DOI: 10.1002/anie.201210238

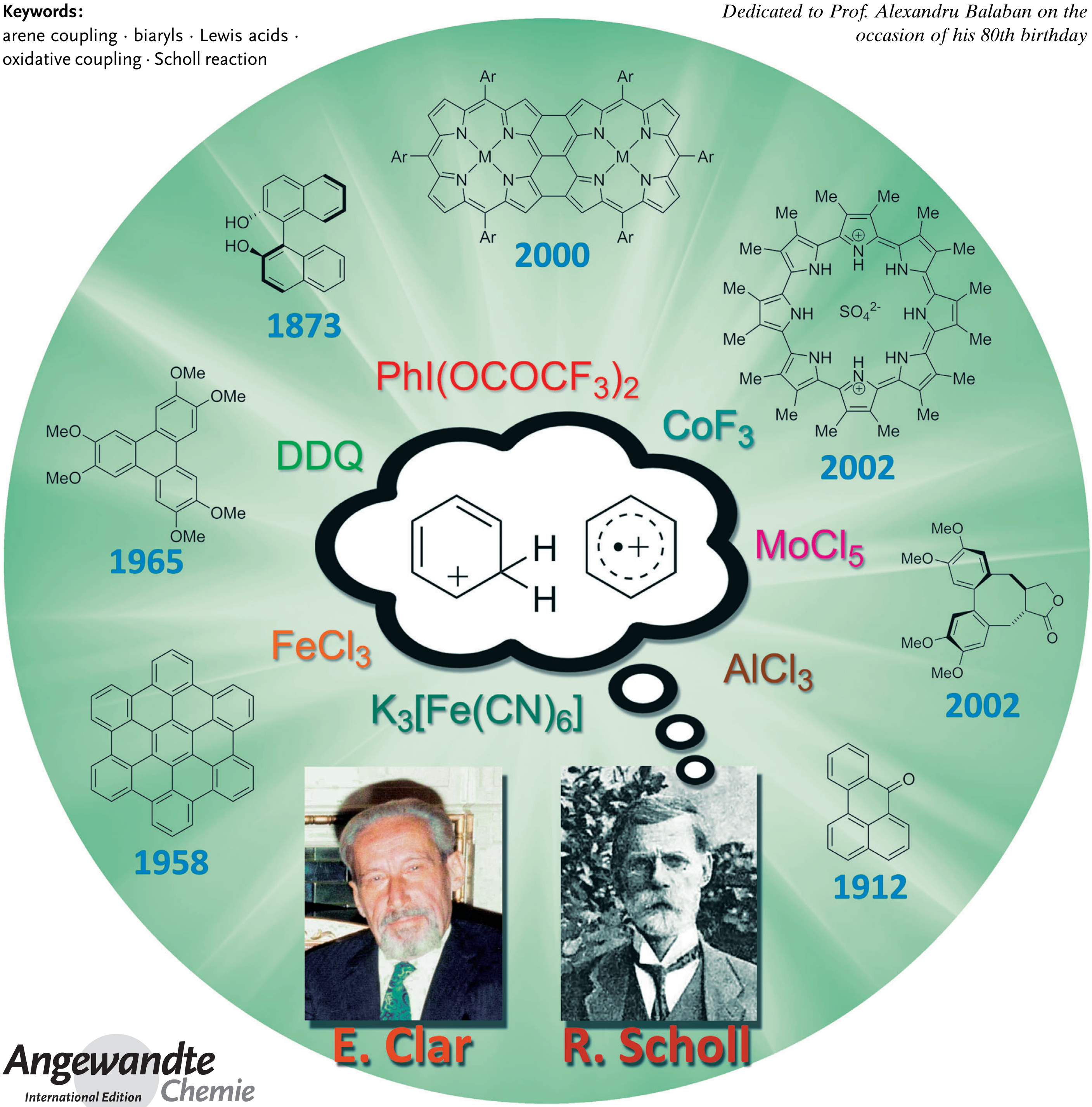
Aromatic Dehydrogenation

Comparison of Oxidative Aromatic Coupling and the Scholl Reaction

Marek Grzybowski, Kamil Skonieczny, Holger Butenschön, and Daniel T. Gryko**

Keywords:
arene coupling · biaryls · Lewis acids · oxidative coupling · Scholl reaction

Dedicated to Prof. Alexandru Balaban on the occasion of his 80th birthday



Does the dehydrogenative coupling of aromatic compounds mediated by $AlCl_3$ at high temperatures and also by $FeCl_3$, $MoCl_5$, PIFA, or $K_3[Fe(CN)_6]$ at room temperature proceed by the same mechanism in all cases? With the growing importance of the synthesis of aromatic compounds by double C–H activation to give various biaryl structures, this question becomes pressing. Since some of these reactions proceed only in the presence of non-oxidizing Lewis acids and some only in the presence of certain oxidants, the authors venture the hypothesis that, depending on the electronic structure of the substrates and the nature of the "catalyst", two different mechanisms can operate. One involves the intermediacy of a radical cation and the other the formation of a sigma complex between the acid and the substrate. The goal of this Review is to encourage further mechanistic studies hopefully leading to an in-depth understanding of this phenomenon.

From the Contents

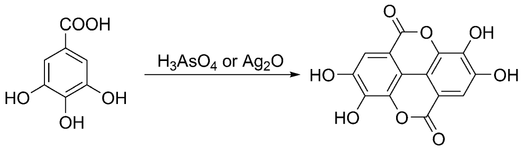
1. Introduction

The first example of an oxidative dimerization of aromatic compounds was published in 1871,[1] and 39 years later Roland Scholl reported that a similar effect can be achieved by heating certain aromatic compounds with $AlCl_3$.[2] For many years, these two reactions were distinguishable, and when Balaban and Nenitzescu published their fundamental review on the Scholl reaction, there was still a clear demarcation between them.[3] Nowadays, however, there is a mix-up in the literature, and the oxidative coupling of electron-rich aromatic substances is often called the Scholl reaction. The aim of this Review is to summarize the development of both reactions, to discuss their mechanisms, and to show their current scope. We will present the historical origin of both of these processes in Section 2, followed by a discussion of their mechanisms in Section 3. In that section we will discuss the similarities and differences between reactions mediated by $AlCl_3$ and reactions mediated by typical oxidants in terms of scope and electronic requirements.[4] In the following two sections we will present representative examples of the Scholl reaction (Section 4), intramolecular oxidative coupling, and intermolecular oxidative coupling reactions (Section 5). We will focus on the most important examples, with special emphasis given to the recent literature. Palladium-catalyzed oxidative aromatic cross-coupling and dehydrogenative coupling by C–H activation by organometallic catalysts are not included in this Review.[5]

2. Historical Development

2.1. Oxidative Aromatic Coupling

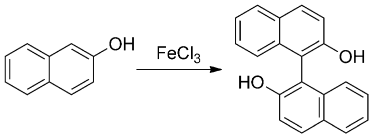
The first known example of the oxidative coupling of aromatic compounds, the formation of ellagic acid (**2**) from gallic acid (**1**), was published in 1868 (Scheme 1).[1] The reaction was mediated by H_3AsO_4 or Ag_2O; however, the yield was not reported.



1 **2**

Scheme 1.

Other examples quickly followed, and in the 1870s it was shown that a variety of phenols and phenyl ethers can be coupled oxidatively using one-electron oxidants such as $FeCl_3$ or $K_3[Fe(CN)_6]$. Seminal examples include the synthesis of 1,1′-bi-2-naphthol (binol, **4**) by the oxidation of 2-naphthol (**3**) with $FeCl_3$ reported in 1873 by Dianin (Scheme 2).[6b] Progress continued into the 20th century and accelerated after the discovery of the role of oxidative aromatic coupling in biogenesis.[7] The early literature has been summarized by



3 **4**, ca. 90 %

Scheme 2.

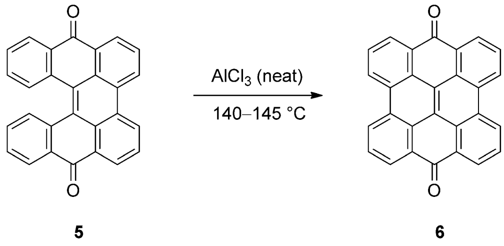
---

[*] M. Grzybowski, K. Skonieczny, Prof. Dr. D. T. Gryko
Institute of Organic Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, Warsaw (Poland)
E-mail: dtgryko@icho.edu.pl
Prof. Dr. H. Butenschön
Institut für Organische Chemie
Leibniz Universität, Hannover
Schneiderberg 1B, 30167 Hannover (Germany)
Prof. Dr. D. T. Gryko
Faculty of Chemistry, Warsaw University of Technology
00-664 Warsaw (Poland)

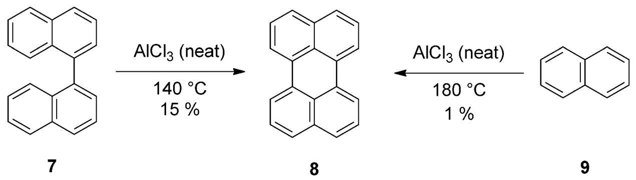
Heuben,[8] and later examples have also been extensively reviewed.[9,10]

2.2. Scholl Reaction

The Scholl reaction was first mentioned as early as 1910, when Scholl and Mansfeld reported the transformation of quinone **5** to the π-extended quinone **6** by treatment with an excess of neat anhydrous aluminum chloride for 45 min at 140–145 °C as a clean reaction, although no yield was given (Scheme 3). The authors mentioned that such a reaction had been observed earlier, for example in the formation of 1,1′-binaphthalene by heating naphthalene with aluminum chloride, but they emphasized that the observation of the formation of quinone **6** under comparatively mild reaction conditions was new.[2] In a subsequent publication, this reaction was applied to the synthesis of perylene (**8**) from 1,1′-binaphthalene (**7**; Scheme 4). Interestingly, Homer described the same reaction at the same time, but without the true formula of the product **8**.[11]



Scheme 3.



Scheme 4.

Perylene (**8**) was also obtained from naphthalene (**9**) without isolation of the intermediate **7**; however, because of some decomposition, the yield of **8** was poor.[12] Later, the reaction of 4,4′-dicyano-1,1′-binaphthalene was reported to give the corresponding coupling product in 72 % yield.[13]

The method was further elaborated and led to the synthesis of benzanthrone (**11**) from ketone **10** and of compound **13** from **12** (no yield was given in the last case, Scheme 5).[14,15] Numerous other examples were published by Scholl and co-workers in the following years.[16,17]

Possible mechanisms were discussed in some of the early reports on the dehydrogenative coupling of aromatic compounds by treatment with anhydrous aluminum chloride; these mechanisms were mainly based on similarities to Friedel Crafts reactions.[15]

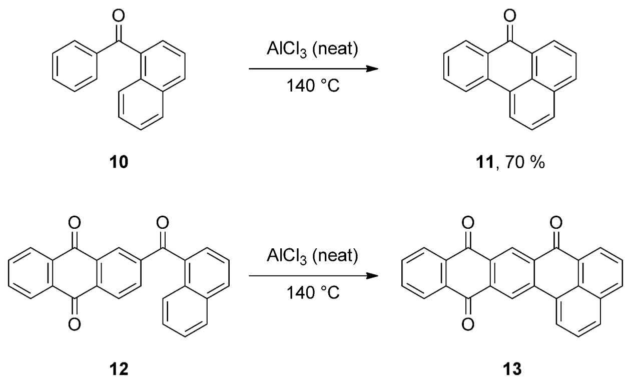
The original procedure by Scholl required baking the organic substrate with $AlCl_3$. This procedure was soon replaced by Kränzlein and Vollmann, who used an equimolar mixture of $AlCl_3$ and NaCl, which is liquid above 100 °C at a low vapor pressure,[18] and this procedure predominates in the later literature. Since the early 1920s, this reaction has been utilized in the industrial synthesis of many antraquinone-derived dyes. It is difficult to overestimate the technical importance of the Scholl reaction. Indanthrene khaki 2G (**15**)

Daniel T. Gryko obtained his PhD from the Institute of Organic Chemistry of the Polish Academy of Sciences in 1997, under the supervision of J. Jurczak. After postdoctoral research with J. Lindsey at North Carolina State University, he started his independent career in Poland. His research interests are focused on the synthesis of porphyrinoids and other functional dyes as well as on two-photon absorption, artificial photosynthesis, and excited-state intramolecular proton transfer.

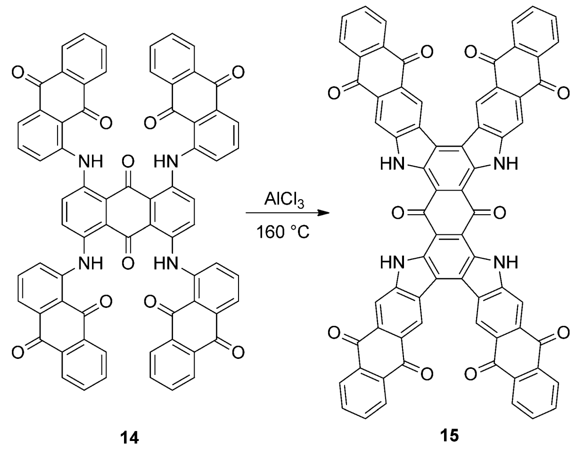
Marek Grzybowski was born in Pionki (Poland) in 1986. He studied chemistry at the Warsaw University of Technology. In 2010 he started PhD studies at the Institute of Organic Chemistry of the Polish Academy of Sciences under the supervision of Prof. Daniel Gryko. His research interests are mainly focused on π-expanded derivatives of diketopyrrolopyrroles for two-photon fluorescence imaging and small-molecule organic electronics.

Holger Butenschön obtained his PhD at the University of Hamburg with Armin de Meijere in 1983, followed by postdoctoral research with K. Peter C. Vollhardt at the University of California at Berkeley. Since 1993 he has been a professor of organic chemistry at the Leibniz University of Hannover. His research interests include preparative organic and organometallic chemistry with an emphasis on ligand- and metal-based reactions of π complexes.

Kamil Skonieczny was born in 1987 in Warsaw. He obtained his MSc in 2011 from Siedlce University. Currently, he is carrying out PhD research at the Institute of Organic Chemistry of the Polish Academy of Sciences under the supervision of Prof. Daniel Gryko. His research interests are focused on dehydrogenative aromatic coupling and on the design and synthesis of imidazole derivatives.



Scheme 5.



Scheme 6.

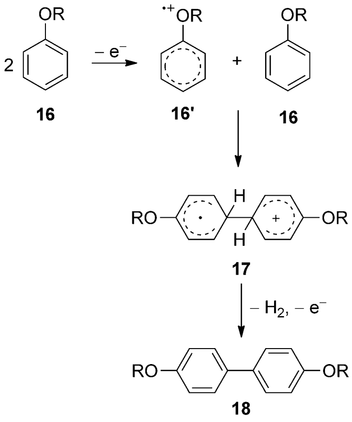
has been produced in millions of kilograms from **14** (Scheme 6).[3,19]

After World War II, the focus shifted and the Scholl reaction started to be used in the synthesis of extended aromatic hydrocarbons. This new direction sparked methodological developments. In 1971, Wick revealed that the cyclization of di-(1-anthraquinonyl)amine into 1,2;7,8-diphthaloylcarbazole (C. I. Vat Yellow 28) proceeds more efficiently in the presence of an $AlCl_3$/pyridine complex than in an $AlCl_3$/NaCl melt.[20] Other variants include the use of $AlCl_3$ in high-boiling solvents such as dichlorobenzene and trichlorobenzene,[21] low-melting complex $AlCl_3/SO_2$,[22] or of $ZrCl_4$.[23] Needless to say, many protocols involve the addition of a certain amount of oxidant such as air, oxygen, nitrobenzene, or potassium *m*-nitrobenzene sulfonate.[24] In 1961, Kovacic and Kyriakis introduced new conditions for the oxidative polymerization of benzene ($AlCl_3/CuCl_2$/neat),[25a] which were later modified by Müllen and co-workers ($AlCl_3/CuCl_2/CS_2$[25b] and $AlCl_3/Cu(OTf)_2/CS_2$),[25c] thus allowing the reaction temperature to be lowered to 25 °C.

3. Mechanistic Considerations

Numerous examples of dehydrogenative coupling reactions of aromatic compounds in the presence of various Lewis acids have recently been published.[26] In most cases, they are assigned as Scholl reactions.[27] Here, we come to the critical question of whether there is a difference between oxidative aromatic coupling and the Scholl reaction.

The typical oxidative aromatic coupling relates to the reaction of electron-rich aromatic compounds such as phenols, alkyl aryl ethers and the like. The broadly accepted mechanism is shown in Scheme 7. It involves the formation of a radical cation from one molecule of the substrate followed by substitution at the neutral second molecule and finally convergence to the biaryl product. This mechanism implies that: 1) the substrate is reasonably electron rich and 2) the attack of the electrophilic radical cation occurs at the most electron-rich position of the second substrate molecule. Other mechanistic pathways have also been discussed for the coupling of phenols, such as oxidation to the radical followed by dimerization and radical substitution.[10]

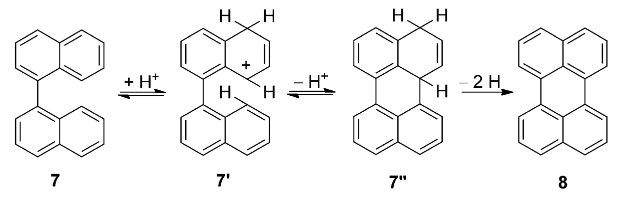


Scheme 7.

According to the definition proposed in very early reviews, the Scholl reaction is a dehydrogenation of aromatic nuclei under the influence of aluminum chloride that results in the formation of a condensed ring system.[28] Balaban and Nenitzescu reformulated it as "the elimination of two aryl-bound hydrogens accompanied by the formation of an aryl–aryl bond under the influence of Friedel–Crafts catalysts".[3]

Baddeley was the first to propose that the mechanism of the Scholl reaction involves the formation of a σ complex between the Lewis acid with the aromatic compound followed by the formation of an arenium cation, an electrophilic attack, and finally a dehydrogenation.[29] This hypothesis was further reformulated by Nenitzescu and Balaban.[30] Kenner, on the other hand was the first to propose a radical cation mechanism for the Scholl reaction.[31] This concept was soon supported by Rooney and Pink[32] and later by Clover.[33]

The arenium cation mechanism implies the protonation of the aryl species, for example, **7**, to form an electrophilic σ complex **7′** (shown with H^+ for simplicity, but this could also

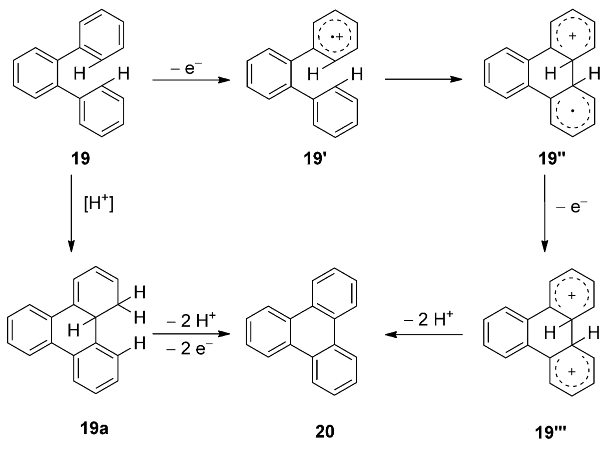


Scheme 8.

be a σ complex with a Lewis acid; Scheme 8). The attack of the latter species at the other aromatic ring to form a new carbon–carbon bond (**7**″) followed by hydrogen elimination regenerates the aromatic system, finally giving **8**.

Numerous experimental results supported this mechanism. Several research groups observed that dehydrogenation of certain aromatic compounds can occur not only in the presence of $AlCl_3$ and similar Lewis acids, but also in media such as anhydrous HF[34,35] or $PhSO_3H$,[30] while radical cations cannot be formed under such conditions. Baddeley and Kenner observed that the presence of hydrogen chloride is essential for the synthesis of benzanthrone (**11**) to occur.[29] Electronic and steric effects in various positions play a considerable role in intramolecular cases. Remarkably, benzophenone does not yield fluorenone upon heating with $AlCl_3$ at 180–220 °C,[15] most likely because this would involve an electrophilic aromatic substitution at the *ortho* position relative to the carbonyl group. On the other hand, milder reaction conditions (100 °C) allowed the synthesis of phenanthrenequinone from benzil.[14] The third step, that is, dehydrogenation/aromatization, is the most controversial one, since studies have shown that only a substoichiometric amount of H_2 was evolved when ketones were subjected to Scholl reaction conditions. To the best of our knowledge, no such study has so far been performed on hydrocarbons. There is an unquestionable positive influence on the yield of products from the Scholl reaction when hydrogen acceptors are added to $AlCl_3$. Various examples include O_2 (conversion of 3,8-dibenzoylpyrene into pyranthrone, 25 % versus 80 %;[36] conversion of 1,5-dibenzoylnaphthalene into 2,3;7,8-dibenzopyrene-1,6-quinone),[10] and nitrobenzene (intermolecular reaction of ethyl 1-naphthyl ether, 0 % versus 70 %).[37] Importantly, the carbonyl group present in many Scholl reaction precursors can serve as a temporary oxidizing agent. In such cases, the corresponding secondary alcohol can be an intermediate, which is then reoxidized by O_2 to a ketone. Balaban and Nenitzescu argue that this may be the reason for the high yields of the intramolecular Scholl reactions with these ketones, despite the electron-withdrawing (hence deactivating) character of the carbonyl group.[3] While discussing possible pathways of rearomatization, one has to remember that $AlCl_3$ itself can catalyze the dehydrogenation of compounds such as 9,10-dihydroanthracene.[37]

The second mechanism advocated by Kenner, Rooney, and Clover implies the formation of radical cations (Scheme 9). Although the mechanism has been studied only occasionally, the schism continued, and in recent years an intense discussion has evolved, prominently between the research groups of King and Rathore. The differentiation between the two mechanisms is clearly not a trivial issue. One of the key difficulties lies in the fact that most of the Lewis acids used in the Scholl reaction are also milder or stronger oxidants. Moreover, aromatic hydrocarbons can also form paramagnetic species in the presence of non-oxidizing $AlCl_3$.[32] The problem with the most commonly used oxidant, namely $FeCl_3$, is that this compound is both a Lewis acid and an oxidant capable of catalyzing or mediating a variety of reactions. For this reason, experiments with $FeCl_3$ or $MoCl_5$ cannot give the definitive answer to the key mechanistic question. One of the iron complexes broadly used in oxidative aromatic coupling,[9] which cannot be considered a Lewis acid, is $K_3[Fe(CN)_6]$, but its relatively low oxidation potential does not allow for direct comparative studies in many cases.

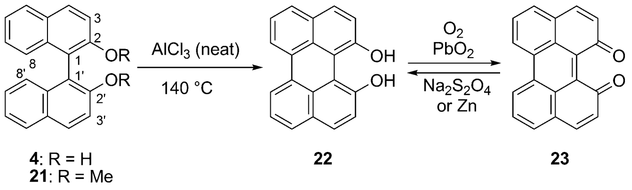


Scheme 9.

King and co-workers published a series of reports that presented both computational and experimental evidence supporting the arenium ion mechanism.[38] Computational studies led to the conclusion that the mechanistic pathway involving the arenium cation is thermodynamically favored under both vacuum and solvated conditions, because of the transition states have lower energy than those found in the radical cation pathway. Additionally, the authors presented computational evidence showing that in the case of the oxidation of hexaphenylbenzene to hexa-*peri*-hexabenzocoronene, the formation of the first C−C bond is the slowest. This explains the lack of observed intermediates in this process. One has to emphasize, however, that the interaction of the reagents with the organic substrate was not taken into account in these calculations. Given that this would probably bring about considerable energy differences, more advanced computational methods have to be applied to gain a more in-depth understanding of this process.

Rathore and co-workers studied the reaction of electron-rich aromatic compounds in the presence of various oxidants in detail, focusing on DDQ-$MeSO_3H$.[39] The same system had been used previously by these authors to efficiently synthesize a number of triphenylenes and hexa-*peri*-hexabenzocoronenes under mild conditions.[40] They presented some important evidence suggesting that, for many *o*-terphenyls such as **19**, the reaction indeed proceeds via radical cation intermediates such as **19**' and **19**'' (Scheme 9). First they showed that various Scholl precursors with oxidation potentials < 1.7 V versus the SCE readily undergo oxidative C–C bond formation with DDQ/H^+ as the oxidant, whereas those with oxidation potentials > 1.7 V versus the SCE do not react. Additionally, they noted that the reaction does not occur in mixtures of CH_2Cl_2 and various acids. These authors also claimed that the necessity of using strong oxidants for this reaction to occur is inconsistent with the arenium ion mechanism, since oxidation of dihydro intermediates such as **19a** (formed through the arenium ion mechanism, Scheme 9) can easily be accomplished even with molecular oxygen. They did not, however, extend their study further to include compounds with lower oxidation potentials and/or larger aromatic systems.

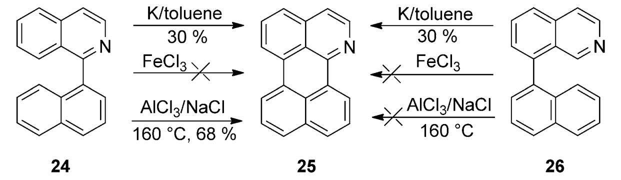
In our opinion, one of the most important compounds with a behavior that may help to understand the difference between typical oxidative aromatic coupling and the Scholl reaction is 2,2′-dihydroxy-1,1′-binaphthyl (**4**). This compound is formed by the oxidative aromatic coupling of 2-naphthol (**3**, Scheme 2). Subjecting **4** to further portions of $FeCl_3$ is ineffective, regardless of the conditions. In contrast, as early as in 1922, Zinke and Dengg performed the reaction of both 2,2′-dihydroxy-1,1′-binaphthyl (**4**) and 2,2′-dimethoxy-1,1′-binaphthyl (**21**) with $AlCl_3$, which resulted in the formation of perylene-1,12-diol (**22**), thus involving a cleavage of the ether functions in the case of **21** (Scheme 10).[41] The authors preferred to start from the dimethoxy derivative **21** as the reaction was initially much more sluggish when starting from the respective diol **4**, presumably because of side reactions of the hydroxy functions with $AlCl_3$. The reaction conditions are remarkable, because neat **4**/**21** and a fourfold excess of $AlCl_3$ are mixed and melted at 140–150 °C for 1 h, with no solvent being used. Phenol **22** undergoes oxidation by basic solutions in air with the formation of the respective quinone **23**.[42]



Scheme 10.

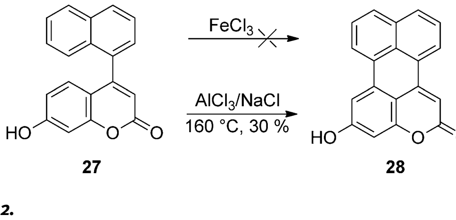
Later, the authors reported the synthesis of crystalline **23** by oxidation of the crude product of quinone **22** with lead(IV) oxide, which was purified by crystallization. Subsequent reduction of **23** with zinc dust or sodium dithionite affords **22** in pure form as bright yellow leaves, which become green on standing in air over longer periods of time.[43] It is clear that the highest electron density in compound **4** is present at positions 3 and 3′, and indeed electrophilic aromatic substitutions were performed at these positions. Oxidative aromatic coupling proceeding through the radical cation mechanism is very sensitive to the distribution of the electron density within the molecule. Numerous examples show that it proceeds: 1) only if the overall electron density of the aromatic molecule is relatively high and 2) only at the position where the electron density is the highest. Consequently, the reaction of diol **4** with $FeCl_3$, which tends to form radical cations, cannot proceed with carbon–carbon bond formation at positions 8 and 8′ (which possess rather moderate electron density). On the other hand, the reaction in the presence of $AlCl_3$ is apparently less sensitive. It can proceed even when the overall electron density is significantly lower (the transformation of ketone **10** into benzanthrone **11** is a good example), and it can also proceed at positions which are not the most electron rich ones in the molecule (especially in an intramolecular fashion). The preparation of 1,12-dihydroxyperylene (**22**) from (1,1′-binaphthalene)-2,2′-diol (**4**) through the action of $AlCl_3$ was later patented by various authors.[44,45]

The reactivity of naphthylisoquinolines is another example that emphasises this fundamental mechanistic difference stated above. We recently discovered the synthesis of 1-azaperylene (**25**) by anion radical coupling of two regioisomeric naphthylisoquinolines, **24** and **26**.[46] These substrates seemed to us to be perfect models to study the interrelation between $AlCl_3$-mediated reactions and $FeCl_3$-mediated reactions, since the oxidation potentials of naphthalene and isoquinoline are rather high. Indeed, both substrates are inert in the presence of stoichiometric or excess amounts of $FeCl_3$ at 25 °C and 80 °C.[47] On the other hand, compound **24** reacts in a $AlCl_3$/NaCl (5:1) melt at 160 °C to afford 1-azaperylene (**25**) in 68 % yield (Scheme 11).[47] In the case of 8-(naphthalen-1-yl)isoquinoline (**26**), such a reaction would require an electrophilic attack at position 1 of the isoquinoline moiety, which is very electron poor. Hence, submitting compound **26** to Scholl reaction conditions does not result in the formation of 1-azaperylene (**25**).[47]



Scheme 11.

An analogous example from our research group is the reaction of compound **27** in the presence of $AlCl_3$/NaCl to afford π-extended coumarin **28** in 30 % yield (Scheme 12).[48] Again, the reaction of coumarin **27** with $FeCl_3$ does not proceeded, most likely because of the electronic effects



Scheme 12.

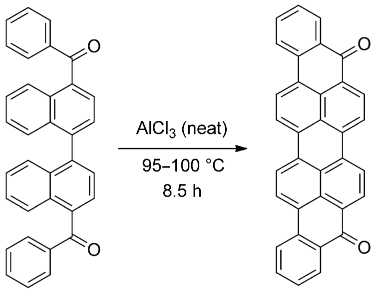
imparted by the OH group, which does not activate a suitable position for reaction to occur.

In the context of the recent discussion concerning the mechanism of the dehydrogenation of aromatic compounds under various conditions, it seems that processes that occur at room temperature with a well-known one-electron oxidant (sometimes mild Lewis acids such as $FeCl_3$ or $MoCl_5$) and processes which proceed at 120–160 °C in the presence of $AlCl_3$ (a strong Lewis acid) most probably undergo a different mechanism. We venture to say that the radical cation mechanism is operating in the first case and the arenium cation mechanism in the second case. The experiments by Nenitzescu and Balaban that show, in some cases, that dehydrogenation proceeds in the presence of a Brønsted acid (and nitrobenzene as the co-oxidant) supports this line of thought.[30] The reaction mediated by $AlCl_3$ can generally proceed with substrates less electron rich than those for oxidative aromatic coupling.

4. Scholl Reaction—Scope, Limitations, and Utilization

The earliest examples of the Scholl reaction focused on the synthesis of large polyaromatic ketones and quinones. 1-Benzoylpyrene is cyclized in an $AlCl_3$/NaCl melt to furnish dibenzo[*def,qr*]chrysene-8-one in approximately 40 % yield.[36]

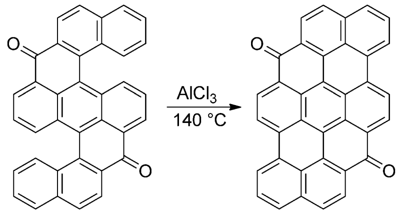
The first example of multiple dehydrogenative coupling was reported by Scholl and Seer in 1913. The authors treated 4,4′-dibenzoyl-1,1′-binaphthyl (**29**) with $AlCl_3$ for 8.5 h at 95-100 °C and obtained the nonacyclic dione “violanthrone” (**30**); however, again no yield was reported (Scheme 13). One of the largest systems ever synthesized by the Scholl reaction is quinone **32** prepared from ketone **31** (no yield given, Scheme 14).[49]



29 **30**

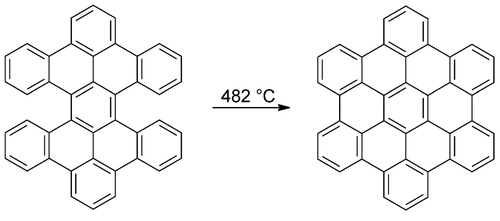
Scheme 13.

The dehydrogenation of aromatic hydrocarbons can also take place upon melting in a vacuum (no yield given, Scheme 15).[50]



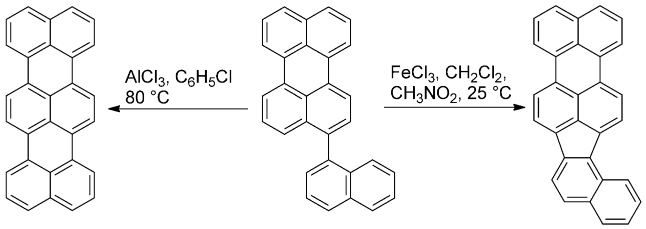
31 **32**

Scheme 14.



33 **34**

Scheme 15.

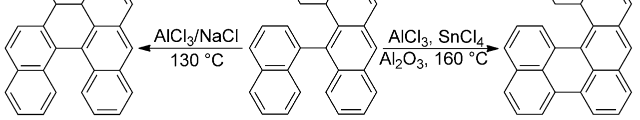


35, 43 % **36** **37**, 46 %

Scheme 16.

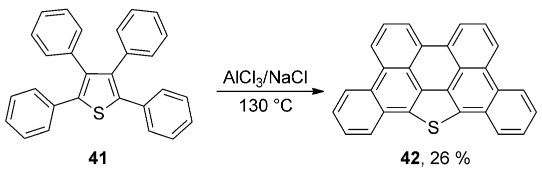
Müllen and co-workers published a very interesting study showing that 3-(1-naphthyl)perylene (**36**) undergoes oxidative coupling to either **35** or **37** depending on the reaction conditions (Scheme 16).[51] Compound **36** in the presence of $FeCl_3$ in dichloromethane forms **37** in 46 % yield, while an analogous reaction with $AlCl_3$ in chlorobenzene gives rise to terrylene (**35**) in 43 % yield. This result further emphasizes that the cyclization of aromatic hydrocarbons in the presence of oxidizing and non-oxidizing Lewis acids usually proceeds by different mechanisms.

Cyclization of 12-(1-naphthyl)benz[*a*]anthracene (**39**) in an $AlCl_3$/NaCl melt furnishes benzo[*def*]naphtha[1,2-*p*]chrysene (**38**; 10 %). However, if $AlCl_3/SnCl_4$ is used, the main product is naphtho[1,2-*a*]perylene (**40**; 60 %, Scheme 17).[52] These results further indicate that the nature of the reactive intermediates can vary quite significantly on changing the reaction conditions slightly.



38, 10 % **39** **40**, 60 %

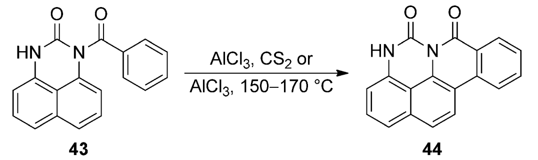
Scheme 17.



Scheme 18.

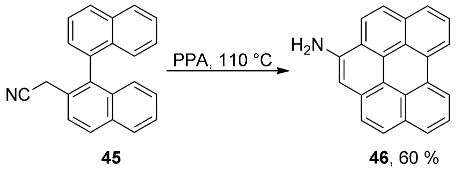
2,3,4,5-Tetraphenylthiophene (**41**), when subjected to classical Scholl conditions ($AlCl_3$/NaCl, 4:1), gives flavophen (**42**) in 26 % yield (Scheme 18).[53]

The reaction can be applied to heterocyclic systems, as has impressively been shown in an American patent disclosing the reaction of *N*-acylurea **43** to afford pentacycle **44** (no yield given, Scheme 19).[54]



Scheme 19.

Weitzenböck and Seer reported that dinaphtho[2,1-*b*:1′,2′-*d*]furan undergoes cyclization to peryleno[1,12-*bcd*]furan in the presence of $AlCl_3$, with the concomittent formation of perylen-1-ol.[13] Polyphosphoric acid has been used to induce the cyclization of precursor **45** (Scheme 20).[55]



Scheme 20.

Amino-substituted benzo[*g*,*h*,*i*]perylene **46** forms in excellent yield in a domino reaction involving an electrophilic substitution followed by a Scholl reaction.

5. Oxidative Aromatic Coupling

5.1. Intermolecular Oxidative Aromatic Coupling

As stated above (see Section 3 and Scheme 7), the reactions of reasonably electron-rich arenes with oxidants that lead to the formation of biaryls usually proceed through the radical cation mechanism. The term "oxidative coupling" will be used in this and the following sections for such reactions. The simplest variant of the oxidative coupling reaction is intermolecular oxidative homocoupling, in which two molecules of one aromatic compound react to form a biaryl. The oxidative cross-coupling of aromatic compounds (the reaction between two different arenes) is much more difficult to achieve. This is due to the poor selectivity of the reaction, which strongly depends on steric factors as well as on the electron density of both aromatic molecules. The conditions must carefully be selected to avoid homocoupling.[56] Nonetheless, significant progress has been made in the field of intermolecular oxidative cross-coupling over recent years, and many interesting examples have been published. Some representative examples of intermolecular oxidative homo- and cross-coupling reactions of arenes from the recent literature are presented in the following sections.

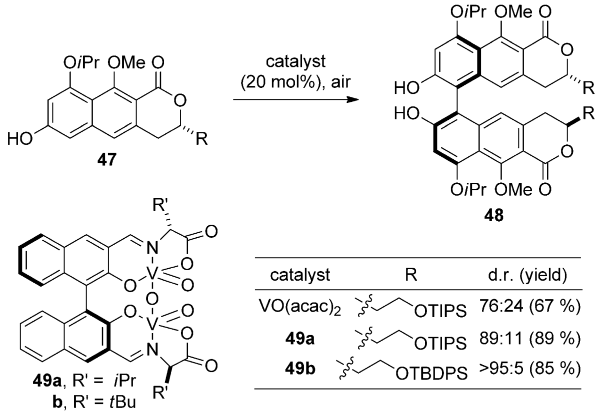
5.1.1. Homocoupling of Naphthalene Derivatives

The oxidative coupling of aromatic compounds often leads to the formation of axially chiral products. Structures of many widely used optically active catalysts are based on biaryl units.[57] Among them, binaphthyl and its derivatives are particularly important. 1,1′-Bi-2-naphthol (**4**), whose first synthesis was described in Section 2.1, is a precursor of many important ligands used in asymmetric catalysis, with binap being the most prominent example.[58] The syntheses of binol (**4**) and other binaphthyls by the oxidative coupling of the corresponding naphthalenes were achieved under various conditions, and racemic products as well as pure enantiomers could be obtained. Many different catalytic systems, oxidants, and metal complexes were examined for this purpose. Besides the classical systems with $FeCl_3$, reasonable yields of binaphthyls were also achieved using reactants such as thallium(III) and mercury(II) trifluoroacetates, $Pb(OAc)_2$, and CoF_3,[59] titanium(IV) chloride,[60] or $CuCl_2$ in the presence of amines.[61] Particularly interesting are the catalyzed homocoupling reactions of naphthalenes to binaphthyls, for example, peroxidase-catalyzed oxidation with H_2O_2,[62] copper(I)- or copper(II)-catalyzed oxidation under oxygen or air,[63] as well as the oxidation catalyzed by methyltrioxorhenium.[64] The syntheses of various binaphthyls have been summarized in recent reviews.[65] Only a few recent examples are presented below.

Shaw and co-workers employed a vanadium catalyst in the air oxidation of the chiral naphthol **47** to binaphthol **48**, a key intermediate in the synthesis of (−)-viriditoxin, which is a promising inhibitor of bacterial cell division.[66] The reaction in the presence of $[VO(acac)_2]$ as the catalyst gave the product **48** in 67 % yield with rather low diastereoselectivity (76:24). When $[VO(acac)_2]$ was replaced by the enantiopure chiral catalysts **49**, which is a binol derivative, both the reaction yield and the diastereoselectivity substantially increased (Scheme 21).

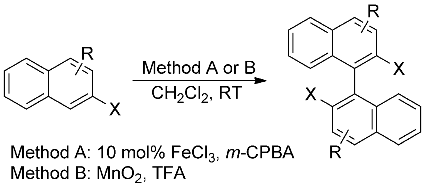
Many interesting copper complexes for the oxidative coupling of naphthols were developed by Kozlowski and co-workers, and and have successfully been applied in the total syntheses of numerous chiral, natural binaphthyl derivatives with high enantioselectivity.[65e,67]

Wang and co-workers recently reported two new systems which are efficient in the oxidation of various 2-naphthols into the corresponding racemic binaphthols (Table 1). In the first



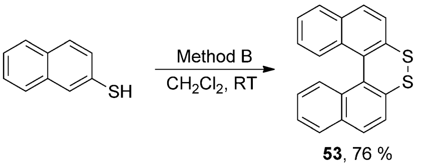
Scheme 21. acac = acetylacetonoate, TBDPS = *tert*-butyldiphenylsilyl.

Table 1:



Product	R	X	Method A [%][a]	Method B [%][b]
4	–	OH	76	73
50	6-Br	OH	58	64
51	3-CO_2Me	OH	47	55
52	–	NH_2	–	55

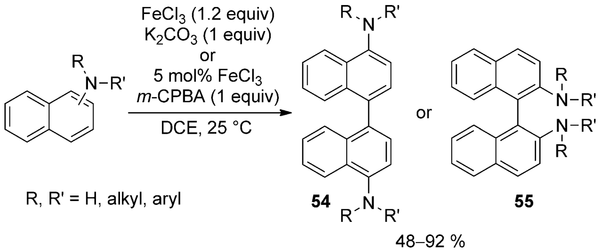
[a] Yield determined by HPLC. [b] Yield of isolated product.



53, 76 %

system, *m*-chloroperoxybenzoic acid (*m*-CPBA) is used as the oxidant, whereas iron(III) chloride serves as the catalyst of this transformation.[68] The second option is an oxidation with a stoichiometric amount of manganese(IV) oxide in a tenfold excess of trifluoroacetic acid (TFA).[69a] Both methods give reasonable yields of biaryls. They can also be employed for the coupling of 2-naphthylamine, 4-methylveratrol, and for various intramolecular cyclizations. The oxidation of naphthalene-2-thiol with MnO_2 leads to the formation of compound **53** possessing an additional ring incorporating a bisulfide functionality. On the other hand, analogous 1,2-diaryl disulfides are transformed into thianthrenes under strongly acidic conditions ($MoCl_5$).[69b]

The efficient synthesis of a variety of bi(naphthylamines) was accomplished by Li et al. in a recent study.[70] 1- and 2-Naphthylamines possessing various substituents at the nitrogen atoms were successfully coupled by treatment with iron(III) chloride as an oxidant and potassium carbonate as a base (Scheme 22). The authors also examined a reaction system similar to that described in the previous section, by using *m*-CPBA as an oxidant and $FeCl_3$ as a catalyst for the oxidative coupling of naphthylamines (Scheme 22). In both cases, the desired bi(naphthylamines) were obtained.

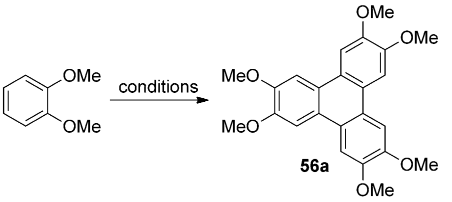


Scheme 22. DCE = 1,2-dichlorethane.

5.1.2. *Triphenylene Syntheses*

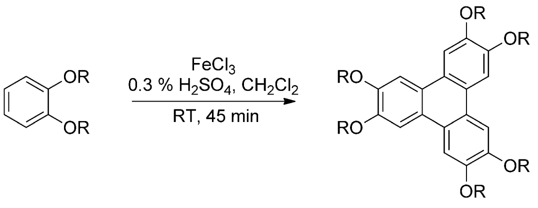
Of course, intermolecular oxidative aromatic coupling is not limited to naphthalene derivatives. Many electron-rich benzene derivatives as well as electron-rich heteroarenes can also be coupled successfully in this way. The classical example is the synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene (**56a**) reported for the first time in 1965.[71] Triphenylene was formed in 73 % yield by the oxidative cyclization of 1,2-dimethoxybenzene (veratrole) upon treatment with chloranil in 70 % aqueous sulfuric acid (Table 2). The authors suggested that in the first step of the reaction, the oxidative dimerization of veratrole occurs, and 3,3′,4,4′-tetramethoxybiphenyl is formed as an intermediate, which subsequently couples to another veratrole molecule, thereby giving triphenylene after another intramolecular coupling reaction. This assumption is supported by the finding that triphenylene **56a** was also obtained when the mixture of veratrole and 3,3′,4,4′-tetramethoxybiphenyl was submitted to the same reaction conditions.[71] The authors found that veratrole does not react with triphenylene under the typical Scholl conditions with

Table 2:



Conditions	Time	Yield [%]	Ref.
chloranil, 70 % $H_2SO_{4(aq)}$, RT	10 days	73	[71]
$AlCl_3$, $PhNO_2$	–	–	[71]
$AlCl_3$, toluene, AcCl, −5 °C	3 h	0.08	[72]
$FeCl_3$, 0.3 % H_2SO_4, CH_2Cl_2, RT	2 h	86	[73]
$FeCl_3$, 70 % $H_2SO_{4(aq)}$, RT	24 h	96	[74]
$FeCl_3$ on Al_2O_3, RT	16 h	89	[75]
$MoCl_5$, CH_2Cl_2, RT	20 min	74	[76]

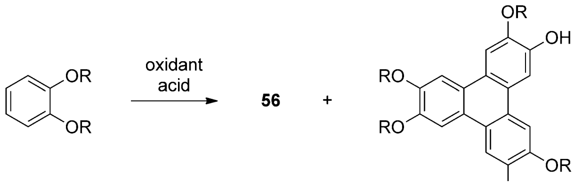
$AlCl_3$ in nitrobenzene, thus suggesting that this reaction proceeds by a radical cation mechanism. However, product **56a** was also separated in 0.08 % yield as a by-product in the Friedel–Crafts acylation of veratrole with acetyl chloride and $AlCl_3$ in toluene.[72] 2,3,6,7,10,11-Hexaalkoxytriphenylenes with longer alkyl chains, for example hexahexyloxytriphenylene (**56d**), show interesting liquid-crystalline properties. Unfortunately, the direct synthesis of higher hexaalkoxytriphenylenes from *o*-dialkoxybenzenes by oxidation with chloranil results in low yields and requires a difficult work-up, which is undoubtedly a disadvantage of the “chloranil method”.[73] As a consequence of this, such compounds are synthesized by an uneconomical, three-step route involving the preparation of **56a**, its demethylation, and base-promoted alkylation of the resulting hexahydroxytriphenylene with alkyl bromides. Another disadvantage of the chloranil method is the fact that it is very time-consuming, as at least a week is needed to achieve satisfactory yields of triphenylenes. These problems were solved by Bushby and co-workers in 1993, who developed an effective, much faster, and more general method for the oxidative cyclization of *o*-dialkoxybenzenes by reaction with iron(III) chloride in 0.3 % sulfuric acid in dichloromethane.[73] Under these conditions, triphenylene **56a** is obtained in 86 % yield in only 2 h. The reaction with *o*-dialkoxybenzenes bearing longer chains is even faster. After only 45 min, hexaalkoxytriphenylenes **56b–f** are obtained in relatively high yields (Scheme 23). Furthermore, the authors claimed that the reaction gives a reasonable yield even without the addition of sulfuric acid, but they did not specify the exact yield. A further improvement of the synthesis of triphenylene **56a** was achieved by Naarmann et al. They obtained **56a** in an excellent 96 % yield by using iron(III) chloride in 70 % sulfuric acid (Table 2).[74] However, this method is less effective than Bushby's method for the synthesis of triphenylenes with longer alkyl chains. Some additional systems that are efficient for the oxidation of *o*-dialkoxybenzenes to hexaalkoxytriphenylenes have been published, such as $FeCl_3$ on alumina,[75] $MoCl_5$ or $VOCl_3$ in dichloromethane,[76,77] and $FeCl_3$ in a mixture of dichloromethane and nitromethane.[78] Bai and Lin recently showed that compounds **56c** and **56d** can be obtained in very high yields (95 % and 80 % respectively) by the solvent-free oxidation of the corresponding dialkoxybenzenes with $FeCl_3$.[79]



56b, R = C_3H_7, 77 %
c, R = C_4H_9, 65 %
d, R = C_6H_{13}, 73 %
e, R = C_8H_{17}, 60 %
f, R = C_9H_{19}, 55 %

Scheme 23.

Kumar and Varshney studied the by-products formed in the oxidative cyclization of *o*-dialkoxybenzenes by the oxidation with $FeCl_3$, $MoCl_5$, and $VOCl_3$. They found that, in all cases, monohydroxypentaalkoxytriphenylene (**57**) is obtained as a side product.[80] Its formation is an effect of the acidic cleavage of one of the alkoxy chains. Further investigation into the cyclotrimerizations performed in $FeCl_3$/nitromethane revealed that the quantity of by-product **57** depends on the concentration of the protic acids in the reaction mixture.[81] Up to 20 % of this product can be obtained when the reaction is carried out in the presence of 0.3 % HCl, TFA, or H_2SO_4 (Scheme 24). Unsymmetrical triphenylenes can be also obtained from 3,3′,4,4′-tetraalkoxybiphenyls and electron-rich benzene derivatives.[71,75,82]



oxidant = $FeCl_3$, $MoCl_5$, $VOCl_3$
acid = HCl, H_2SO_4, TFA

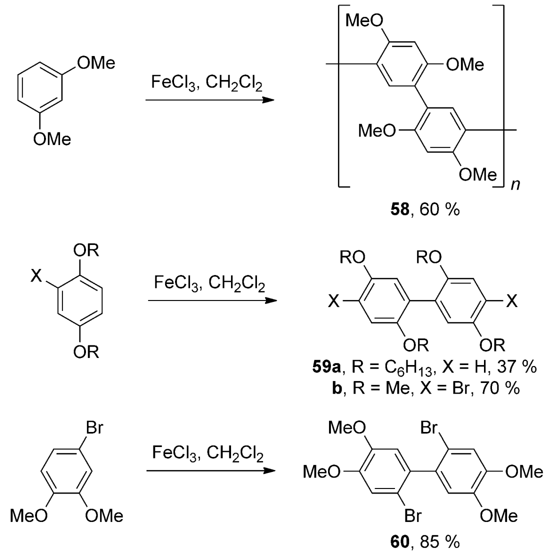
57, R = alkyl, up to 20 %

Scheme 24.

5.1.3. Intermolecular Oxidative Homocoupling of Other Simple Benzene Derivatives

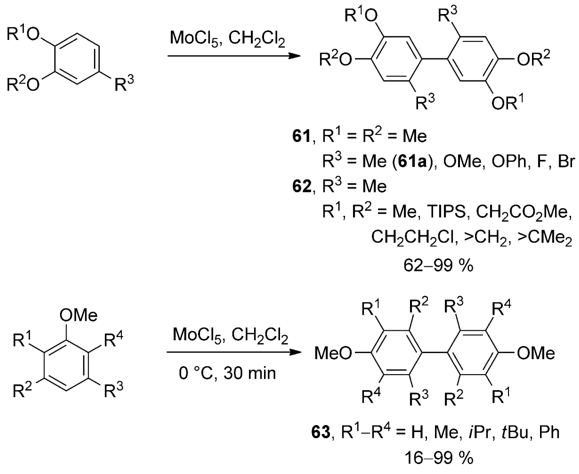
The oxidation of veratrole and other *o*-dialkoxybenzenes leads almost exclusively to the formation of triphenylene derivatives. However, when *meta*- or *para*-dialkoxybenzenes are treated with an oxidant, the reaction proceeds in a completely different way. *m*-Dimethoxybenzene reacts with $FeCl_3$ in dichloromethane to form polymer **58**, which is soluble in chlorinated solvents, whereas *p*-dihexyloxybenzene forms biphenyl **59a** as a main product.[83] The authors claimed that the yield of this reaction is low due to the fact that the initially formed product **59a** still has free reactive sites at C4 and C4’ and can be consumed in further coupling reactions. These assumptions are supported by the observation that, when these positions are blocked by bromine, the yield of biphenyl **59b** is much higher. Similarly, the introduction of a bromine atom at C4 of veratrole prevents the oxidative cyclization and, instead of triphenylene, the corresponding dimer **60** is obtained in high yield (Scheme 25).

In 2000 Waldvogel and co-workers introduced the oxophilic Lewis acid molybdenum(V) chloride as a new, efficient oxidant.[83–85] $MoCl_5$ is moisture and air sensitive, but since molybdenum salts are considered to be biocompatible, the use of this reagent is environmentally acceptable. Systematic studies on $MoCl_5$ revealed that it is a one-electron oxidant and that the rate of its reaction is greatly enhanced in the presence of two alkoxy groups in the 1- and 2-positions of the aromatic substrate.[84a,b] Aromatic oxidative coupling in the



Scheme 25.

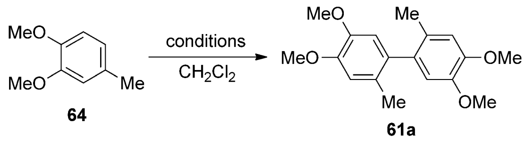
presence of MoCl$_5$ can be performed within a few minutes, moreover, 2-chloroethyl and triisopropylsilyl (TIPS) are suitable protecting groups for phenols being subjected to this reagent.[84c] Waldvogel and Trosien claim that MoCl$_5$ forms clusters, which coordinate to oxygen-donor functions followed by inner sphere electron transfer.[84b] MoCl$_5$ was found to be an efficient oxidant for the homocoupling of variously substituted *o*-dialkoxybenzenes and anisoles.[84] Under these conditions, the lowest yield of homocoupling was noticed with simple anisole, which gives 4,4′-dimethoxybiphenyl in only 16 % yield. More complex starting materials often react much more facilely, and the desired dimers are obtained in 60 % and higher yields, which makes this route an effective and quite general method for the preparation of alkoxy-substituted biphenyls (Scheme 26). Recently, Waldvogel and co-workers discovered the beneficial effect of the addition of TiCl$_4$ as a supporting Lewis acid, which helps to keep the oxidative reagent (i.e. MoCl$_5$) active.[85a] Additional advantages of MoCl$_5$ are its compatibility with the presence of alkyl groups (which usually do not survive in strongly electrophilic media and give rise to *tert*-butylated products),[84a] iodine,[85c] and ketals.[85f] However, one has to keep in mind that prolonged exposure of organic substrates to MoCl$_5$ can lead to their oxidative decomposition, and the concomitant chlorination of some substrates represents a limitation of its scope.[84b]



Scheme 26.

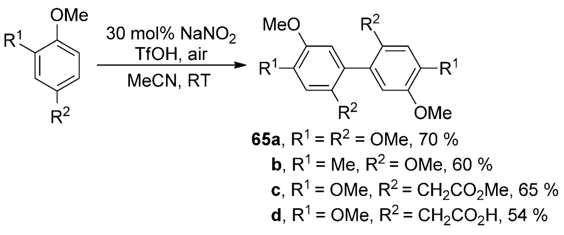
The oxidation of 1,2-dimethoxy-4-methylbenzene (**64**) to 2,2′-dimethyl-4,4′,5,5′-tetramethoxybiphenyl (**61a**) can also be achieved in reasonable yields by other methods, and in this Review it will be used as a representative reaction to compare the reaction conditions and yields of oxidative coupling (Table 3). Wang et al. reported that **64** is oxidized by manganese(IV) oxide to give biphenyl **61a** in 56 % yield.[69] The yield increased slightly when *m*-CPBA was used as the oxidant in the presence of FeCl$_3$ as a catalyst (58 % yield).[68] Much higher yields of this reaction can be achieved by oxidants such as phenyliodine bis(trifluoroacetate) (PIFA)[85,86] and DDQ[39,40] (93 % and 99 %, respectively).

Table 3:



Conditions	Time	Yield [%]	Ref.
MoCl$_5$, RT	30 min	67	[84a,b]
MnO$_2$, TFA, RT	1.2 h	56	[69]
10 mol % FeCl$_3$, *m*-CPBA, RT	1 h	58	[68]
PIFA, BF$_3$·OEt$_2$, −40 °C	1.5 h	93	[85]
DDQ, MsOH, 0 °C	5 min	99	[39,40]

PIFA/BF$_3$·OEt$_2$ is also effective for the coupling of various alkoxyiodobenzenes.[87] Wang and co-workers recently published the results of their investigation of the application of sodium nitrite as an efficient catalyst for the oxidative coupling of arenes.[88] They mostly examined an intramolecular variant of the reaction. Nevertheless, some examples of intermolecular homocoupling reactions were also presented (Scheme 27). Intermolecular coupling reactions of electron-rich benzene derivatives require higher loadings of the sodium nitrite catalyst (30 mol %) to achieve reasonable reaction yields compared to intramolecular cyclizations (5 to

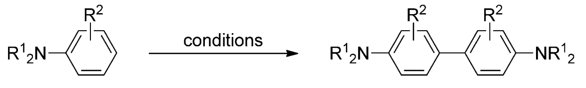


Scheme 27. Tf = CF$_3$SO$_2$.

20 mol %). However, the yields of the coupling reactions are slightly lower.

As electron-rich species, anilines can also be oxidatively coupled. Early on, cerium(IV) ammonium nitrate (CAN) and cerium(IV) sulfate were found to facilitate the homocoupling of *N,N*-dimethylaniline, but the yields were rather low.[89] More efficient protocols for the oxidative coupling of *N,N*-dialkylanilines have been developed in recent decades. *N,N,N′,N′*-Tetraalkylbenzidines of type **66** can be synthesized in good yields by treatment of the corresponding anilines with $TiCl_4$ in dichloromethane,[90] copper(II) perchlorate in acetonitrile,[91a] CuBr in the presence of H_2O_2,[91b] or naphthalene-1,8-diylbis(diphenylmethylium) perchlorate (**68**; Table 4).[91c]

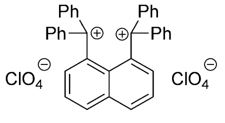
Table 4:



66, R^1 = alkyl
67, R^1 = aryl

Conditions	R^1	R^2	Yield [%]	Ref.
$TiCl_4$, CH_2Cl_2, 0–25 °C	alkyl	H	57–92	[90]
$Cu(ClO_4)_2$, MeCN, RT	Me, Et	H	83–86	[91a]
CuBr, H_2O_2, H_2O, 0 °C	alkyl	H, 3,5-Me_2	49–76	[91b]
68, CH_2Cl_2, −78 °C to RT	alkyl, allyl, Bn	H, Me, OMe, CO_2Me, Cl, Br	10–95	[91c]
CAN, H_2O, RT	alkyl	H, 2-Me	53–85	[91d]
CAN, RT, grinding	alkyl	H, 2-Me, 3-Me	43–78	[91e]
$Cu(ClO_4)_2$, MeCN, RT	aryl	H	81–94	[91f]

CAN = $(NH_4)_2Ce(NO_3)_6$



68

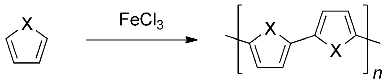
Furthermore, methods in which CAN is used as the oxidant have significantly been improved; biaryls can be obtained by reaction with CAN in water[91d] or by solvent-free grinding of the aniline with CAN.[91e] *N,N*-Diarylanilines may also be coupled to give the corresponding benzidines **67**. This goal is achieved by using copper(II) perchlorate as the oxidant (Table 4).[91f]

Oxidative aromatic coupling can also be performed by using electrochemical methods.[92] Electrochemical approaches for redox transformations are highly attractive for ecological and economic reasons, since only electrons are used and virtually no reagent waste is produced. Numerous hydrocarbons have been oxidatively coupled in this way, prominently by the research groups of Schäfer and Parker.[92] In these cases it is easier to determine the mechanistic pathway. It was then proved that the initially formed radical cation reacts with the starting compound to form biaryls. It was also established that the typical solvent of choice is CH_2Cl_2, and that the addition of TFA enhances the stability of the radical cation and supresses the nucleophilicity of water. Many hydrocarbons lacking electron-donating groups, such as 9-phenylanthracene, have been oxidized in this way.[93] Phenols (usually in alkaline media) and aryl alkyl ethers were also studied extensively. In the case of phenols, carbon–oxygen coupling often competes with the desired carbon–carbon coupling.[94] In contrast, alkyl aryl ethers can often be coupled very selectively, and the yields of the products are typically very high (85 % for 1,2,4-trimethoxybenzene,[95] 95 % for 9-methoxyanthracene).[96]

5.1.4. *Oxidative Homocoupling of Simple Heteroarenes*

Heteroarenes such as pyrrole, thiophene, indole, etc. are electron-rich aromatic compounds, and can undergo oxidative coupling reactions like the other arenes mentioned in this section. 2,2′-Bipyrrole is a structural motif of many important and useful natural and synthetic products.[97] Poly-2,2′-pyrroles (PPy, **69**), poly-2,2′-furans (PF, **70**), and poly-2,2′-thiophenes (PTs, **71**) show good electrical conductivity and have found applications in electronics.[98] These polymers are usually synthesized in good yields by the electrochemical oxidation of pyrrole, furan, or thiophene, respectively. This method provides polymers of high purity and conductivity; nonetheless, chemical methods have also been developed for the synthesis of conducting polyheteroarenes.[99] Among them, the oxidative coupling of furan, thiophene, or pyrrole seems to be the simplest synthetic method. Iron(III) chloride is the most common oxidant used for these purposes (Scheme 28). Unfortunately, polymers **69**, **70**, and **71** synthesized by chemical oxidation show lower electrical conductivity than polymers obtained by electropolymerization.[99] It was found that the polymers derived from the chemical oxidation contain some amount of reduced polymers (e.g. pyrrolidine in the case of polymer **69**), which break the π conjugation of the polymer chain and thus reduce the conductivity.

As shown in Scheme 28, the reaction of thiophene (and other heteroarenes) with $FeCl_3$ and similar oxidants leads to the formation of polymers, but not of simple biaryls. This is due to the lower oxidation potential of 2,2′-bithiophene compared to the corresponding thiophene. Thus, the dimer is more easily oxidized than the monomer and undergoes further coupling reactions more readily to produce the polymer.[100] Hence, the synthesis of bithiophene must be performed in a different way than the oxidative coupling of thiophene with $FeCl_3$, and has been carried out by transition-metal-mediated reactions such as Ullmann, Suzuki, Stille, and Negishi coupling reactions.[101] The major disadvantage of all of these methods is the requirement for a preactivation of thiophene. Thus, the oxidative coupling of thiophene would be an easier method of bithiophene synthesis, but the further

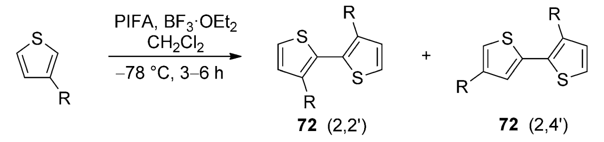


69, X = NH
70, X = O
71, X = S

Scheme 28.

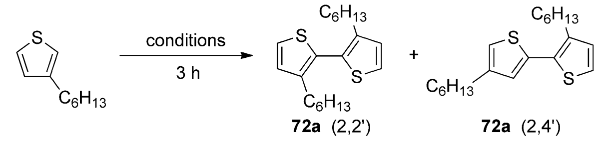
polymerization of bithiophene must somehow be prevented to achieve this goal. Kita and co-workers solved this problem by the using PIFA as the oxidant. Various 3-substituted thiophenes were successively coupled by reaction with PIFA in the presence of BF$_3$·OEt$_2$ to afford bithiophenes in moderate yields, although the selectivity of the reaction is low and mixtures of 2,2′- and 2,4′-disubstituted isomers are obtained (Table 5).[102] The oxidant, Lewis acid, and solvent were further optimized by the Kita research group, and the selectivity was significantly improved, so that the 2,4′-disubstituted isomer can be prepared almost exclusively.[103] The synthesis of bithiophene **72a** under various conditions is shown in Table 6 as a representative example. The highest selectivity is obtained when the reaction is performed in 1,1,1,3,3,3-hexafluoropropane-2-ol (HFIP) as the solvent with trimethylsilyl bromide (Me$_3$SiBr) as the Lewis acid and Koser's reagent [PhI(OH)OTs, HTIB][103a] or an adamantane derivative **74** as the oxidant.[103b] Although compound **74** has a complex structure and its synthesis is difficult, it has the advantage that the corresponding iodo derivative precipitates from the reaction mixture and can be easily filtered off and recycled.

Table 5:

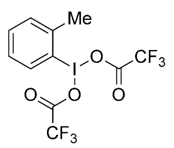


R	Product	Yield [%]	2,2′/2,4′
C$_6$H$_{13}$	**72a**	72	54:46
Me	**72b**	50	40:60
*n*Bu	**72c**	67	43:57
C$_8$H$_{17}$	**72d**	66	50:50
cyclopentyl	**72e**	55	42:58

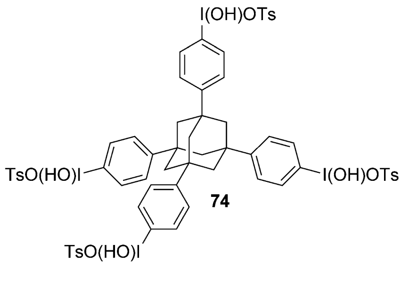
Table 6:



Conditions	Temperature [°C]	Yield [%]	2,2′/2,4′
PIFA, BF$_3$·OEt$_2$, CH$_2$Cl$_2$	−78	72	54:46
PIFA, Me$_3$SiOTf, CH$_2$Cl$_2$	−78	41	94:6
73, Me$_3$SiOTf, CH$_2$Cl$_2$	−78	72	81:19
74, Me$_3$SiBr, HFIP	RT	75	1:99
HTIB, Me$_3$SiBr, HFIP	RT	78	only 2,4′

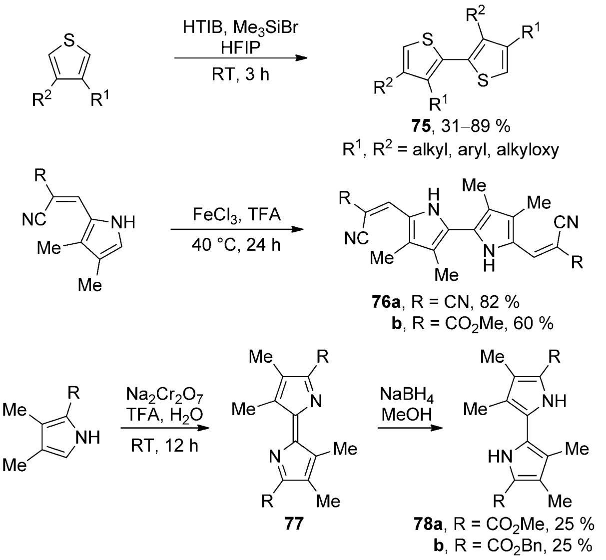


73



74

The reaction system HTIB/Me$_3$SiBr/HFIP is very effective and many different bithiophenes bearing a variety of substituents have been synthesized in this way (Scheme 29).[103d,e] Usually the 2,4′-disubstituted isomer is produced by this method.



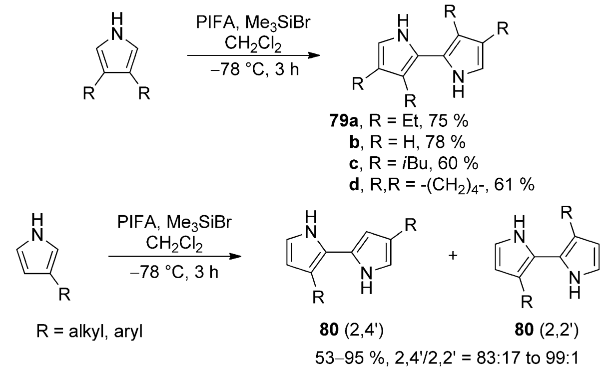
Scheme 29. Bn = benzyl.

Falk and Flödl reported the coupling of pyrroles substituted with electron-withdrawing groups at the 2-position by oxidation with FeCl$_3$ or Na$_2$Cr$_2$O$_7$ in TFA.[104] The presence of the 2-substituent prevents further coupling reactions; thus, bipyrroles **76** and **78** were obtained in reasonable yields (Scheme 29). The reaction with Na$_2$Cr$_2$O$_7$ initially leads to the formation of over-oxidized intermediate **77**, which can subsequently be reduced to the desired product by the addition of NaBH$_4$.

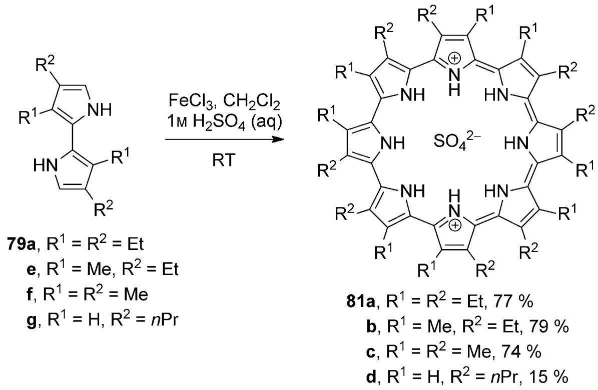
Analogously to thiophene derivatives, pyrroles unsubstituted at the 2- and 5-positions can be transformed into their homocoupling products by hypervalent iodine(III) oxidants. This goal was achieved by the use of PIFA in the presence of Me$_3$SiBr. As in the case of thiophene, unsymmetrically substituted pyrroles also react to form 2,4′-disubstitutedbipyrroles **80** predominantly (Scheme 30).[103b,c,105]

2,2′-Bipyrroles unsubstituted at positions 5 and 5′ (such as compounds **79a** and **80**) can undergo further oxidative oligomerization. Sessler and co-workers have found that 3,3′,4,4′-tetraalkylbipyrroles react with FeCl$_3$ in a biphasic system consisting of 1 M aqueous sulfuric acid and dichloromethane to give aromatic macrocycles **81a–d**, named cyclo[8]pyrroles, in very high yields (up to 79%, Scheme 31).[106,107]

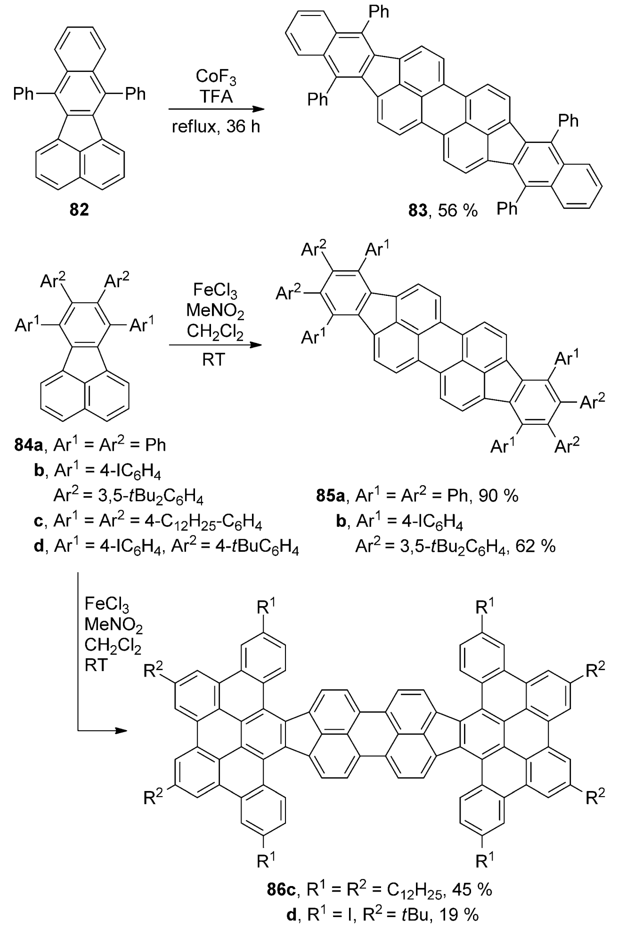
The same transformation has also been achieved by electrochemical oxidation.[108] Compounds **81a–d** were iso-



Scheme 30.



Scheme 31.



Scheme 32.

lated as the sulfate salts, and the structure of **81b** was confirmed by single-crystal X-ray diffraction analysis. In the crystal structure, **81b** adopts a nearly planar, diprotonated, dicationic form with the sulfate anions coordinated by eight strong hydrogen bonds inside the macrocycle. Since the sulfate anion fits so well into the cavity of the macrocycle, the suggestion arises that the sulfate serves as a templating agent during the reaction, so that the formation of a macrocycle consisting of eight pyrrole rings is favored. This might be an explanation for the surprisingly high yields of cyclo[8]pyrroles. Similarly, naphthobipyrrole reacts with FeCl$_3$ in the presence of H$_2$SO$_4$ to give cyclo[4]naphthobipyrrole in up to 30% yield.[109]

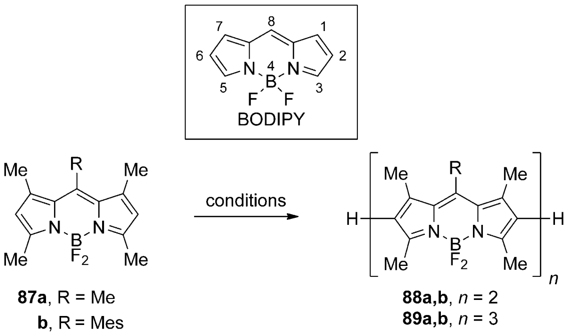
5.1.5. Oxidative Homocoupling of Higher Arenes and Dyes

There are several examples of the oxidative aromatic coupling of higher arenes or dyes. Almost all such cases were published during the last decade.[110,111] For example, fluoranthene derivative **82** can be oxidized effectively to the highly expanded π system **83** by reaction with cobalt(III) fluoride in trifluoroacetic acid (Scheme 32).[112] In the same way, fluoranthenes **84a** and **84b** substituted with phenyl or sterically hindered 4-*tert*-butylphenyl groups react with iron(III) chloride to give the corresponding dimers **85a**,**b**. The oxidation of sterically less-congested **84c** and **84d** leads to the formation of polyaromatic hydrocarbons **86c**,**d** as a result of both inter- and intramolecular oxidative coupling (Scheme 32).[109,113]

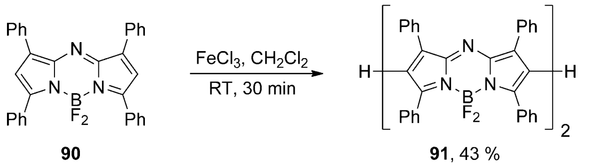
4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) is an important group in heterocyclic organic dyes that shows interesting optical properties and has found many practical applications. The BODIPY chromophore consists of two pyrrole moieties connected by a methyne bridge and a difluoro-substituted boron atom incorporated between the two pyrrolic nitrogen atoms. As was recently published, depending on the substituents, BODIPY dyes can be oxidatively coupled to give variously linked dimers. BODIPY **87a**,**b**, which are unsubstituted at C2 and C6, react with iron(III) chloride[114] or PIFA[115] to afford the corresponding 2,2′-coupled products **88a**,**b**. These still possess free reactive sites, and further coupling reactions are possible. Therefore, the yields of the dimers are low and trimers **89a**,**b** can also be isolated from the reaction mixture (Table 7). The yield of the dimer increases slightly when one of the free sites of the starting material is blocked by an iodo or a *p*-tolyl substituent.[114] The 2,2′-dimer can be also obtained, when aza-BODIPY **90** is used in the reaction with FeCl$_3$.[114] 3-Unsubstituted BODIPY is oxidized by FeCl$_3$ to the 3,3′-dimer.[116]

The 1,1′ dimer can also be obtained by the oxidation of BODIPY. In this way, compound **93** is synthesized in 32%

Table 7:

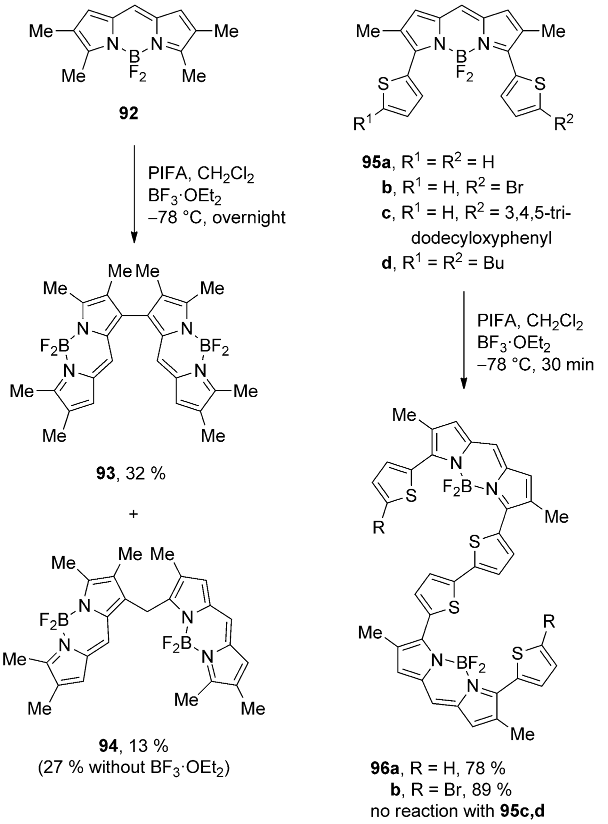


Conditions	R	Substrate	Yield [%] (**88**/**89**)	Ref.
$FeCl_3$, CH_2Cl_2, RT, 20 min	Me	**87a**	27:9	[113]
$FeCl_3$, CH_2Cl_2, RT, 25 min	Mes	**87b**	10:3	[113]
PIFA, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C, 30 min	Me	**87a**	10:4	[114]

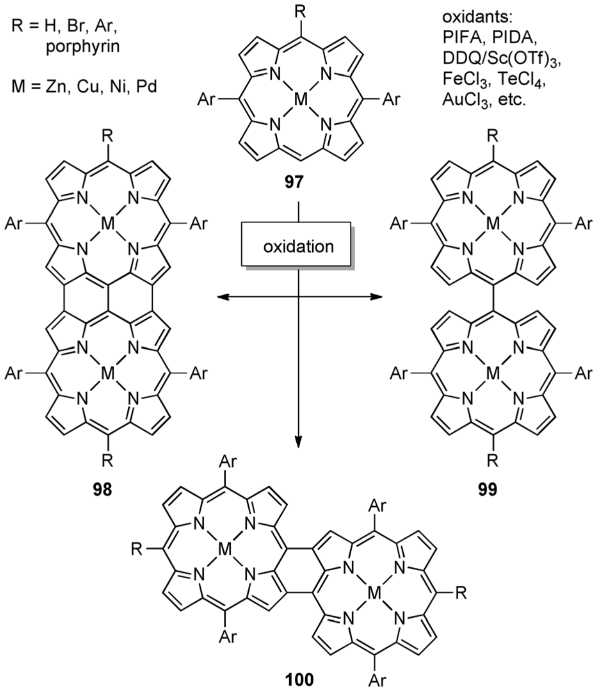


yield from 1,7,8-unsubstituted BODIPY **92** by the reaction with PIFA and boron trifluoride diethyl etherate.[117] The authors also isolated the regioisomeric coupling product **94** (13 % yield), in which two molecules of **92** are connected by a methylene bridge (Scheme 33). Moreover, dye **94** is obtained in 27 % yield as the only product when the reaction is performed without the addition of $BF_3{\cdot}OEt_2$. 3,5-Dithienyl-BODIPYs **95a–d** were also investigated in the reaction with PIFA/$BF_3{\cdot}OEt_2$ to obtain 1,1′ dimers. However, only **95a** and **95b** react under these conditions and, surprisingly, the isolated products **96a**,**b** are not the desired 1,1’ coupling products, but rather those formed by the coupling of thiophene substituents (Scheme 33).[117]

Porphyrins of type **97** can be oxidatively coupled to give **98**, **99**, or **100** (Scheme 34).[118] The type of product obtained depends on the substituents, coordinated metal, and conditions of the reaction. Dimers of types **98** and **100** are almost planar and, as a consequence of substantial chromophore expansion, their photophysical properties are considerably different from those of the starting porphyrins. In contrast, dimers **99** exhibit photophysical properties similar to those of their precursors, presumably because the planes of the porphyrin fragments adopt a twisted conformation and the π conjugation between them is interrupted. This aspect was extensively covered in two recent reviews.[119]

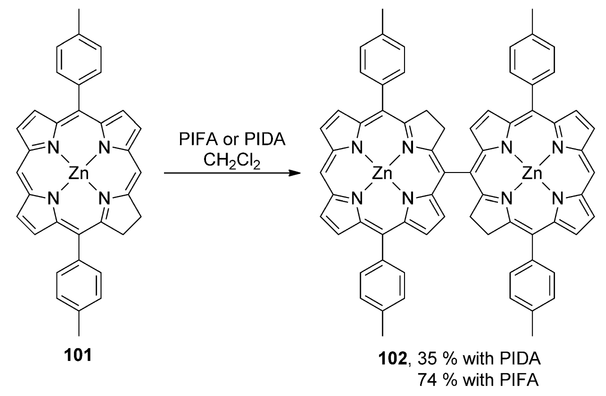


Scheme 33.



Scheme 34. DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone.

An interesting discovery was made by Zheng and coworkers, who examined the reactivity of various oxidants toward chlorins—analogues of porphyrins with one reduced double bond. They found that zinc chlorin **101** can be oxidatively coupled to compound **102** with phenyliodine diacetate (PIDA) or PIFA in 35 % and 75 % yield, respectively.[120] The chlorin macrocycles in the product remain unoxidized, that is, the dimer preserves two sp^3 carbon atoms in the skeleton of each chlorin unit (Scheme 35). Only the zinc complex of chlorin **101** undergoes coupling with PIFA or PIDA. Oxidation of the free-base form of **101** as well as of its

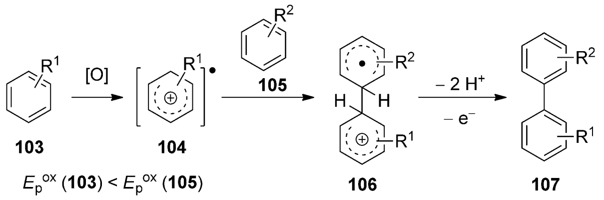


Scheme 35.

Pd, Ni, and Cu complexes does not occur, nor does it lead to the formation of the corresponding porphyrin monomer. Porphyrins are also obtained when DDQ is used as the oxidant.

5.1.6. *Intermolecular Oxidative Cross-Coupling of Aromatic Compounds*

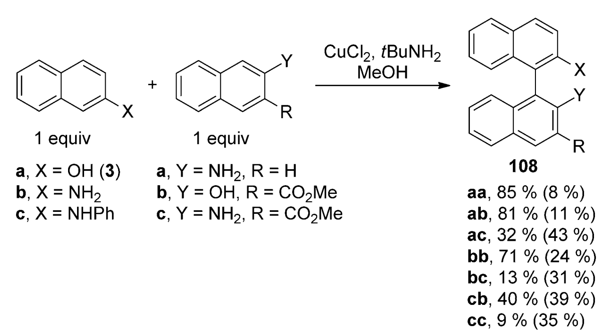
The intermolecular oxidative cross-coupling of arenes is more difficult to perform and is less predictable than homocoupling. The conditions of the reaction, as well as the starting materials, should be precisely selected to obtain cross-coupling products in reasonable yields and selectivity. The following reaction mechanism is proposed:[56,121] Two starting arenes usually differ in their oxidation potential E_p^{ox}, thus the oxidation of the more electron rich component **103** (with the lower oxidation potential) is preferred and the electrophilic radical cation **104** is formed. A high yield of the desired heterodimer **107** can only be obtained when **104** undergoes electrophilic attack at the less electron rich arene molecule **105**, which results in the formation of a radical intermediate **106**. Then, the abstraction of two protons and the second electron takes place to give a cross-coupled biaryl **107** (Scheme 36).



Scheme 36.

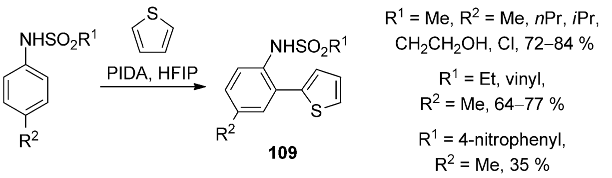
Analyzing the above mechanism, one can conclude that the radical cation **104**, as an electrophile, would prefer to react with the more electron rich arene **103** rather than with **105**, which possesses a lower electron density. As a consequence, the homodimer of **103** would be the main product of the reaction. Indeed, this is the major problem of intermolecular oxidative cross-coupling, which is likely to be responsible for the fact that the number of efficient synthetic protocols published in the literature is rather limited for such reactions. Nevertheless, such effective protocols exist, and the problem mentioned above can be overcome in several ways. The use of an excess of the more electron deficient arene seems to be the easiest of them. This approach is discussed in this Section along with other methods.

Early examples of oxidative aromatic cross-coupling were published by Hovorka et al. and by Smrcina et al.[122] They found that variously substituted naphthols or naphthylamines can cross-couple on treatment with copper(II) chloride in the presence of *tert*-butylamine. High yields of the desired cross-coupling products were obtained in the cases of binaphthyls **108 aa**, **ab**, and **bb**. In the remaining reactions, homocoupling products were obtained in higher or similar yields (Scheme 37). The authors performed frontier molecular orbital calculations, which suggested that the reaction takes place between the radical cation of the more electron rich naphthalene derivative and a second component. The relative proportions of cross- and homocoupled products obtained in the reaction were successively predicted by frontier molecular orbital calculations. The yields of cross-coupled products were high in cases where the singly occupied molecular orbital (SOMO) of the nucleophilic radical was calculated to have a stronger interaction energy with the frontier molecular orbitals of the less electron rich naphthyl reactant.[121b] Further improvement of the copper-mediated cross-coupling of naphthols was made by Habaue and co-workers.[123] Analogously to systems used by Kozlowski and co-workers,[67] they used copper only in catalytic amounts, and the reaction was performed in the presence of chiral diamines under air as the oxidant (Glaser-like conditions). Using these conditions, the authors were able to achieve high yields of the cross-coupling products with moderate enantioselectivities.



Scheme 37. Yields of homocoupled by-products are shown in brackets.

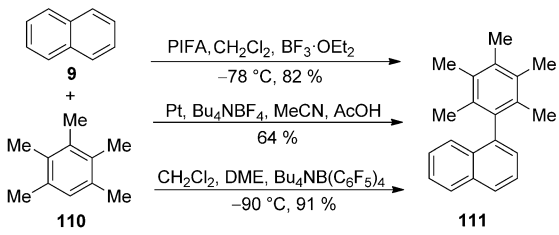
Hypervalent iodine reagents developed by Kita and co-workers has proven to be very effective for the homocoupling of arenes (e.g. PIFA; see Section 5.1.4, Scheme 30). Canesi and co-workers have extended these protocols and subsequently applied them in the oxidative cross-coupling reactions of aromatic substrates.[124] They found that the *ortho* positions of *N*-sulfonylated *p*-substituted anilines can be coupled with thiophenes by reaction with PIDA in HFIP. In this way, variously substituted heterobiaryls **109** were prepared in high



Scheme 38.

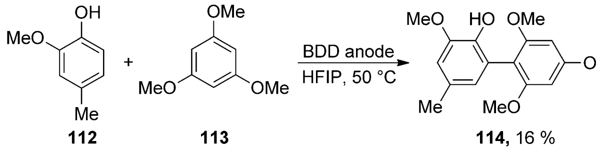
yields (Scheme 38). The procedure also works for *N*-mesyl-2-naphthylamine and bromo- or methylthiophenes.

Kita and co-workers studied the cross-coupling reaction between naphthalene and pentamethylbenzene (**110**) under diverse oxidative conditions.[125a] Oxidants such as FeCl$_3$, CAN, DDQ, Dess–Martin periodinane (DMP), pentafluorophenyliodine bis(trifluoroacetate) (FPIFA), PIFA, and HTIB were examined for this purpose. The best yield of the cross-coupling product **111** was obtained with PIFA in the presence of BF$_3$·OEt$_2$ (82 %, Scheme 39). The higher affinity of hypervalent iodine reagents to naphthalenes compared to benzene rings is key to the selectivity of this reaction. In this way, naphthalene (and not the more electron rich arene **110**) is oxidized to the corresponding radical cation, which can later react with **110** to give the desired cross-coupling product. The authors suggested that the oxidation of **110** with PIFA is additionally prevented by steric hindrance. The optimized procedure was used for the synthesis of numerous other biaryls from various naphthalenes and monocyclic arenes, for example, 1,3,5-triisopropylbenzene and mesitylene. Shafir and co-workers reported that the latter reacts with naphthalene to form a mixture, which contains certain amounts of single or higher homocoupling products as well as the desired biaryl.[125b]



Scheme 39.

A selective electrochemical phenol–arene cross-coupling reaction using boron-doped diamond (BDD) electrodes was very recently reported by Waldvogel and co-workers.[126a,b] The crucial prerequisite is the presence of a hydroxy group, because the phenoxyl radical intermediate plays a key role in this process. 4-Methylguiacol has been coupled with a range of electron-rich benzene derivatives by using this approach to give cross-coupled products in moderate yields (**114**, Scheme 40). It is noteworthy that the same method has also been applied to the oxidative homocoupling of various phenols to afford products in 44–84 % yield.[126c] These reactions occur only in hexafluoroisopropanol as the solvent.

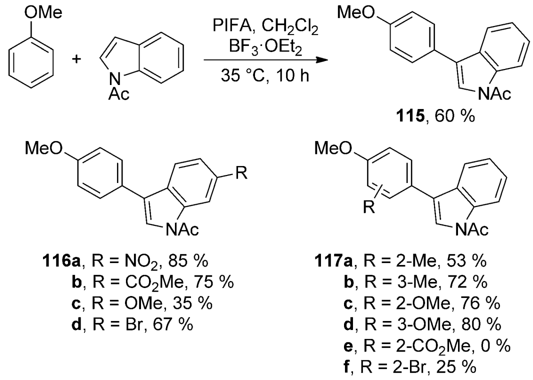


Scheme 40.

The second electrochemical breakthrough was developed by Yoshida and co-workers.[126d] This "radical cation pools" method is based on the generation and accumulation of radical cations of the aromatic compound (by low-temperature electrolysis) followed by reaction with a second organic substrate. Performing the reaction at −90 °C with 1,2-dimethoxyethane as an additive made it possible to obtain the whole range of cross-coupled biaryls (including derivatives of indole and benzothiophene) in 36–87 % yield (an example is shown in Scheme 39). The authors claim on the basis of DFT calculations that the observed high regioselectivity of the cross-coupling results from the spin density of the radical cation and the HOMO coefficient of the nucleophilic partner. The same transformation under operationally simpler electrochemical conditions was reported by Nyberg in 1973[126e] (Scheme 39).

1,4-Dimethoxynaphthalene and 3,5-dimethoxytoluene can be cross-coupled using various PIFA analogues.[127] The best yield was obtained when FPIFA was used as the oxidant.

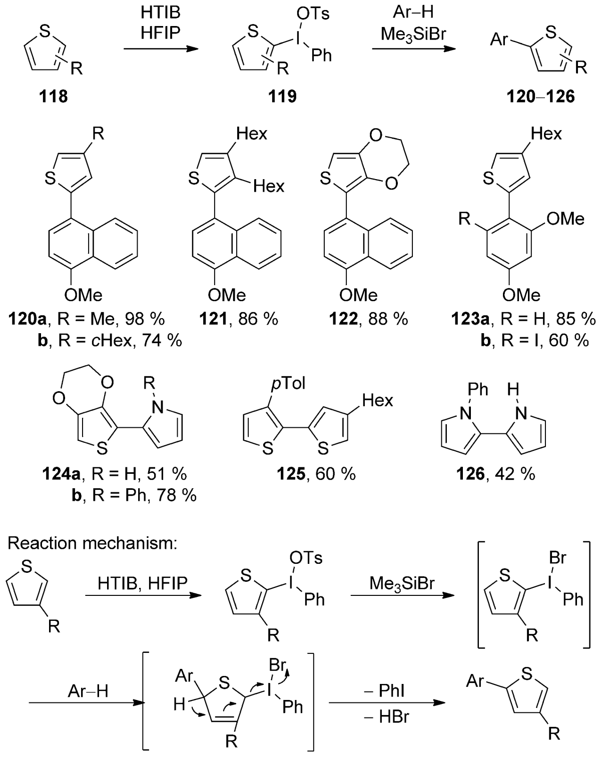
PIFA in the presence of boron trifluoride etherate was also used by Gu and Wang for the oxidative coupling of indole derivatives with variously substituted anisoles.[128] The reaction conditions were optimized for the cross-coupling of *N*-acetylindole with anisole. The authors found that the best yield of compound **115** is achieved when the reaction is carried out at 35 °C in dichloromethane as the solvent (Scheme 41). Under the same conditions, *N*-acetylindoles possessing electron-withdrawing substituents at C6 react with anisole to give the corresponding biaryls **116a**,**b**,**d** in higher yields than their 6-unsubstituted analogues. The more electron rich 6-methoxy-*N*-acetylindole gives the desired coupling product **116c** in only 35 % yield. The opposite trend was



Scheme 41.

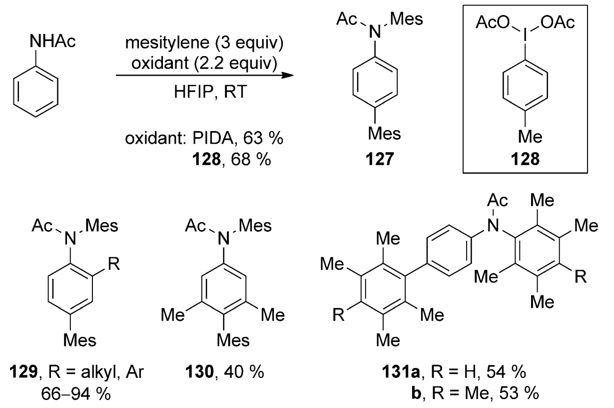
observed in the case of anisole substitution patterns: the highest yields of the coupling product **117** are obtained with anisoles bearing additional electron-donating substituents. In all cases, the substitution takes place at the most electron rich position (C3) of the indole.

In 2007, Kita and co-workers published a simple and effective method for the synthesis of diaryliodonium(III) salts by the reaction of arenes with HTIB in 2,2,2-trifluoroethanol.[129] Further studies on the reactivity of these salts led the researchers to the discovery of an interesting synthesis of heterobiaryls. Diaryliodonium salts can be prepared in situ from thiophene derivatives **118** and, after the subsequent addition of an electron-rich arene and Me_3SiBr, the reaction takes place to give cross-coupling products **120–126** in excellent yields (Scheme 42).[130] In particular, thiophene can be coupled with pyrrole derivatives or another thiophene to provide cross-coupling products **124a**,**b** and **125** in reasonable yields. This method was also applied to the synthesis of unsymmetrical bipyrrole **126**, which was obtained in 40% yield. The reaction does not proceed without the addition of Me_3SiBr. The authors showed that the initially formed diaryliodonium(III) salt **119** is unreactive as long as tosylate is its counterion. After the addition of Me_3SiBr, tosylate is exchanged by bromide, which activates the salt toward the reaction with electron-rich arenes. The reaction mechanism proposed by the authors is presented in Scheme 42.



Scheme 42. Ts = $4\text{-}CH_3C_6H_4SO_2$.

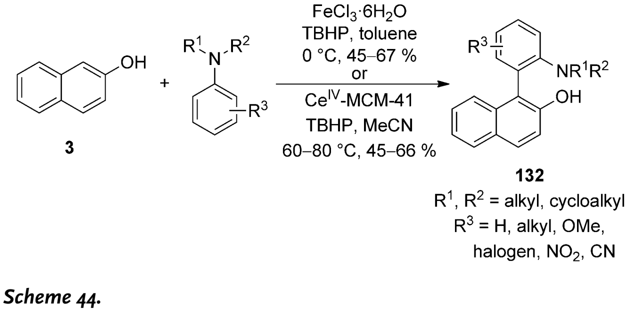
Recently, Antonchick and co-workers reported an interesting result related to the oxidative arylation of acetanilide.[131] They found that its reaction with mesitylene in the presence of an excess of PIDA (2.2 equivalents) in HFIP leads to the formation of the diarylated product **127** in 63% yield. Two mesityl substituents were introduced into the product: first at the nitrogen atom and second at the *para* position of the benzene ring of acetanilide (Scheme 43). The use of (4-methylphenyl)iodine diacetate (**128**) instead of PIDA improved the yield of **127** to 68%. Additionally, **128** prevents the formation of an *N*-iodophenylation by-product, which was detected when PIDA was used.



Scheme 43. Mes = $MeSO_2$.

Therefore, the authors decided to use compound **128** as the oxidant in further experiments. They examined the reaction of mesitylene with a variety of substituted acetanilides, with **128** used as the oxidant. The desired diarylated products **129** and **130** were obtained in high yields. In a second series, the authors studied the reactivity of a variety of benzene derivatives in the reaction with acetanilide and **128**. Again, the expected products, such as **131a** and **b**, were isolated from the reaction mixture in satisfactory yields.

As shown above, the intermolecular oxidative cross-coupling of aromatic substrates is dominated by the hypervalent iodine(III) reagents, which was mainly developed by the research group of Kita.[85,86,102,103,105,124,126,128,129] Metal catalysts, however, are also used for this purpose. 2-Naphthol (**3**) can be coupled with variously substituted *N*,*N*-dialkylanilines by oxidation with *tert*-butyl hydrogen peroxide (TBHP) catalyzed by iron(III) chloride.[132] In this reaction, anilines undergo substitution at their *ortho* positions relative to the amine group. Numerous examples of biaryls **132** can be obtained by this method in reasonable yields (Scheme 44).



Scheme 44.

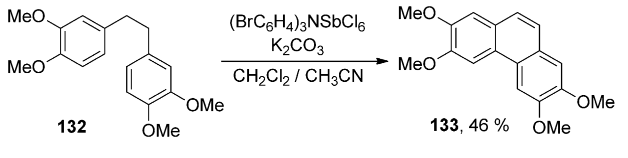
Recently, cerium(IV) was also employed for the oxidative coupling of anilines with 2-naphthol (**3**).[133] The authors used mesoporous silica MCM-41 with embedded cerium(IV) as the catalyst for this reaction (Scheme 44).

5.2. Intramolecular Oxidative Aromatic Coupling

The oxidant-mediated coupling of electron-rich arene rings has served for several decades as a valuable procedure to access biaryl units. The complex mixtures of isomers that often plagued the earliest studies have gradually given way to synthetically useful product distributions through the application of more-selective coupling protocols. Continuous advances in the nature of the oxidant (and its attendant ligands) and more precisely defined reaction conditions have led to increasing levels of control over C–C bond formation. Chemoselective (C–C versus C–O bond formation with phenols; suppression of product oxidation), regioselective (2,2′, 2,4′, or 4,4′) C–C bond formation), and, more recently, stereoselective (atropisomer-selective) biaryl bond formation can now be achieved in many well-defined systems. A survey of the more recent advances in these areas is presented below.

5.2.1. Homoaromatic Compounds

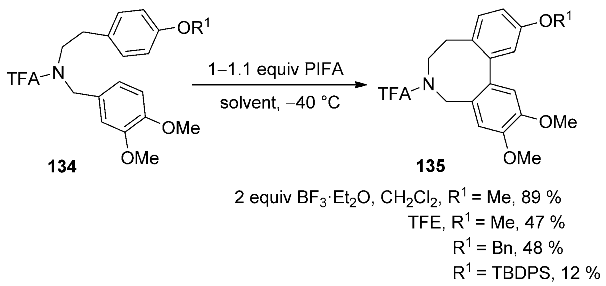
Ronlán and Parker described the electrochemical oxidation of a bibenzyl to the corresponding phenanthrene derivative.[134] Kricka and Ledwith prepared phenanthrene as a major product by treatment of bibenzyl with two equivalents of tris-(*p*-bromophenyl)ammonium hexachloroantimonate.[135] Isomeric tetramethoxybibenzyls and the corresponding benzils were largely unreactive. The use of PIFA/$BF_3{\cdot}Et_2O$ in CH_2Cl_2 as an oxidant significantly increases the yield of the product **133** (91 %, Scheme 45).[136,137]



Scheme 45.

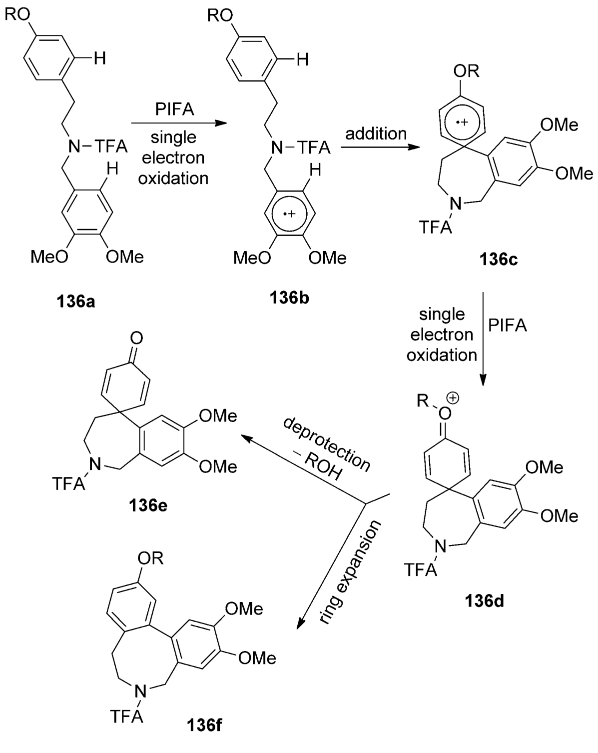
Wang also described $FeCl_3$-catalyzed intramolecular oxidative coupling reactions for the direct construction of the phenanthrene ring in excellent yields by using *m*-chloroperbenzoic acid as the oxidant at 25 °C. The catalyst acts as a one-electron oxidant, and the reduced catalyst is reoxidized by *m*-CPBA.[68]

Most intramolecular oxidative biaryl C–C coupling reactions result in the formation of six-membered rings. Larger rings, however, can also be formed by this approach. Kita et al. observed the selective formation of seven- and eight-membered rings by using phenyliodine bis(trifluoroacetate) (PIFA) as the oxidant (Scheme 46).[138] PIFA alone does not promote these transformations, but activation by $BF_3{\cdot}Et_2O$ or trifluoroethanol (TFE) appears to enhance the electrophilicity of the iodine reagent.



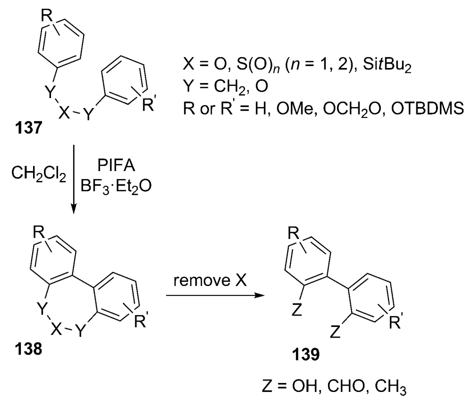
Scheme 46. TFA = trifluoroacetyl.

According to the authors, the mechanism involves a single-electron oxidation of the more electron rich aromatic ring in **136a** to give **136b**, followed by an S_EAr transformation to **136c**, oxidation to arenium cation **136d**, and finally a ring expansion with rearomatization to give the desired product **136f** in addition to the spiro-anellated derivative **136e** (Scheme 47). It is well known that, because of the formation of quinone-type by-products, cyclization to form eight-membered rings is difficult.[139] In this case, the choice of suitable substituents favored cyclization over oxidation to quinones.



Scheme 47.

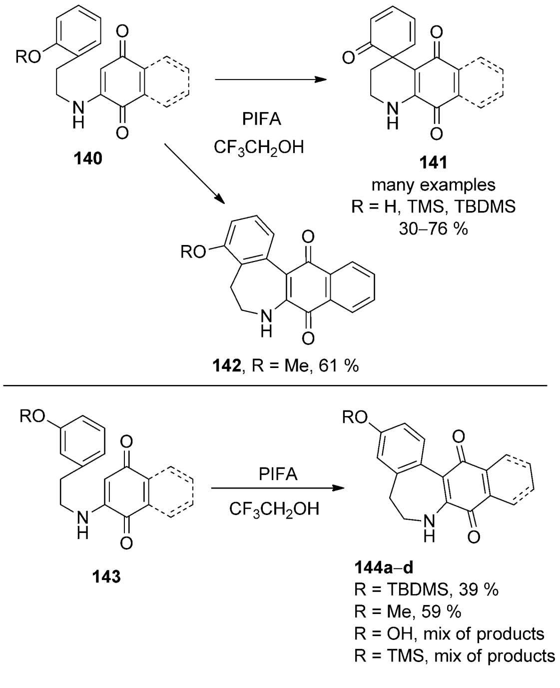
Oxidation of suitable precursors **137** with the PIFA/$BF_3{\cdot}OEt_2$ system allows fused heterocyclic compounds **138a–c** to be obtained, which can easily be converted into



Scheme 48. TBDMS = *tert*-butyldimethylsilyl.

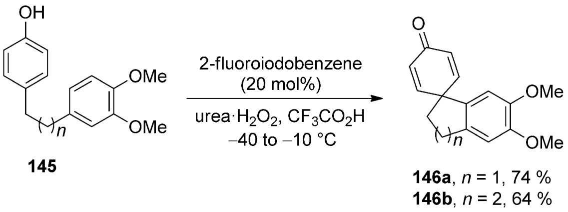
2,2′-substituted biaryls possessing hydroxy **139a**, formyl **139b**, and methyl groups **139c** (Scheme 48). 2,2′-disubstituted symmetrical and unsymmetrical biphenyls have attracted considerable interest because of the presence of these moieties in a number of natural products, such as vancomycin, elladitannins, and dibenzocyclooctalignans, and also as the ligand of metal catalysts in asymmetric synthesis.[137c]

Kita and co-workers examined the reactivity of phenol derivatives bearing an additional aminoquinone moiety.[140] The difference in reactivity among these derivatives in the presence of PIFA/trifluoroethanol has been investigated. Reaction of an *o*-substituted phenol or protected phenol derivatives (TMS, TBDMS) with PIFA in CF_3CH_2OH at 25 °C gives the azacarbocyclic spirodienone derivatives **141** in good yields (Scheme 49). On the other hand, methyl ether derivatives give only the rearrangement product, namely the 2,3-dihydro-1*H*-azepine **142** in 61 % yield. As a result, the final product with a seven-membered ring contains an electron-donating group (OMe) in the *meta* position. However, the *m*-substituted phenol derivatives **143** give 2,3-dihydro-1-azepine systems **144a–d** selectively.



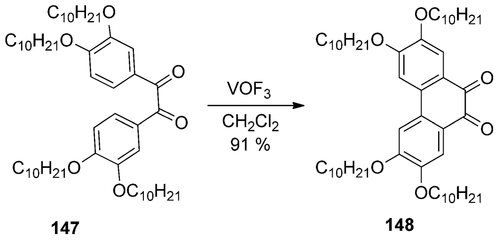
Scheme 49.

The same authors developed a new H_2O_2/acid anhydride system for the iodoarene-catalyzed intramolecular cyclization of phenolic derivatives.[141] In situ generated trifluoroperacetic acid oxidizes iodoarenes to a well-known oxidizing iodine(III) reagent, which acts as the catalyst in the synthesis of a series of spirocyclic dienones (Scheme 50).



Scheme 50.

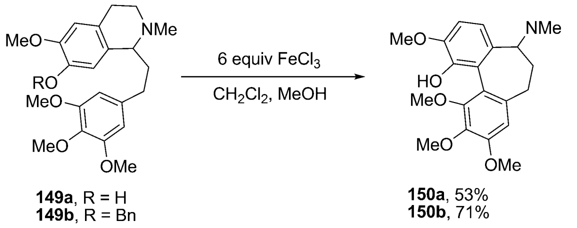
Aromatic oxidative coupling of benzils is a more complex endeavor since an electron-withdrawing carbonyl group is inherently present and deactivates the substrate. A study performed by Wegner and co-workers showed that such cyclization to form alkyl- and alkoxy-substituted phenanthrenedione products **148** is possible (Scheme 51).[142a] The yields are rather low unless VOF_3 is used as the oxidant. Very recently Trosien and Waldvogel proved that $MoCl_5/TiCl_4$ is an even more efficient reagent for this transformation.[142b]



Scheme 51.

The use of VOF_3 in a mixture of CH_2Cl_2 and TFA allowed Comins et al. to complete the total synthesis of tylophorine, first in racemic form and then as the enantiopure (−) enantiomer.[143] The oxidative cyclization of septicine leads directly to tylophorinein in 68 % yield.

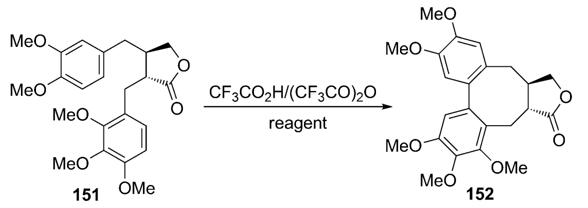
An analogous coupling in the tetrahydroisoquinoline alkaloid family studied by Herbert et al. led to the synthesis of alkaloid kreysigine (**150a**), which can be synthesized from compounds **149a,b** by the formation of a seven-membered ring mediated by $FeCl_3$ (6 equiv, anhydrous) in dichloromethane (Scheme 52).[144] The reaction with phenol **149a** gives a lower yield (53 %). A significantly better yield of kreysigine is obtained with the benzyl-protected compound **149b** (71 %).



Scheme 52.

The most comprehensive study of the formation of seven-membered rings by intramolecular aromatic oxidative coupling was performed by Planchenault, Dhal, and Robin.[145,146] This investigation explored commonly used oxidizing reagents such as thallium(III) and vanadium(V) derivatives, as well as other metals ranging from ruthenium to tellurium in the synthesis of stegane (**152**, Table 8). The authors concluded that the intramolecular oxidative coupling of the stegane precursor **151** is best accomplished with either ruthenium or rhenium reagents. Analogous transformations can also be carried out efficiently by using $MoCl_5$ as the sole reagent.[85g]

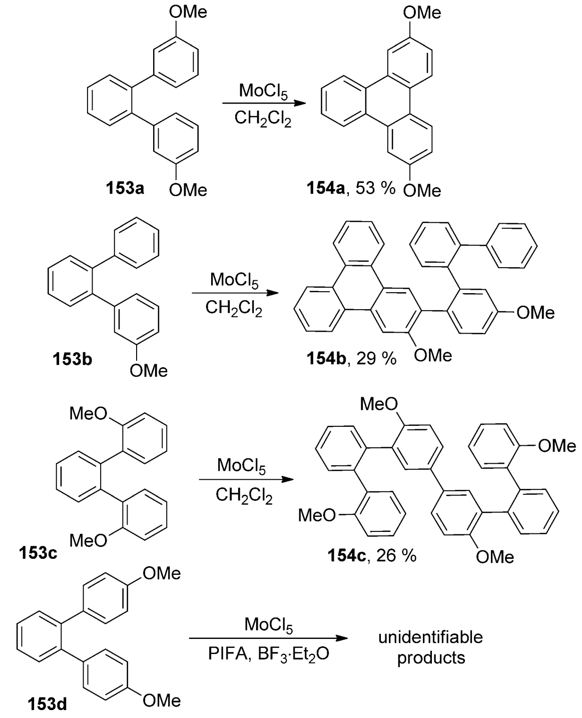
Table 8:



Oxidant	Equiv	Time	Yield **152** [%]
$RuO_2 \cdot 2H_2O$	2	18 h	98
Tl_2O_3	0.52	30 min	73
$Mn(OAc)_3 \cdot H_2O$	1.9	15 min	84
$Ce(OH)_4$	4.8	3 h	72
V_2O_5	4.8	5 days	87
Re_2O_7	1.9	3 h	98
$Fe(OH)(OAc)_2$	3.8	5 h	62
Co_3O_4	9.5	3 days	78
CF_3CO_2Ag	14	1 day	86
CrO_3	3.8	6 days	71
$Rh_2O_3 \cdot 5H_2O$	4.8	14 days	39
IrO_2	4.8	16 days	77
Pr_2O_{11}	11.6	64 h	74
SeO_2	5.	8 h	70
TeO_2	10	2 days	80
$Cu(OAc)_2 \cdot H_2O$	3.8	1 day	22

Numerous electron-rich aromatic compounds have been oxidized electrochemically in an intramolecular fashion to afford biphenyls with connecting rings of different size.[92] The coupling sites and yields are dependent not only on the specific structure of the substrate but also on the choice of the electrolyte/electrode system, the pH value of the medium, the current density, and the oxidation potential. Again, the beneficial effect of TFA can clearly be observed in many cases, since in its presence the radical cations of the products are stable and do not decompose, thus allowing for the final reduction to the neutral product with zinc powder.[134]

King and co-workers systematically studied the cyclization of terphenyls with different directing group effects so as to allow the outcome of reactions of substituted substrates to be predicted.[38b] They used $MoCl_5$ (introduced by Waldvogel and co-workers[84]) and PIFA/$BF_3 \cdot Et_2O$ as general and effective reagents. According to general expectations, activating *o*,*p*-directing groups (e.g. OMe) direct the bond formation to the *ortho* or *para* positions either intramolecularly or intermolecularly. For example, the oxidation of 3,3′-dimethoxy-*o*-terphenyl (**153a**) with $MoCl_5$ in CH_2Cl_2 gives 2,7-dimethoxytriphenylene (**154a**) in 53 % yield (Scheme 53).

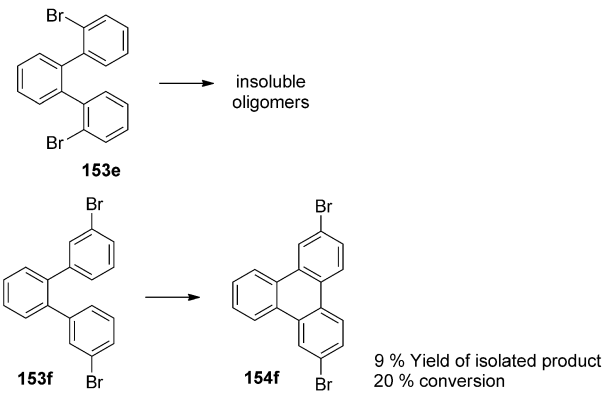


Scheme 53.

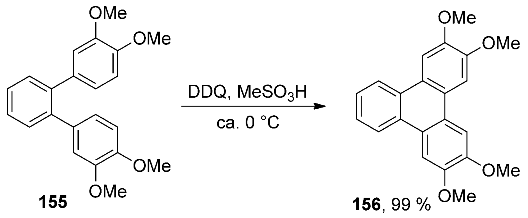
The oxidation of the tetramethoxy derivative occurs in an analogous way, thereby leading to 1,3,10,12-tetramethoxytriphenylene in 30% yield. Unexpectedly, the use of PIFA/$BF_3 \cdot Et_2O$ results in lower conversion and more oligomeric material. The oxidation of 3-methoxy-*o*-terphenyl (**153b**) and *o*-terphenyls **153c,d** by using $MoCl_5$/CH_2Cl_2 and/or PIFA/$BF_3 \cdot Et_2O$ gives either an intractable mixture or unexpected products such as **154c**.

The same authors also examined the influence of electron-withdrawing substituents. They found that a bromo substituent also directs bond formation, but yields are lower (Scheme 54). The presence of strongly electron-withdrawing groups suppresses the reaction.

In 2009, Rathore and co-workers introduced a new reagent for oxidative aromatic coupling, namely DDQ/



Scheme 54.



Scheme 55.

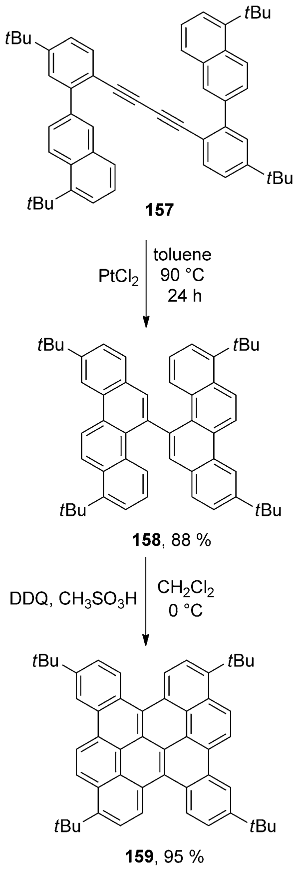
$MeSO_3H$, which enabled the transformation of tetramethoxy derivative **155** into **156** (Scheme 55).[40]

A complex example of the synthesis of polynuclear aromatic hydrocarbon **159** under these conditions was recently revealed by Chen and Liu.[147] The two-step synthesis starts from bis(biaryl)diyne **157**, which undergoes an initial $PtCl_2$-catalyzed aromatization to form **158**, and a subsequent oxidation by DDQ (Scheme 56). The highest yields are obtained by combining DDQ with methanesulfonic acid in dichloromethane as the solvent.

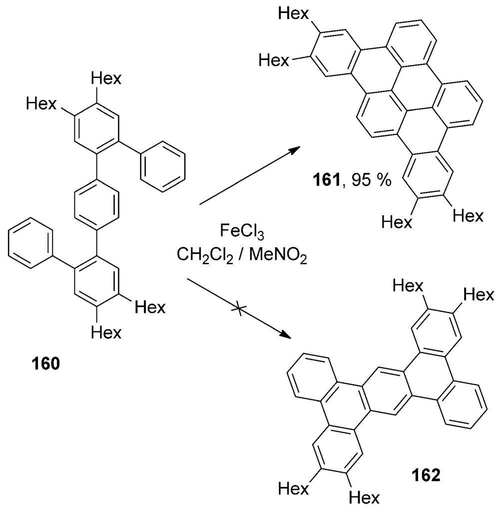
The research groups of Müllen[148] and Hilt[149] reported that tribenzo[*fg*,*ij*,*rst*]pentaphene derivatives such as **161** are formed exclusively rather than tetrabenzoanthracene **162** (CH_2Cl_2/$MeNO_2$ solution, Scheme 57) in the oxidation of triphenylene precursors **160**.[14b] In one of these cases, the authors noted that neither $AlCl_3$ nor $MeSO_3H$ are effective under these conditions.

Very recently, Durola and co-workers described even more intriguing examples of peculiar regioselectivity.[27b] For example, derivative **163** of quinquephenyl is converted into **164** and **165** (Scheme 58). The steric hindrance imparted by the *tert*-butyl groups has only a small influence on the ratio of the two products since compound **165** is predominant.

Hexa-*peri*-hexabenzocoronene (HBC) was obtained by Clar et al. for the first time in 1958.[50,150] Symmetrical HBC **167** can be easily obtained by cyclotrimerization of di(4-alkylphenyl)ethynes catalyzed by a dicobalt octacarbonyl catalyzed process,[151] and the resulting hexa(4-alkylphenyl)-benzenes **166** can be cyclodehydrogenated with $CuCl_2$/$AlCl_3$ or $Cu(OTf)_2$/$AlCl_3$ in CS_2,[152] or with $FeCl_3$ dissolved in nitromethane (Scheme 59).[153]

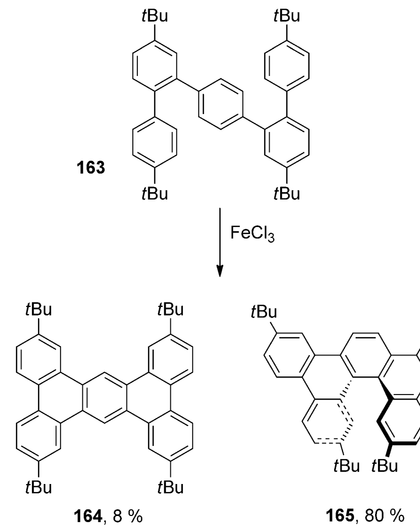


Scheme 56.

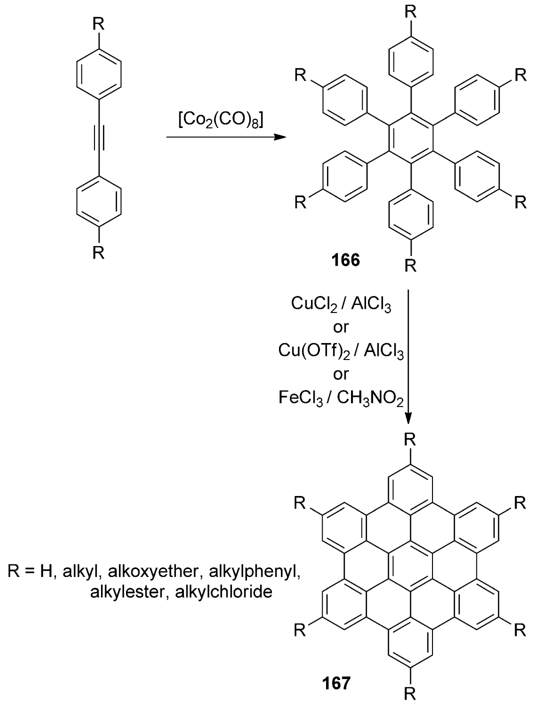


Scheme 57.

Despite the simultaneous formation of six carbon–carbon bonds, the yield of these oxidative couplings are usually nearly quantitative. Unsubstituted HBC (**167**, R = H) is obtained in > 90 % yield by using a $CuCl_2$/$AlCl_3$ mixture in CS_2 at room temperature. Scholl reaction conditions ($AlCl_3$/NaCl melt) give only 3 % of these products.[154] It is noteworthy that the highest yield for the cyclization of hexaphe-



Scheme 58.

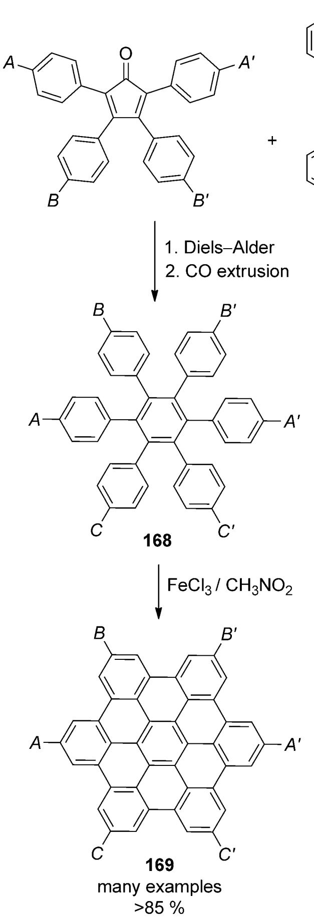


Scheme 59.

nylbenzene to hexa-*peri*-hexabenzocoronene (99 %) was achieved using $MoCl_5$.[38c]

A key development in the preparation of HBCs was the use of $FeCl_3$, which improved the functional-group tolerance. However, the iron trichloride route often resulted in the formation of chlorinated side products. This general fact was observed for the first time already in 1919 by Bratz and Niementowski during the attempted oxidation of 8-hydroxyquinoline.[155] A detailed study of the oxidative cyclodehydrogenation process by controlling the quantity of the oxidant and the reaction time revealed that the reaction occurs exclusively in an intramolecular fashion without the formation of organic side products. The intermediate can be separated, thus indicating that the cyclodehydrogenation is a step-wise process.[156]

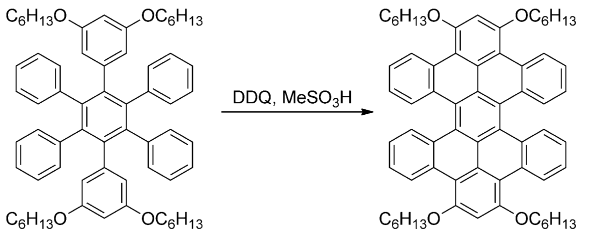
The HBC derivatives **169** with reduced symmetry were synthesized by an alternative way, starting from tetraphenylcyclopentadienone and substituted diphenylethynes. The second step is the standard $FeCl_3$ reaction with hexaphenylbenzene derivatives **168**.[157] HBCs carrying solubilizing alkyl chains and one or multiple bromine functionalities with different symmetries can be synthesized by using the above synthetic strategy (Scheme 60).



Scheme 60.

Miao and co-workers showed that hexaphenylbenzene **170** cannot be oxidized to a hexa-*peri*-hexabenzocoronene by using Rathore's system (DDQ/$MeSO_3H$). The product of this reaction is compound **171**, which lacks two bonds (Scheme 61).[158] Interestingly, this product cannot be further oxidized with either DDQ/$MeSO_3H$ or $FeCl_3$.

This procedure was recently utilized by Mughall and Kuck, who fused the bowl-shaped tribenzotriquinacene with hexa-*peri*-hexabenzocoronene by using a $Cu(OTf)_2/AlCl_3/CS_2$ system.[159] Interestingly, the use of $FeCl_3$ gives only the starting materials.

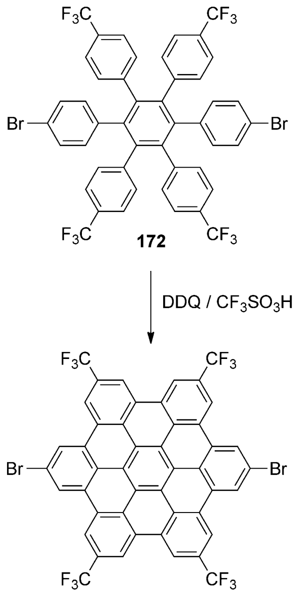


170

171, 72 %

Scheme 61.

Very recently, Jones et al. proved that even electron-deficient arenes can be coupled by using a system consisting of an oxidant and a super acid.[160a] Hexaphenylbenzene **172** bearing electron-withdrawing Br, F, and CF$_3$ groups can be cyclized by using the DDQ/CF$_3$SO$_3$H system to afford hexa-*peri*-hexabenzocoronene **173** in moderate yields (Scheme 62).

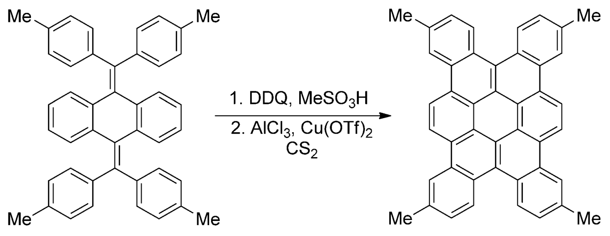


173, 81 %

Scheme 62.

Rearrangements during the synthesis of HBCs were first observed by Müllen and co-workers during the planned synthesis of dimethoxy-substituted HBCs.[160b] The reaction of a *para*-dimethoxy-substituted precursor with FeCl$_3$ in MeNO$_2$ provided a mixture of *meta*-dimethoxy-HBC product and bis(spirocyclic) dienone. An analogous case has been observed by Wadumethrige and Rathore. During the attempted oxidation of hexakis(4-methoxyphenyl)benzene with FeCl$_3$, only spirocyclic indenofluorene was isolated in quantitative yield.[160c]

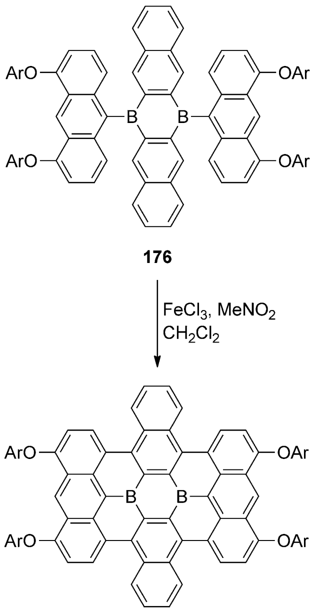
The dehydrogenation reaction was recently applied by Tao and co-workers to the synthesis of tetrabenzo-[*a*,*d*,*j*,*m*]coronenes.[161] The authors noted that the cyclization of intermediate **174** to afford tetrabenzocoronene **175** proceeds better if, after the action of DDQ/MeSO$_3$H, the CuCl$_2$/AlCl$_3$/CS$_2$ system is used rather than FeCl$_3$, which causes concomitant chlorination (Scheme 63).



174

175, 44 %

Scheme 63.



177, 51 %

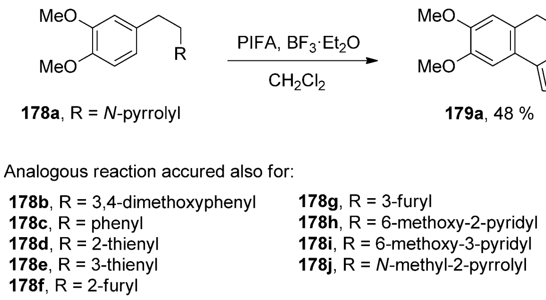
Scheme 64.

Very recently, Yamaguchi and co-workers published the first example of an intramolecular oxidative coupling in a polyaromatic system containing boron (Scheme 64).[162] The oxidative aromatic coupling of compound **176** with an excess of FeCl$_3$ proceeds successfully to form dye **177** as a deep-purple solid in 51 % yield. Again, electron-donating phenoxy groups are incorporated at appropriate positions to provide the electron density necessary for this reaction to occur.

5.2.2. *Heterocyclic Compounds*

Dominguez used hypervalent iodine reagents for a biaryl coupling reaction leading to the formation of heterobiaryl connections (Scheme 65).[137]

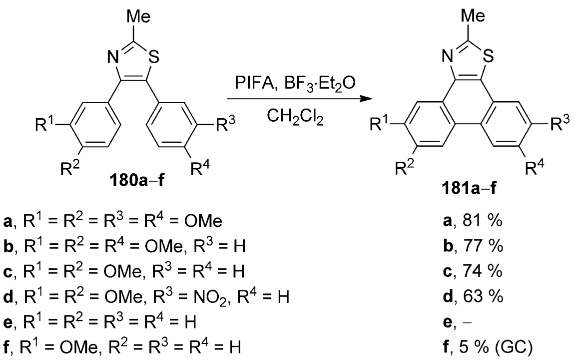
Only electron-rich aromatic rings are able to provide the corresponding fused systems. The authors showed that not only the tetramethoxyphenanthrene **179b** but also the naphthothiophene **179d** and the pyrroloisoquinoline **179a** can be prepared in moderate to high yields in this way. On the other hand, in those cases in which the aryl ring is not



Scheme 65.

sufficiently nucleophilic, the coupling product is the only one detected (**179h**, **179j**) as a result of a homocoupling biaryl process. Finally, it is worth noting that some of the substrates (**178c**, **178e**, **178f**, **178g**, and **178i**) decompose under the same reaction conditions to give complex mixtures of unidentified compounds.

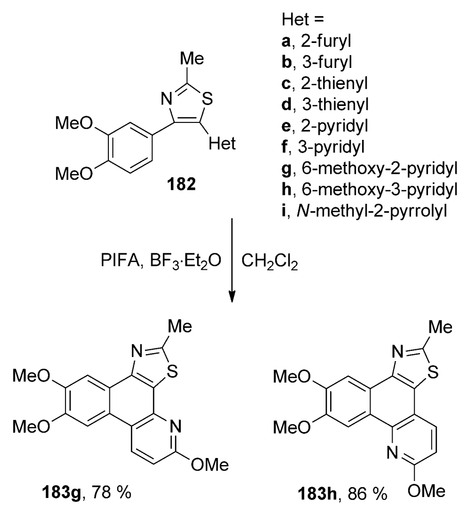
Dominguez and co-workers also studied the effectiveness of the oxidative cyclization of a series 4,5-diarylthiazoles (**180a–f**), including highly activated (**180a**, **180b**, **180g**), moderately activated (**180c**), non-activated (**180e**, **180f**), and deactivated (**180d**) aromatic rings (Scheme 66). The key conclusion was that it is possible to achieve the desired products by cyclization, provided that at least two methoxy groups are present in one of the rings (**180a–c**, **180g**). If only one methoxy group is present in the ring, the yield decreases dramatically (less than 5% for **180f**). Surprisingly, product **181d**, in which one of the rings is highly deactivated by the nitro group, could also be prepared in good yield (63%).



Scheme 66.

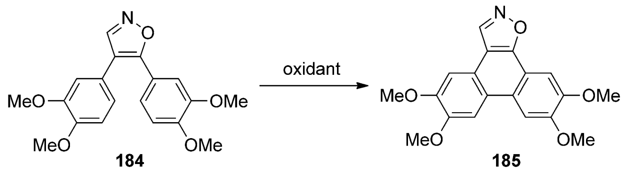
The same authors also prepared a series of fused thiazoles of type **183** (Scheme 67). Intramolecular oxidative coupling occurred in moderate to high yields, except for the case of pyridine-2-yl-thiazole **182e**. Clearly, the electron-poor pyridine ring does not provide sufficient electron density for this reaction to occur. Placing an electron-donating group (OMe) on the pyridine ring leads to the successful synthesis of the fused pyridylthiazoles **183g,h**.

In 1999, Dominguez and co-workers showed that phenanthro[9,10-*d*]-fused isoxazoles and related pyrimidines could be obtained from the biarylisoxazoles and biarylpyrimidines respectively, with PIFA as the oxidant (Table 9).[164] This reagent proved to be the most efficient one and afforded product mixtures from which the desired biaryl products could be more easily isolated compared to those obtained with other oxidants [thallium tris(trifluoroacetate) (TTFA) 42–72%, RuO$_2$ 71%, VOF$_3$ 49–69%, FeCl$_3$ 80%].



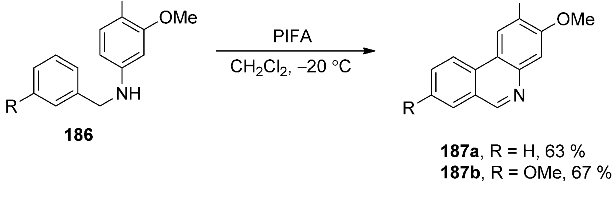
Scheme 67.

Table 9:



Reaction conditions	Time [h]	**185** [%]
TTFA (1.1 equiv), CH$_2$Cl$_2$, RT	6.5	42
TTFA (1.1 equiv), TFAA, TFA, BF$_3$·Et$_2$O, 0 °C	4	67
TTFA (1.1 equiv), CH$_3$CN, CCl$_4$, BF$_3$·Et$_2$O, −40 °C	75	72
RuO$_2$·2 H$_2$O (4 equiv), TFAA, TFA, BF$_3$·Et$_2$O, −10 °C	7	71
VOF$_3$ (3.3 equiv), BF$_3$·Et$_2$O, CH$_2$Cl$_2$, RT	0.15	49
VOF$_3$ (3 equiv), TFA, CH$_2$Cl$_2$, −45 °C to RT	6	69
FeCl$_3$ (6 equiv), CH$_2$Cl$_2$, RT	6.7	80
PIFA (1.1 equiv), BF$_3$·Et$_2$O, CH$_2$Cl$_2$, −40 °C	0.25	85

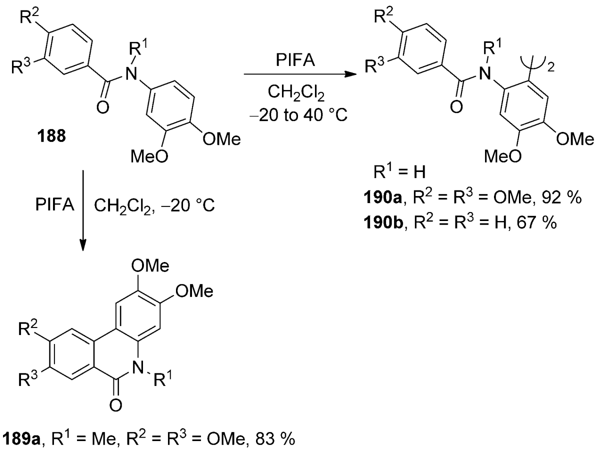
Dominguez and co-workers also presented the synthesis of phenanthridines and phenanthridinones starting from suitably substituted amines and amides under oxidative cyclization conditions (Scheme 68).[165] The reaction starting



Scheme 68.

from a secondary amine as the precursor results in the formation of a biaryl bond followed by a spontaneous aromatization process under oxidative reaction conditions.

On the other hand, secondary amides do not yield the expected products in most cases. Regardless of the reaction conditions, a dimerization process occurs and leads to **190a**,**b** (Scheme 69). These results can be explained in terms of the stabilization of the amides in a *trans* conformation, which prevents the proximity of both rings needed for the desired intramolecular coupling. The transformation of amides **188a**,**b** into the corresponding *N*-methyl derivatives alter the preferred conformation, thus leading to the expected phenanthridinone **189** in very high yield (83 %).

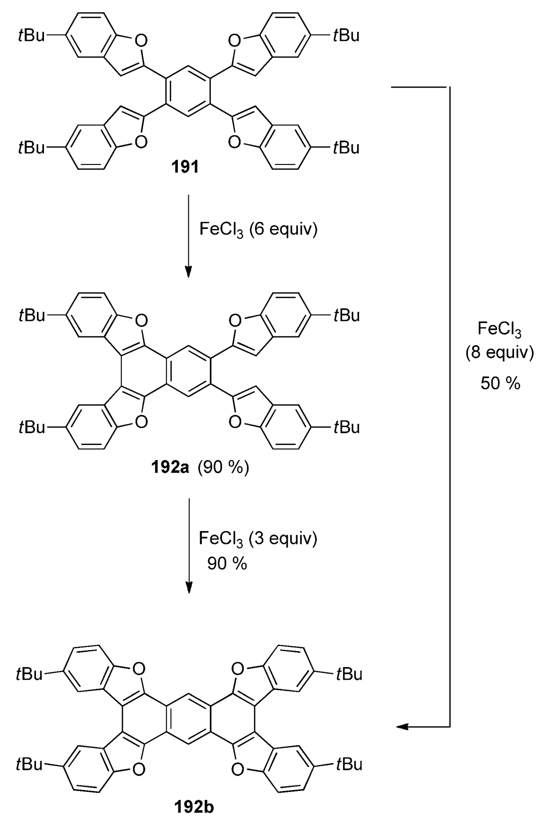


Scheme 69.

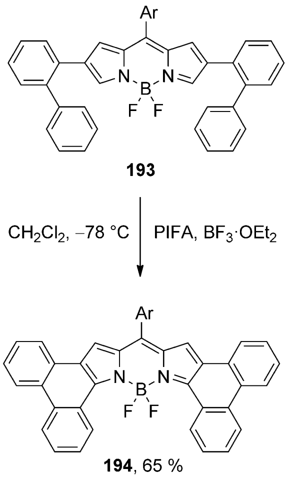
Sullivan and Faul investigated the intramolecular coupling of bis(indol-3-yl)maleimides to prepare indolo[2,3-*a*]carbazoles. Modest yields were obtained, but the strategy nevertheless proved to be successful.[166]

The authors also tested various Lewis acids (CSA, HBF_4, TFA), but only BF_3 activated the oxidant and allowed the fused products to be obtained. The oxidation of bisindolylmaleimides with PIFA was unsuccessful when monosubstituted indoles (6-Cl, 6-F) were employed.

Cao and co-workers[167] synthesized novel compounds **192** containing fused oligobenzofuran substructures. Oxidation was performed using $FeCl_3$ in a mixture of $CH_2Cl_2/MeNO_2$. Compound **191** generally undergoes intramolecular aromatic oxidative coupling in one position only. The best result in terms of the full oxidation to form **192b** was observed when eight equivalents of oxidant were used, but only moderate yields were obtained (50 %). Higher concentrations of oxidant resulted in decomposition of the substrate, while lower concentrations led to the product of monooxidation. Interestingly, the yield of **192b** was higher when the oxidation was performed in a stepwise manner (Scheme 70). Oxidation to compound **192a** proceeded under mild reaction conditions and in high yield. The final fusion takes place in the next step, also in high yield.



Scheme 70.



Scheme 71.

Shinokubo and co-workers reported an oxidative coupling of aryl substituents at the β position of **193** as a strategy to expand the π system of a BODIPY unit (Scheme 71).[168] The reaction proceeds very efficiently despite the fact that none of the reacting units are electron rich. This is an example of a cyclization of a relatively electron-poor substrate.

Wu and co-workers successfully fused an anthracene unit to the BODIPY core by a $FeCl_3$-mediated oxidative cyclization.[169] The product of the intermolecular oxidative coupling at the β position of the pyrrole ring was also observed.

Interestingly, the coupled product was obtained only in the case of a derivative containing 2,4,6-trimethylphenoxy groups on the anthracene ring. Attempts towards the fusion of such a system without these groups were not successful, as BODIPY oligomers and other decomposed BODIPY side products were obtained. The authors think that this failure may be ascribed to the relatively low reactivity at the 1,8-positions of the anthracene unit. A similar problem was also encountered in the synthesis of anthracene-fused porphyrins.[170]

Porphyrins fused with other aromatic units at the meso and β positions have recently emerged as a hot topic of research. Their synthesis typically starts with the preparation of precursors by either Suzuki coupling of a meso-bromoporphyrin or mixed-aldehyde condensation, and is followed by an oxidative aromatic coupling, often using high-valent metal reagents, with DDQ/Sc(OTf)$_3$ and Fe^{III} salts being among the most popular. In recent years, porphyrins have been oxidatively coupled not only with well-known aromatic hydrocarbons such as naphthalene[171] and pyrene,[172] but also with more complex heterocyclic fragments, including indole, phenanthro[1,10,9,8-*cdefg*]carbazole,[173] and BODIPY.[174] A subtle relationship exists between the output of intramolecular oxidative coupling and the nature of the second aromatic moiety, the cation in the porphyrin cavity, the oxidant, and the type of remaining meso substituent.

6. Summary and Outlook

Over the past 140 years, tremendous knowledge has been accumulated regarding the dehydrogenative inter- and intramolecular coupling of aromatic compounds. This economically advantageous process attracts attention as the ultimate method for the formation of biaryls. Electron-rich and electron neutral compounds/moieties can both react to form one or more carbon–carbon single bonds. The presentation of various aspects of oxidation leading to the formation of aryl–aryl linkages has allowed us to state the hypothesis that, depending on the structure of the substrates, two mechanisms have to be considered. The fact that this process can be mediated by both a strong Lewis acid at high temperature and by mild oxidants (both Lewis acids and not) under mild conditions has caused certain confusion in recent years. We, therefore, propose to call this process dehydrogenative aromatic coupling when the mechanism is unclear. We also propose to reserve the name “Scholl reaction” only for those cases when non-oxidizing Brønsted or Lewis acids are used to perform the reaction (with the use of an additional oxidant or without). We also think that it would be good to reserve the name “oxidative aromatic coupling” to cases when the reaction occurs with electron-rich substrates at room temperature and is mediated by oxidants. Moreover, by drawing on our own examples, we have shown that the Scholl reaction can occur in many cases with substrates having low oxidation potentials, but are still able to provide the final products in good yield. Needless to say, a great deal of additional effort (especially focused on electrochemically mediated oxidative aromatic coupling, experiments with Brønsted acids, and computational studies)[175] is needed to clarify the mechanisms of these processes. We hope that this Review, in addition to organizing the knowledge on this topic, will serve as a catalyst to spark further studies.

We thank the Regional Development Fund (Foundation for Polish Science, TEAM-2009-4/3) for financial support.

Received: December 22, 2012

[1] J. Löwe, *Z. Chemie*, **1868**, *4*, 603–604.

[2] R. Scholl, J. Mansfeld, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734–1746.
Roland Scholl was born on September 30, 1865 in Zürich. He studied chemistry and physics in Würzburg and—after his army service—in Zürich, and obtained his PhD in 1890 in Basel. In 1897 he moved to Karlsruhe, where he became an extraordinary professor in 1904. In 1907 Scholl moved to Graz as a full professor. He served in World War I as a volunteer from 1914 till 1916, when he resigned as the consequence of a disease caused by the army service. He became a professor and the director of the Institute of Organic Chemistry and Organic Chemical Engineering of the Technische Hochschule Dresden. In 1934 he retired and became an emeritus professor. Roland Scholl died from the consequences of the air raids in a refugee camp near Dresden on August 22, 1945. As a young scientist, Scholl did some research in the field of fulminic acid and related compounds. Later he undertook fundamental investigations in the chemistry of aromatic compounds and cooperated with the *Badische Anilin- und Sodafabrik* in the field of dye chemistry. His name is connected with the coupling of aromatic compounds, known as the Scholl reaction, which made numerous polyaromatic compounds readily accessible. A highlight in his research was the synthesis of coronene by degradation of a dibenzocoronene in 1932. Scholl enjoyed a reputation as an excellent experimentalist, and some of his activity was devoted to microanalysis using a microbalance.

[3] “Dehydrogenation Condensation of Aromatics (Scholl and Related Reactions)”: A. T. Balaban, C. D. Nenitzescu, *Friedel–Crafts and Related Reactions*, *Vol. 2* (Ed.: G. Olah), Wiley, New York, **1964**, pp. 979–1047.

[4] R. J. Mullins, M. T. Corbett, *Name reactions for carbocyclic ring formations* (Ed.: J. J. Li), Wiley, New York, **2010**, pp. 409–422.

[5] F. W. Patureau, J. Wencel-Delord, F. Glorius, *Aldrichimica Acta* **2012**, *45*, 31–41.

[6] a) V. von Richter, *Ber. Dtsch. Chem. Ges.* **1873**, *6*, 1249–1260; b) A. P. Dianin, *Zh. Russ. Fiz.-Khim. O-va.* **1874**, 183.

[7] H. R. Barton, T. Cohen in *Festschrift Prof. Dr. Arthur Stoll zum siebzigsten Geburtstag, 8. Januar 1957*, Birkhäuser-Verlag, Basel, **1957**, p. 117.

[8] *Die methoden der Organische Chemie* (Ed.: J. Heuben), *Vol. II, 3rd ed.*, Georg Thieme, Leipzig, **1925**, p. 110, 781, 782.

[9] “Oxidation of phenols”: *The Chemistry of Phenols Chemistry of Functional Groups* (Ed.: Z. Rappoport), Wiley-Interscience, Chichester, **2003**, pp. 234–345.

[10] a) “Oxidative coupling of phenols and phenol ethers”: D. A. Whiting in *Comprehensive Organic Synthesis*, *Vol. 3.* (Eds.: B. M. Trost, I. Fleming, G. Pattenden), Pergamon, Oxford, **1991**, pp. 659–703; b) S. R. Waldvogel, D. Mirk, *Handbook of CH-Transformations*, *Vol. 1* (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**, pp. 251–261.

[11] A. Homer, *J. Chem. Soc.* **1910**, *97*, 1141–1154.

[12] R. Scholl, C. Seer, R. Weitzenbock, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2202–2209.

[13] R. Weitzenböck, C. Seer, *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 1994–2000.

[14] R. Scholl, C. Seer, *Monatsh. Chem.* **1912**, *33*, 1–8.

[15] R. Scholl, C. Seer, *Justus Liebigs Ann. Chem.* **1912**, *394*, 111–177.

[16] a) R. Scholl, H. Neumann, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 118–126; b) R. Scholl, G. Schwarzer, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 324–330.

[17] a) C. Seer, O. Dishendorfer, *Monatsh. Chem.* **1913**, *34*, 1493–1502; b) R. Scholl, O. Dischendorfer, *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 452–453.

[18] a) G. Kränzlein, H. Vollmann, Germ. Pat. 518,316 (Dec. 31, **1931**); *Chem. Zentr.*, II, 3267 (**1932**); b) G. Kränzlein, H. Vollmann, E. Diefenbach, Germ. Pat. 555,180, (July 19, **1932**); Chem. Zentral., II, 3267 (**1932**).

[19] a) Farbwerke Hoechst A. G. vorm. Meister Luciuc & Brauning, Germ. Pat. 262788 (Mar. 25, **1913**); Frdl. 11, 615 (**1915**); b) Du Pont de Nemours, E. I., & Co., Br. Pat. 439,296 (Jan. 2, **1936**); Chem. Zentr. **1936**, I, 3028.

[20] A. K. Wick, *Helv. Chim. Acta* **1971**, *54*, 769–782.

[21] a) G. M. Smith, J. F. Cullinan, U.S. Patent. 2,434,056 (Jan 6, **1948**; C. A. **1948**, *42*, 2113; b) Soc. For Chem. Ind. In Basle, Br. Pat. 585,798 (Feb. 25, **1947**); C. A. **1947**, *41*, 7128.

[22] F. Wiener, W. Mieg, U.S. Pat. 2212965 (Aug. 27, **1941**); C. A. 35, **1941**, 1240.

[23] H. Z. Lecher, M. Scalera, W. S. Forster, U.S. Patent, 2416931 (Mar. 4, **1947**); C. A. **1947**, *41*, 5151.

[24] M. Scalera, U. S. Patent 2,432,972 (Dec. 16, **1947**); C. A. **1948**, *42*, 2779.

[25] a) P. Kovacic, A. Kyriakis, *Tetrahedron Lett.* **1962**, 467; b) M. Müller, H. Mauermann-Düll, M. Wagner, V. Enkelmann, K. Müllen, *Angew. Chem.* **1995**, *107*, 1751–1754; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1583–1586; c) C. D. Simpson, J. D. Brand, A. J. Berresheim, L. Przybilla, H. J. Räder, K. Müllen, *Chem. Eur. J.* **2002**, *8*, 1424–1429.

[26] a) A. A. O. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730–2744; b) A. Pradhan, P. Dechambenoit, H. Bock, F. Durola, *J. Org. Chem.* **2013**, *78*, 2266–2274; c) M. Takase, T. Narita, W. Fujita, M. S. Asano, T. Nishinaga, H. Benten, K. Yoza, K. Müllen, *J. Am. Chem. Soc.* **2013**, *135*, 8031–8040.

[27] a) M. Danz, R. Tonner, G. Hilt, *Chem. Commun.* **2012**, *48*, 377–379; b) A. Pradhan, P. Dechambenoit, H. Bock, F. Durola, *Angew. Chem.* **2011**, *123*, 12790–12793; *Angew. Chem. Int. Ed.* **2011**, *50*, 12582–12585; c) D. Myśliwiec, B. Donnio, P. J. Chmielewski, B. Heinrich, M. Stępień, *J. Am. Chem. Soc.* **2012**, *134*, 4822–4833.

[28] a) G. Kränzlein, *Aluminiumchlorid in der organischen Chemie, 3rd ed.*, Chemie, Berlin, **1939**, p. 146; b) C. A. Thomas, *Anhydrous Aluminium Chloride in Organic Chemistry*, Reinhold, New York, **1941**, p. 648.

[29] a) G. Baddeley, J. Kenner, *J. Chem. Soc.* **1935**, 303–309; b) G. Baddeley, *J. Chem. Soc.* **1950**, 994–997.

[30] C. D. Nenitzescu, A. T. Balaban, *Chem. Ber.* **1958**, *91*, 2109–2116.

[31] J. Kenner, *J. Soc. Chem. Ind.* **1933**, *42*, 470.

[32] J. J. Rooney, R. C. Pink, *Proc. Chem. Soc.* **1961**, 142–143.

[33] G. A. Clover, *J. Chem. Soc. C* **1968**, 2519–2526.

[34] J. H. Simons, R. E. McArthur, *J. Ind. Eng. Chem.* **1947**, *39*, 364–367.

[35] J. M. Tinker, V. M. Weinmar, A. L. Linch, U.S. Pat. 2,258,394 (Oct. 7, **1942**): C. A. 36, 492, (**1942**).

[36] H. Vollmann, H. Becker, M. Corell, H. Streeck, *Justus Liebigs Ann. Chem.* **1937**, *531*, 1–159.

[37] R. Scholl, C. Seer, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 330.

[38] a) P. Rempala, J. Kroulik, B. T. King, *J. Am. Chem. Soc.* **2004**, *126*, 15002–15003; b) B. T. King, J. Kroulik, C. R. Robertson, P. Rempala, C. L. Hilton, J. D. Korinek, L. M. Gortari, *J. Org. Chem.* **2007**, *72*, 2279–2288; c) P. Rempala, J. Kroulik, B. T. King, *J. Org. Chem.* **2006**, *71*, 5067–5081.

[39] L. Zhai, R. Shukla, S. H. Wadumethrige, W. Rathore, *J. Org. Chem.* **2010**, *75*, 4748–4760.

[40] L. Zhai, R. Shukla, R. Rathore, *Org. Lett.* **2009**, *11*, 3474–3477.

[41] A. Zinke, R. Dengg, *Monatsh. Chem.* **1922**, *43*, 125–128.

[42] A. Zinke, K. J. von Schieszl, F. Hanus, *Monatsh. Chem.* **1936**, *67*, 196–202.

[43] A. Zinke, F. Hanselmayer, *Monatsh. Chem.* **1925**, *45*, 231–234.

[44] a) A. Corbellini, G. Aymar, *Giorn. Chim. Ind. Appl.* **1928**, *10*, 196; b) H. Pereira, Germ. Pat. 394,437 (Apr. 17, **1924**); Chem. Zentr. **1924**, II, 404; c) A. Zinke, Br. Pats. 165770 (Aug. 24, **1921**); *Chem. Zentr.* **1921**, *IV*, 1009.

[45] H. Pereira, Br. Pat. 191,363 (Feb. 28, **1923**); Chem. Zentr. **1924**, I, 1869.

[46] D. T. Gryko, J. Piechowska, M. Gałęzowski, *J. Org. Chem.* **2010**, *75*, 1297–1300.

[47] D. T. Gryko, E. Sebai, unpublished results.

[48] D. T. Gryko, K. Morawska, M. Tasior, unpublished results.

[49] a) R. Scholl, H. K. Meyer, *Chem. Ber.* **1934**, *67*, 1229–1235; b) R. Scholl, H. K. Meyer, J. Donat, *Chem. Ber.* **1937**, *70*, 2180–2189.

[50] E. Clar, C. T. Ironside, *Proc. Chem. Soc.* **1958**, 150–150.

[51] Y. Avlasevich, C. Kohl, K. Müllen, *J. Mater. Chem.* **2006**, *16*, 1053–1057.

[52] F. A. Vingiello, L. Ojakaar, *Tetrahedron* **1966**, *22*, 847–860.

[53] G. M. Badger, B. J. Christie, J. M. Pryke, W. H. F. Sasse, *J. Chem. Soc.* **1957**, 4417–4419.

[54] W. Mieg, R. Heidenreich, U.S. Pat. 1,749,955 (Mar. 11, 1930); Chem. Zentr., **1930**, II, 627.

[55] G. Pieters, A. Gaucher, D. Prim, T. Besson, J. G. Planas, F. Teixidor, C. Viñas, M. E. Light, M. B. Hursthouse, *Chem. Commun.* **2011**, *47*, 7725–7727.

[56] J. A. Ashenhurst, *Chem. Soc. Rev.* **2010**, *39*, 540–548.

[57] D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 6438–6461; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361.

[58] a) S. Schenker, A. Zamfir, M. Freund, S. B. Tsogoeva, *Eur. J. Org. Chem.* **2011**, 2209–2222; b) S. G. Telfer, R. Kuroda, *Coord. Chem. Rev.* **2003**, *242*, 33–46.

[59] A. McKillop, A. G. Turrell, D. W. Young, E. C. Taylor, *J. Am. Chem. Soc.* **1980**, *102*, 6504–6512.

[60] J. Doussot, A. Guy, C. Ferroud, *Tetrahedron Lett.* **2000**, *41*, 2545–2547.

[61] a) B. Feringa, H. Wynberg, *Bioorg. Chem.* **1978**, *7*, 397–408; b) J. Brussee, J. L. G. Groenendjik, J. M. te Koppele, A. C. A. Jansen, *Tetrahedron* **1985**, *41*, 3313–3319; c) M. Smrcina, M. Lorenc, V. Hanus, P. Sedmera, P. Kocovsky, *J. Org. Chem.* **1992**, *57*, 1917–1920; d) M. Smrcina, J. Polakova, S. Vyskocil, P. Kocovsky, *J. Org. Chem.* **1993**, *58*, 4534–4538.

[62] M. M. Schmitt, E. Schüler, M. Braun, D. Häring, P. Schreier, *Tetrahedron Lett.* **1998**, *39*, 2945–2946.

[63] a) T. Sakamoto, H. Yonehara, C. Pac, *J. Org. Chem.* **1997**, *62*, 3194–3199; b) M. Nakajima, I. Miyoshi, K. Kanayama, S. Hashimoto, *J. Org. Chem.* **1999**, *64*, 2264–2271.

[64] V. B. Sharma, S. L. Jain, B. Sain, *Tetrahedron Lett.* **2003**, *44*, 2655–2656.

[65] a) Y. Chen, S. Yekta, A. K. Yudin, *Chem. Rev.* **2003**, *103*, 3155–3211; b) G. Bringmann, A. J. P. Mortimer, P. A. Keller, M. J. Gresser, J. Garner, M. Breuning, *Angew. Chem.* **2005**, *117*, 5518–5563; *Angew. Chem. Int. Ed.* **2005**, *44*, 5384–5427; c) T. W. Wallace, *Org. Biomol. Chem.* **2006**, *4*, 3197–3210; d) M. C. Kozlowski, B. J. Morgan, E. C. Linton, *Chem. Soc. Rev.* **2009**, *38*, 3193–3207; e) S. Takizawa, *Chem. Pharm. Bull.* **2009**, *57*, 1179–1188; f) M. Diéguez, O. Pàmies, *Acc. Chem. Res.* **2010**, *43*, 312–322; g) M. Klussman, D. Sureshkumar, *Synthesis* **2011**, 353–369; and references cited therein.

[66] a) Y. S. Park, C. I. Grove, M. Gonzalez-Lopez, S. Urgaonkar, J. C. Fettinger, J. T. Shaw, *Angew. Chem.* **2011**, *123*, 3814–3817;

Angew. Chem. Int. Ed. **2011**, *50*, 3730–3733; b) C. I. Grove, J. C. Fettinger, J. T. Shaw, *Synthesis* **2012**, *44*, 362–371.

[67] a) Z. Xu, M. C. Kozlowski, *J. Org. Chem.* **2002**, *67*, 3072–3078; b) X. Li, J. Yang, M. C. Kozlowski, *Org. Lett.* **2001**, *3*, 1137–1140; c) X. Li, J. B. Hewgley, C. Mulrooney, J. Yang, M. C. Kozlowski, *J. Org. Chem.* **2003**, *68*, 5500–5511; d) C. A. Mulrooney, X. Li, E. S. DiVirgilio, M. C. Kozlowski, *J. Am. Chem. Soc.* **2003**, *125*, 6856–6857; e) M. C. Kozlowski, E. C. Dugan, E. S. DiVirgilio, K. Maksimenka, G. Bringmann, *Adv. Synth. Catal.* **2007**, *349*, 583–594; f) B. J. Morgan, X. Xie, P.-W. Phuan, M. C. Kozlowski, *J. Org. Chem.* **2007**, *72*, 6171–6182; g) J. B. Hewgley, S. S. Stahl, M. C. Kozlowski, *J. Am. Chem. Soc.* **2008**, *130*, 12232–12233; h) E. E. Podlesny, M. C. Kozlowski, *Org. Lett.* **2012**, *14*, 1408–1411.

[68] K. Wang, M. Lu, A. Yu, X. Zhu, Q. Wang, *J. Org. Chem.* **2009**, *74*, 935–938.

[69] a) K. Wang, Y. Hu, Z. Li, M. Wu, Z. Liu, B. Su, A. Yu, Y. Liu, Q. Wang, *Synthesis* **2010**, 1083–1090.

[70] X.-L. Li, J.-H. Huang, L.-M. Yang, *Org. Lett.* **2011**, *13*, 4950–4953.

[71] I. M. Matheson, O. C. Musgrave, C. J. Webster, *Chem. Commun.* **1965**, 279–279.

[72] F.-H. Marquardt, *J. Chem. Soc.* **1965**, 1517–1518.

[73] N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge, M. V. Jesudason, *Liq. Cryst.* **1993**, *15*, 851–858.

[74] H. Naarmann, M. Hanack, R. Mattmer, *Synthesis* **1994**, 477–478.

[75] G. Cooke, V. Sage, T. Richomme, *Synth. Commun.* **1999**, *29*, 1767–1771.

[76] S. Kumar, S. K. Varshney, *Liq. Cryst.* **1999**, *26*, 1841–1843.

[77] S. Kumar, M. Manickam, *Chem. Commun.* **1997**, 1615–1616.

[78] S. J. Mahoney, M. M. Ahmida, H. Kayal, N. Fox, Y. Shimizu, S. H. Eichhorn, *J. Mater. Chem.* **2009**, *19*, 9221–9232.

[79] W. Bai, J. Lin, *Synth. Commun.* **2011**, *41*, 903–906.

[80] S. Kumar, S. K. Varshney, *Synthesis* **2001**, 0305–0311.

[81] S. Kumar, B. Lakshmi, *Tetrahedron Lett.* **2005**, *46*, 2603–2605.

[82] a) N. Boden, R. J. Bushby, A. N. Cammidge, *J. Chem. Soc. Chem. Commun.* **1994**, 465–466; b) N. Boden, R. J. Bushby, A. N. Cammidge, G. Headdock, *Synthesis* **1995**, 31–32; c) N. Boden, R. J. Bushby, Z. Lu, G. Headdock, *Tetrahedron Lett.* **2000**, *41*, 10117–10120.

[83] a) S. R. Waldvogel, R. Fröhlich, C. A. Schalley, *Angew. Chem.* **2000**, *112*, 2580–2583; *Angew. Chem. Int. Ed.* **2000**, *39*, 2472–2475; b) S. R. Waldvogel, *Synlett* **2002**, 0622–0624.

[84] a) D. Mirk, B. Wibbeling, R. Fröhlich, S. R. Waldvogel, *Synlett* **2004**, 1970–1974; b) S. R. Waldvogel, S. Trosien, *Chem. Commun.* **2012**, *48*, 9109–9119; c) B. Kramer, R. Fröhlich, K. Bergander, S. R. Waldvogel, *Synthesis* **2003**, 91–96.

[85] a) B. Kramer, A. Averhoff, S. R. Waldvogel, *Eur. J. Org. Chem.* **2003**, 3549–3554; b) B. Kramer, S. R. Waldvogel, *Angew. Chem.* **2004**, *116*, 2501–2503; *Angew. Chem. Int. Ed.* **2004**, *43*, 2446–2449; c) S. R. Waldvogel, E. Aits, C. Holst, R. Fröhlich, *Chem. Commun.* **2002**, 1278–1279; d) K. Hackeloer, G. Schnakenburg, S. R. Waldvogel, *Org. Lett.* **2011**, *13*, 916–919; e) A. Spurg, G. Schnakenburg, S. R. Waldvogel, *Chem. Eur. J.* **2009**, *15*, 13313–13317; f) N. M. Boshta, M. Bomkamp, S. R. Waldvogel, *Tetrahedron* **2009**, *65*, 3773; g) B. Kramer, A. Averhoff, S. R. Waldvogel, *Angew. Chem.* **2002**, *114*, 3103–3104; *Angew. Chem. Int. Ed.* **2002**, *41*, 2981–2982.

[86] a) H. Tohma, H. Morioka, S. Takizawa, M. Arisawa, Y. Kita, *Tetrahedron* **2001**, *57*, 345–352; b) T. Dohi, A. Maruyama, M. Yoshimura, K. Morimoto, H. Tohma, Y. Kita, *Angew. Chem.* **2005**, *117*, 6349–6352; *Angew. Chem. Int. Ed.* **2005**, *44*, 6193–6196.

[87] D. Mirk, A. Willner, R. Fröhlich, S. R. Waldvogel, *Adv. Synth. Catal.* **2004**, *346*, 675–681.

[88] B. Su, L. Li, Y. Hu, Y. Liu, Q. Wang, *Adv. Synth. Catal.* **2012**, *354*, 383–387.

[89] a) V. Sterba, Z. Sagner, M. Matrka, *Coll. Czech. Chem. Commun.* **1965**, *30*, 2477; b) G. Galliani, B. Rindene, C. Scolastico, *Synth. Commun.* **1975**, *5*, 319–323.

[90] M. Periasamy, K. N. Jaykumar, P. Bharathi, *J. Org. Chem.* **2000**, *65*, 3548–3550.

[91] a) M. Kirchgessner, K. Sreenath, K. R. Gopidas, *J. Org. Chem.* **2006**, *71*, 9849–9852; b) Y. Jiang, C. Xi, X. Yang, *Synlett* **2005**, 1381–1384; c) T. Saitoh, S. Yoshida, J. Ichikawa, *J. Org. Chem.* **2006**, *71*, 6414–6419; d) C. Xi, Y. Jiang, X. Yang, *Tetrahedron Lett.* **2005**, *46*, 3909–3911; e) X. Yang, C. Xi, Y. Jiang, *Synth. Commun.* **2006**, *36*, 2413–2419; f) K. Sreenath, C. V. Suneesh, V. K. R. Kumar, K. R. Gopidas, *J. Org. Chem.* **2008**, *73*, 3245–3251.

[92] "Electrolytic oxidative coupling": H. J. Schäfer in *Organic Electrochemistry, 4th ed.* (Eds.: H. Lund, O. Hammerich), Marcel Dekker, New York, **2001**, pp. 883–967.

[93] V. D. Parker, *Acta Chem. Scand.* **1970**, *24*, 3171–3177.

[94] J. M. Bobbitt, I. Noguchi, H. Yagi, K. H. Weisgraber, *J. Org. Chem.* **1976**, *41*, 845–850.

[95] H. G. H. Erdtman, *Proc. R. Soc. London Ser. A* **1933**, *143*, 191–222.

[96] O. Hammerich, V. D. Parker, *Acta Chem. Scand. Ser. B* **1982**, *36*, 519–527.

[97] S. E. Korostova, A. I. Mikhaleva, B. A. Trofimov, *Russ. Chem. Rev.* **1999**, *68*, 459–482.

[98] a) R. J. Waltman, J. Bargon, *Can. J. Chem.* **1986**, *64*, 76–95; b) K. Gurunathan, A. V. Murugan, R. Marimuthu, U. P. Mulik, D. P. Amalnekar, *Mater. Chem. Phys.* **1999**, *61*, 173–191; c) A. K. Bakhshi, J. Ladik, M. Seel, *Phys. Rev. B* **1987**, *35*, 704–712; d) D. Kumar, R. C. Sharma, *Eur. Polym. J.* **1998**, *34*, 1053–1060.

[99] a) R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93–116; b) L.-X. Wang, X.-G. Li, Y.-L. Yang, *React. Funct. Polym.* **2001**, *47*, 125–139; c) M. J. González-Tejera, E. Sánchez de La Blanca, I. Carrillo, *Synth. Met.* **2008**, *158*, 165–189.

[100] F. Barbosa, L. Eberson, G. Gescheidt, S. Gronowitz, A. Hörnfeldt, L. Juliá, O. Persson, *Acta Chem. Scand.* **1998**, *52*, 1275–1284.

[101] J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1470 and references cited therein.

[102] H. Tohma, M. Iwata, T. Maegawa, Y. Kiyono, A. Maruyama, Y. Kita, *Org. Biomol. Chem.* **2003**, *1*, 1647–1649.

[103] a) T. Dohi, K. Morimoto, Y. Kiyono, A. Maruyama, H. Tohma, Y. Kita, *Chem. Commun.* **2005**, 2930–2932; b) T. Dohi, K. Morimoto, C. Ogawa, H. Fujioka, Y. Kita, *Chem. Pharm. Bull.* **2009**, *57*, 710–713; c) T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Tetrahedron* **2009**, *65*, 10797–10815; d) K. Morimoto, N. Yamaoka, C. Ogawa, T. Nakae, H. Fujioka, T. Dohi, Y. Kita, *Org. Lett.* **2010**, *12*, 3804–3807; e) K. Morimoto, T. Nakae, N. Yamaoka, T. Dahi, Y. Kita, *Eur. J. Org. Chem.* **2011**, 6326–6334.

[104] H. Falk, H. Flödl, *Monatsh. Chem.* **1988**, *119*, 247–252.

[105] T. Dohi, K. Morimoto, A. Maruyama, Y. Kita, *Org. Lett.* **2006**, *8*, 2007–2010.

[106] D. Seidel, V. Lynch, J. L. Sessler, *Angew. Chem.* **2002**, *114*, 1480–1483; *Angew. Chem. Int. Ed.* **2002**, *41*, 1422–1425.

[107] T. Köhler, D. Seidel, V. Lynch, F. O. Arp, Z. Ou, K. M. Kadish, J. L. Sessler, *J. Am. Chem. Soc.* **2003**, *125*, 6872–6873.

[108] M. Buda, A. Iordache, C. Bucher, J.-C. Moutet, G. Royal, E. Saint-Aman, J. L. Sessler, *Chem. Eur. J.* **2010**, *16*, 6810–6819.

[109] a) V. V. Roznyatovskiy, J. M. Lim, V. M. Lynch, B. S. Lee, D. Kim, J. Sessler, *Org. Lett.* **2011**, *13*, 5620–5623; b) T. Sarma, P. K. Panda, *Chem. Eur. J.* **2011**, *17*, 13987–13991.

[110] D. T. Gryko, M. Tasior, B. Koszarna, *J. Porphyrins Phthalocyanines* **2003**, *7*, 239–248.

[111] a) M. Takase, V. Enkelmann, D. Sebastiani, M. Baumgarten, K. Müllen, *Angew. Chem.* **2007**, *119*, 5620 – 5623; *Angew. Chem. Int. Ed.* **2007**, *46*, 5524 – 5527; b) B. Koszarna, D. T. Gryko, *Chem. Commun.* **2007**, 2994 – 2996.

[112] J. D. Debad, J. C. Morris, V. Lynch, P. Magnus, A. J. Bard, *J. Am. Chem. Soc.* **1996**, *118*, 2374 – 2379.

[113] M. Wehmeier, M. Wagner, K. Müllen, *Chem. Eur. J.* **2001**, *7*, 2197 – 2205.

[114] A. B. Nepomnyashchii, M. Bröring, J. Ahrens, A. J. Bard, *J. Am. Chem. Soc.* **2011**, *133*, 8633 – 8645.

[115] S. Rihn, M. Erdem, A. De Nicola, P. Retailleau, R. Ziessel, *Org. Lett.* **2011**, *13*, 1916 – 1919.

[116] A. B. Nepomnyashchii, M. Bröring, J. Ahrens, A. J. Bard, *J. Am. Chem. Soc.* **2011**, *133*, 19498 – 19504.

[117] A. Poirel, A. De Nicola, P. Retailleau, R. Ziessel, *J. Org. Chem.* **2012**, *77*, 7512 – 7525.

[118] a) M. Kamo, A. Tsuda, Y. Nakamura, N. Aratani, K. Furukawa, T. Kato, A. Osuka, *Org. Lett.* **2003**, *5*, 2079 – 2082; b) L.-M. Jin, L. Chen, J.-J. Yin, C.-C. Guo, Q.-Y. Chen, *Eur. J. Org. Chem.* **2005**, 3994 – 4001; c) A. K. Sahoo, Y. Nakamura, N. Aratani, K. S. Kim, S. B. Noh, H. Shinokubo, D. Kim, A. Osuka, *Org. Lett.* **2006**, *8*, 4141 – 4144; d) Q. Ouyang, Y.-Z. Zhu, C.-H. Zhang, K.-Q. Yan, Y.-C. Li, J.-Y. Zheng, *Org. Lett.* **2009**, *11*, 5266 – 5269.

[119] a) J. P. Lewtak, D. T. Gryko, *Chem. Commun.* **2012**, *48*, 10069 – 10086 and references cited herein; b) A. M. V. M. Pereira, S. Richeter, C. Jeandon, J.-P. Gisselbrecht, J. Wytko, R. Ruppert, *J. Porphyrins Phthalocyanines* **2012**, *16*, 464 – 478; c) "Single-molecule photophysical properties of various directly linked porphyrin arrays": D. Kim, A. Osuka, *Multiporphyrin arrays* (Ed.: D. Kim), Pan Stanford, Singapore, **2012**, pp. 1 – 54.

[120] Q. Quyang, K.-Q. Yan, Y.-Z. Zhu, C.-H. Zhang, J.-Z. Liu, C. Chen, J.-Y. Zheng, *Org. Lett.* **2012**, *14*, 2746 – 2749.

[121] P. Kovacic, M. B. Jones, *Chem. Rev.* **1987**, *87*, 357 – 379.

[122] a) M. Hovorka, J. Günterová, J. Závada, *Tetrahedron Lett.* **1990**, *31*, 413 – 416; b) M. Smrcina, S. Vyskocil, B. Máca, M. Polásek, T. A. Claxon, A. P. Abbott, P. Kocovsky, *J. Org. Chem.* **1994**, *59*, 2156 – 2163.

[123] a) T. Temma, S. Habaue, *Tetrahedron Lett.* **2005**, *46*, 5655 – 5657; b) S. Habaue, Y. Takahashi, T. Tomma, *Tetrahedron Lett.* **2007**, *48*, 7301 – 7304.

[124] A. Jean, J. Cantan, D. Bérard, D. Bouchu, S. Canesi, *Org. Lett.* **2007**, *9*, 2553 – 2556.

[125] a) T. Dohi, M. Ito, K. Morimoto, M. Iwata, Y. Kita, *Angew. Chem.* **2008**, *120*, 1321 – 1324; *Angew. Chem. Int. Ed.* **2008**, *47*, 1301 – 1304; b) E. Faggi, R. M. Sebasyián, R. Pleixats, A. Vallribera, A. Shafir, A. Rodríguez-Gimeno, C. R. de Arellano, *J. Am. Chem. Soc.* **2010**, *132*, 17980 – 17982.

[126] a) A. Kirste, G. Schnakenburg, F. Stecker, A. Fischer, S. R. Waldvogel, *Angew. Chem.* **2010**, *122*, 983 – 987; *Angew. Chem. Int. Ed.* **2010**, *49*, 971 – 975; b) A. Kirste, B. Elser, G. Schnakenburg, F. Stecker, S. R. Waldvogel, *J. Am. Chem. Soc.* **2012**, *134*, 3571 – 3576; c) A. Kirste, G. Schnakenburg, F. Stecker, S. R. Waldvogel, *Org. Lett.* **2011**, *13*, 3126 – 3129; d) T. Morofuji, A. Shimizu, J. Yoshida, *Angew. Chem.* **2012**, *124*, 7371 – 7374; *Angew. Chem. Int. Ed.* **2012**, *51*, 7259 – 7262; e) K. Nyberg, *Acta Chem. Scand.* **1973**, *27*, 503 – 509.

[127] T. Dohi, M. Ito, I. Itani, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Org. Lett.* **2011**, *13*, 6208 – 6211.

[128] Y. Gu, D. Wang, *Tetrahedron Lett.* **2010**, *51*, 2004 – 2006.

[129] T. Dohi, M. Ito, K. Morimoto, Y. Minamitsuji, N. Takenaga, Y. Kita, *Chem. Commun.* **2007**, 4152 – 4154.

[130] Y. Kita, K. Morimoto, M. ito, C. Ogawa, A. Goto, T. Dohi, *J. Am. Chem. Soc.* **2008**, *130*, 1668 – 1669.

[131] R. Samanta, J. Lategahn, A. P. Antonchick, *Chem. Commun.* **2012**, *48*, 3194 – 3196.

[132] M. Chandrasekharam, B. Chiranjeevi, K. S. V. Gupta, B. Sidhar, *J. Org. Chem.* **2011**, *76*, 10229 – 10235.

[133] A. M. Akondi, R. Trivedi, B. Sreedhar, M. L. Kantam, S. Bhargava, *Catal. Today* **2012**, *198*, 35 – 44.

[134] A. Ronlán, V. D. Parker, *J. Chem. Soc. D* **1970**, 1567 – 1568.

[135] L. J. Kricka, A. Ledwith, *J. Chem. Soc. Perkin Trans. 1* **1973**, 294 – 297.

[136] I. Moreno, I. Tellitu, R. SanMartin, E. Dominguez, *Synlett* **2001**, 1161 – 1163.

[137] I. Isabel, I. Tellitu, E. Dominguez, R. SanMartin, *Eur. J. Org. Chem.* **2002**, *13*, 2126 – 2135.

[138] a) Y. Kita, T. Takada, M. Gyoten, H. Tohma, M. H. Zenk, J. Eichhorn, *J. Org. Chem.* **1996**, *61*, 5857 – 5864; b) Y. Kita, M. Gyoten, M. Ohtsubo, H. Tohma, T. Takada, *Chem. Commun.* **1996**, 1481 – 1482; c) T. Takada, M. Arisawa, H. Gyoten, R. Hamada, H. Tohma, Y. Kita, *J. Org. Chem.* **1998**, *63*, 7698 – 7706; d) Y. Kita, T. Dohi, K. Morimoto, *J. Synth. Org. Chem. Jpn.* **2011**, *69*, 1241 – 1250.

[139] a) L. Yet, *Chem. Rev.* **2000**, *100*, 2963 – 3008; b) G. A. Molander, *Acc. Chem. Res.* **1998**, *31*, 603; c) G. Illuminati, L. Mandolini, *Acc. Chem. Res.* **1981**, *14*, 95 – 102.

[140] T. Takada, M. Ibaraki, M. Gyoten, S. Mihara, S. Fujita, H. Tohma, Y. Kita, *J. Org. Chem.* **1996**, *61*, 223 – 227.

[141] T. Dohi, Y. Minamitsuji, A. Maruyama, S. Hirose, Y. Kita, *Org. Lett.* **2008**, *10*, 3559 – 3562.

[142] a) B. Mohr, V. Enkelmann, G. Wegner, *J. Org. Chem.* **1994**, *59*, 635 – 638; b) S. Trosien, S. R. Waldvogel, *Org. Lett.* **2012**, *14*, 2976 – 2979.

[143] a) D. L. Comins, L. A. Morgan, *Tetrahedron Lett.* **1991**, *32*, 5919 – 5922; b) D. L. Comins, X. Chen, L. A. Morgan, *J. Org. Chem.* **1997**, *62*, 7435 – 7438.

[144] R. B. Herbert, A. E. Kattah, A. J. Murtagh, P. W. Sheldrake, *Tetrahedron Lett.* **1995**, *36*, 5649 – 5650.

[145] D. Planchenault, R. Dhal, J.-P. Robin, *Tetrahedron* **1993**, *49*, 5823 – 5830.

[146] D. Planchenault, R. Dhal, J.-P. Robin, *Tetrahedron* **1995**, *51*, 1395 – 1404.

[147] T.-A. Chen, R.-S. Liu, *Chem. Eur. J.* **2011**, *17*, 8023 – 8027.

[148] L. Dössel, L. Gherghel, X. Feng, K. Müllen, *Angew. Chem.* **2011**, *123*, 2588 – 2591; *Angew. Chem. Int. Ed.* **2011**, *50*, 2540 – 2543.

[149] M. Danz, G. Hilt, *Adv. Synth. Catal.* **2011**, *353*, 303 – 308.

[150] E. Clar, C. T. Ironside, M. Zander, *J. Chem. Soc.* **1959**, 142 – 147.

[151] J. A. Hyatt, *Org. Prep. Proced. Int.* **1991**, *23*, 460 – 463.

[152] A. Stabel, P. Herwig, K. Müllen, J. P. Rabe, *Angew. Chem.* **1995**, *107*, 1768 – 1770; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1609 – 1611.

[153] M. Müller, C. Kübel, K. Müllen, *Chem. Eur. J.* **1998**, *4*, 2099 – 2109.

[154] A. Halleux, R. H. Martin, G. S. D. King, *Helv. Chim. Acta* **1958**, *41*, 1177 – 1183.

[155] L. T. Bratz, S. Niementowski, *Chem. Ber.* **1919**, *52*, 189.

[156] C. Kübel, K. Eckhardt, V. Enkelmann, G. Wegner, K. Müllen, *J. Mater. Chem.* **2000**, *10*, 879 – 886.

[157] S. Ito, M. Wehmeier, J. D. Brand, C. Kübel, R. Epsch, J. P. Rabe, K. Müllen, *Chem. Eur. J.* **2000**, *6*, 4327 – 4342.

[158] J. Luo, X. Xu, R. Mao, Q. Miao, *J. Am. Chem. Soc.* **2012**, *134*, 13796 – 13803.

[159] E. U. Mughall, D. Kuck, *Chem. Commun.* **2012**, *48*, 8880 – 8882.

[160] a) D. J. Jones, B. Purushothaman, S. Ji, A. B. Holmes, W. W. H. Wang, *Chem. Commun.* **2012**, *48*, 8066 – 8068; b) X. Dou, X. Yang, G. J. Bodwell, M. Wagner, V. Enkelmann, K. Müllen, *Org. Lett.* **2007**, *9*, 2485 – 2488; c) S. H. Wadumethrige, R. Rathore, *Org. Lett.* **2008**, *10*, 5139 – 5142.

[161] S. Pola, C.-H. Kuo, W.-T. Peng, M. M. Islam, I. Chao, Y.-T. Tao, *Chem. Mater.* **2012**, *24*, 2566 – 2571.

[162] C. Dou, K. Matsuo, I. Hisaki, S. Yamaguchi, S. Saito, *Angew. Chem.* **2012**, *124*, 12372–12376; *Angew. Chem. Int. Ed.* **2012**, *51*, 12206–12210.

[163] a) D. J. Gregg, E. Bothe, P. Hofer, P. Passaniti, S. M. Draper, *Inorg. Chem.* **2005**, *44*, 5654–5660; b) S. M. Draper, D. J. Gregg, R. Madathil, *J. Am. Chem. Soc.* **2002**, *124*, 3486–3487.

[164] R. Olivera, R. SanMartin, S. Pascual, M. Herrero, E. Dominguez, *Tetrahedron Lett.* **1999**, *40*, 3479–3480.

[165] I. Moreno, I. Tellitu, J. Etayo, R. SanMartin, E. Dominguez, *Tetrahedron* **2001**, *57*, 5403–5411.

[166] K. A. Sullivan, M. M. Faul, *Tetrahedron Lett.* **2001**, *42*, 3271–3273.

[167] Y. Chai, E.-Q. Yang, Y.-L. Zhang, A.-L. Xie, X.-P. Cao, *Synthesis* **2012**, *44*, 439–445.

[168] Y. Hayashi, N. Obata, M. Tamaru, S. Yamaguchi, Y. Matsuo, A. Saeki, S. Seki, Y. Kureishi, S. Saito, S. Yamaguchi, H. Shinokubo, *Org. Lett.* **2012**, *14*, 866–869.

[169] L. Zeng, C. Jiao, X. Huang, K.-W. Huang, W.-S. Chin, J. Wu, *Org. Lett.* **2011**, *13*, 6026–6029.

[170] a) N. K. S. Davis, M. Pawlicki, H. L. Anderson, *Org. Lett.* **2008**, *10*, 3945–3947; b) N. K. S. Davis, M. Pawlicki, H. L. Anderson, *Org. Lett.* **2010**, *12*, 2124–2127; c) N. K. S. Davis, M. Pawlicki, H. L. Anderson, *J. Am. Chem. Soc.* **2011**, *133*, 30–31.

[171] a) D. L. Hughes, A. N. Cammidge, P. J. Scaife, *Org. Lett.* **2005**, *7*, 3413–3416; b) J. P. Lewtak, D. Gryko, D. Bao, E. Sebai, O. Vakuliuk, M. Ścigaj, D. T. Gryko, *Org. Biomol. Chem.* **2011**, *9*, 8178–8181.

[172] O. Yamane, K. Sugiura, H. Miyasaka, K. Nakamura, T. Fujimoto, T. Kaneda, Y. Sakata, M. Yamashita, *Chem. Lett.* **2004**, *33*, 40–41.

[173] C. Jiao, K. W. Huang, Z. Guan, Q.-H. Xu, J. Wu, *Org. Lett.* **2010**, *12*, 4046–4049.

[174] C. Jiao, L. Zhu, J. Wu, *Chem. Eur. J.* **2011**, *17*, 6610–6614.

[175] J. J. Brown, S. L. Cockroft, *Chem. Sci.* **2013**, *4*, 1772–1780.