in the preparation of unique dyads possessing interesting optical properties. Among other successes, I covalently linked diketopyrrolopyrroles with corroles, which was never done before. I also introduced tetrafluorophenoxy linker, which was never used before in this field of research, and which is able to electronically disconnect all subunits of the multichromophoric system and at the same time it displays stabilizing effect on corroles due to its electron-withdrawing character. Its additional advantage over typical amide based linkers lies in a very straightforward synthesis.

I investigated in-depth the reaction of oxidative nucleophilic substitution of pyrrole to acridine. In the course of this study I have developed an efficient method for the preparation of non-oxidized adduct. I prepared adducts of pyrrole with dipyrranes. Although yellow dyes thus obtained have moderate molar absorption coefficient they display large Stokes shift. The introduction of acridin-9-yl substituent into dipyrrin derivative forms new chromophore with absorption shifted

$\sim$ 40 nm versus parent dipyrrins. I also proved that a transformation of acridine into highly fluorescent, strongly absorbing dyads can be achieved with the help of direct arylation of pyrrole moiety.

Altogether eighteen new dyads displaying efficient energy-transfer to corrole were prepared. On the other hand for majority of them as it turned out, electrochemically established first reduction potentials were too high to achieve electron-transfer to corrole core. In some cases these dyads possess non-typical, rigid spatial arrangement of secondary chromophore versus corrole plane.

For my most important achievement I consider the synthesis of two triads. One of them possessing, in addition to corrole and perylene bisimide, also bis(4-ethoxyphenyl)aniline moiety was prepared after investigating various possible synthetic routes. This triad, according to predictions made based on absorption spectra and electrochemical potentials of all subunits, should display double electron-transfer: first from easily oxidizable triarylamine to corrole followed by second one from corrole to perylene bisimide. Consequently, it should display longer charge-separation time than previously prepared dyads and triads containing corrole unit (photophysical measurements are under progress in the group of Prof. Lucia Flamigni). The second triad consists of Zn-porphyrin, corrole and substituted naphthalene imide.

In conclusion, the chemistry described herein demonstrates that there are many open possibilities in design and synthesis of models for electron- and energy-transfer based on *meso*-substituted corroles combined with various organic dyes.

Glossary

AQI anthraquinone imide.

BAIB bis(acetoxy)iodobenzene.

cod 1,5-cyclooctadiene.

CT charge transfer.

DBI dibromoisocyanuric acid.

DBU 1,8-diazabicyclo[5.4.0]undec-7-ene.

DCM dichloromethane.

DCVC dry column vacuum chromatography.

DDQ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

DIEA *N,N*-diisopropylethylamine, Hünig's base.

DIPA diisopropylamine.

DMA *N,N*-dimethylacetamide.

DMF *N,N*-dimethylformamide.

DMSO dimethyl sulfoxide.

HOMO highest occupied molecular orbital.

LUMO lowest unoccupied molecular orbital.

MS mass spectrometry.

NBS *N*-bromosuccinimide.

NDI naphthalene diimide.

NIR near-infrared.

NLO nonlinear optics.

NMR nuclear magnetic resonance.

OFET organic field-effect transistor.

OLED organic light-emitting diode.

OSC organic semiconductor.

OTFT organic thin-film transistor.

OTS *n*-octadecyltrichlorosilane.

PDI perylene diimide.

PTC phase transfer catalysis.

R_f retention factor.

SEC size-exclusion chromatography.

SHE standard hydrogen electrode.

TAA triarylamine.

$TBAPF_6$ tetrabutylammonium hexafluorophosphate.

TEMPO 2,2,6,6-tetramethylpiperidine 1-oxyl.

TFA trifluoroacetic acid.

THF tetrahydrofuran.

TLC thin layer chromatography.

TMS tetramethylsilane.

TPA two-photon absorption.

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