

Diazatriphenylenes and their thiophene analogues: synthesis and applications

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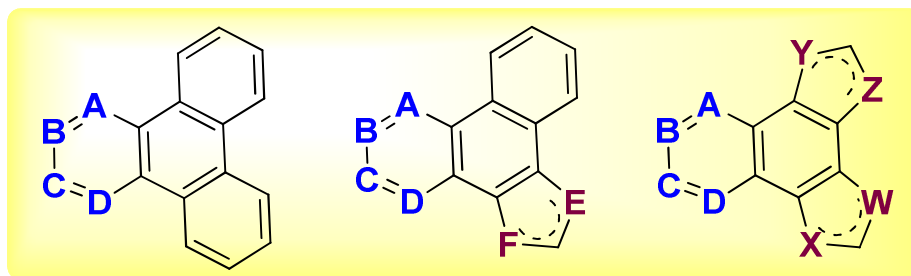
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Abstract

This review highlights the recent advances in the field of the synthesis of diazatriphenylenes and their structural analogues, such as phenanthrenes, fused with the thiophene ring, and naphthalenes, condensed with two thiophene rings. Also applications of these compounds are considered.



A = B = N, C = D = CH; E = S, F = CH; W = Z = S, X = Y = CH;
 C = D = N, A = B = CH; F = S, E = CH. X = Y = S, W = Z = CH;
 B = C = N, A = D = CH; W = Y = S, X = Z = CH;
 A = C = N, B = D = CH; X = Z = S, W = Y = CH.
 A = D = N, B = C = CH.

Keywords: Pyridazines; pyrimidines; pyrazines; triphenylenes; phenanthreno[9,10-*b*]thiophene; diazanaphthalenes

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1. Introduction

Over the last two decades polycyclic aromatic hydrocarbons (PAHs) have gained a growing attention of chemists due to their unique electronic and optoelectronic properties, which can find applications in organic electronics.¹⁻¹⁹ In this series triphenylenes²⁰⁻³⁷ and their thiophene analogues (*viz.* phenanthro[9,10-*b*]-thiophenes,³⁸⁻⁴² naphtho[1,2-*b*:4,3-*b'*]dithiophenes,^{26,43,44} naphtho[2,1-*b*:3,4-*b'*]dithiophenes^{42,44,45-49} and naphtho[1,2-*b*:3,4-*b'*]dithiophenes⁵⁰) (Figure 1) are of particular interest, because these compounds proved to have a great potential for use in supramolecular chemistry and material science. A rapid growth of publications in this promising field, concerning both synthetic aspects and properties of PAHs is well documented in the literature. Indeed, 4843 references concerning triphenylenes are available in SciFinder database for the 1st of May, 2017).

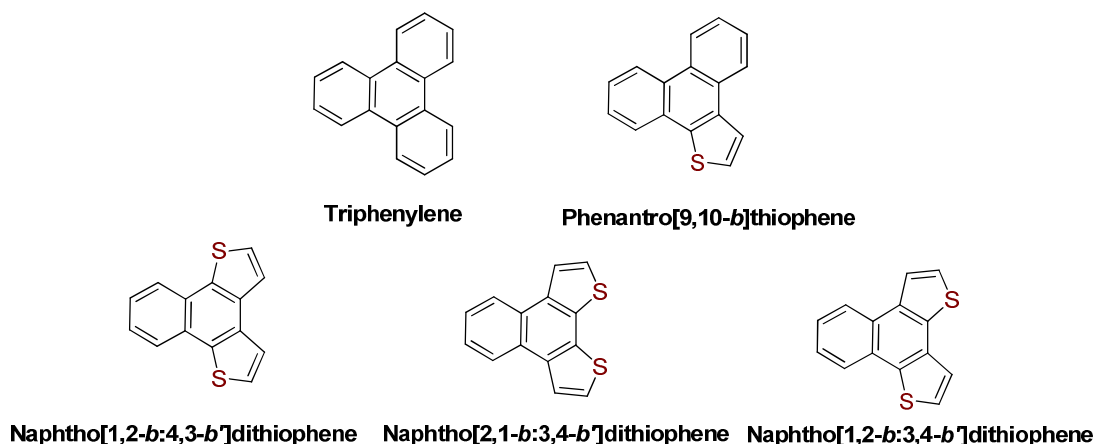


Figure 1. Structures of triphenylene, phenanthro[9,10-*b*]thiophene, naphthodithiophenes.

A first-rate review on the chemistry of the above mentioned heteroaromatic systems, focusing on their synthesis, electronic properties, and applications in materials science, has recently been published.⁵¹ However, no reviews dealing with the chemistry and applications of triphenylenes, phenanthro[9,10-*b*]thiophenes and naphthodithiophenes, bearing pyridazine (**I-XVII**; Section 2 of this review), pyrimidine (**XVIII-XXVI**; Section 3) or pyrazine rings (**XXVII-XXXII**; Section 4) have so far been published.

2. Synthesis of 1,2- and 2,3-Diazatriphenylenes and Related Thiophene-containing Systems

There are theoretically 17 tetracyclic diazatriphenylene structures (I-XVII), bearing two neighboring aza-groups (see Figure 2), however only dibenzo[*f,h*]cinnoline (I) and dibenzo[*f,h*]phthalazine (II) derivatives have so far been described in the literature.^{52,53} Both compounds are considered to be promising materials and ligands for using as dopants in organic light emitting diodes.^{52,53}

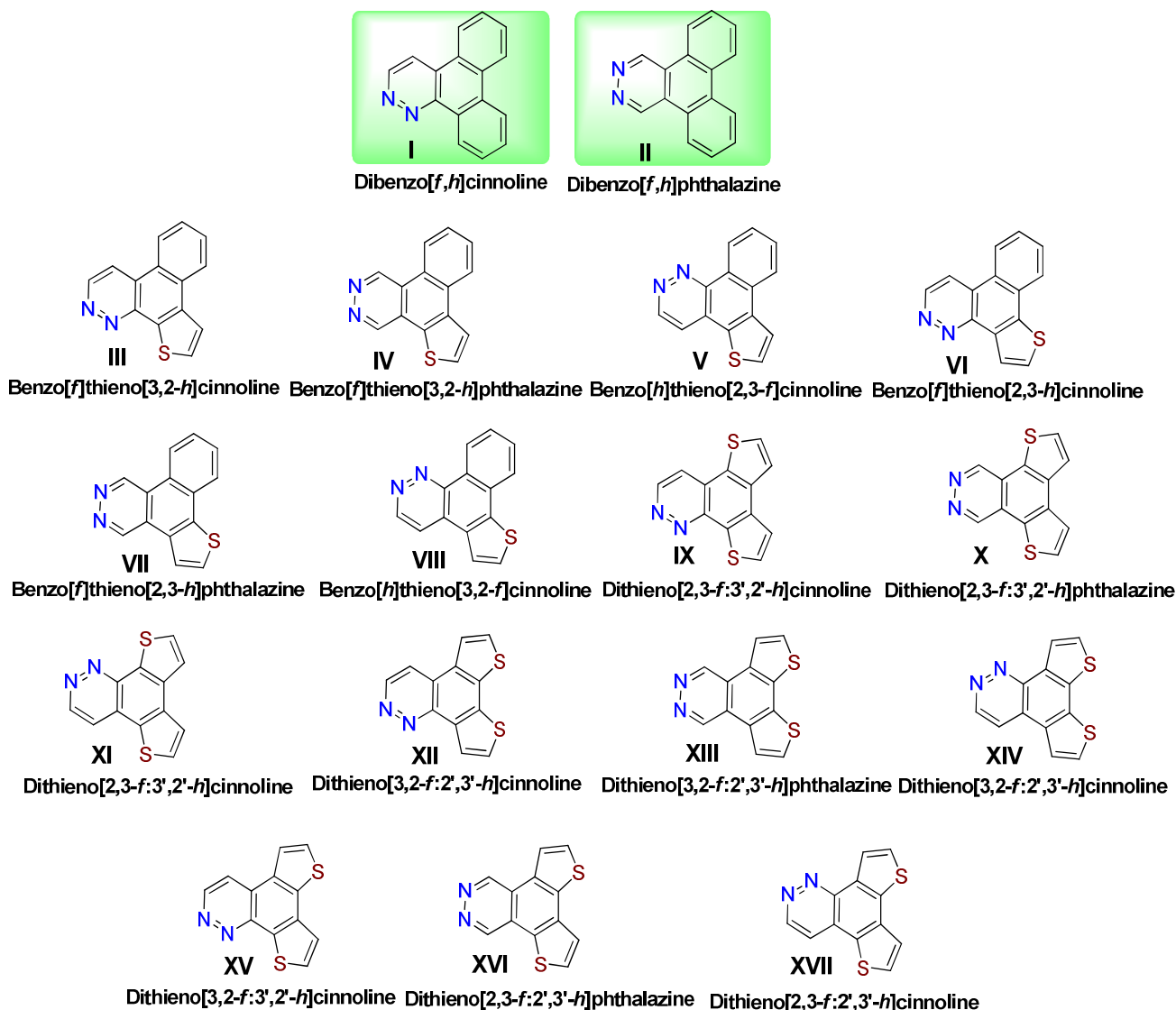
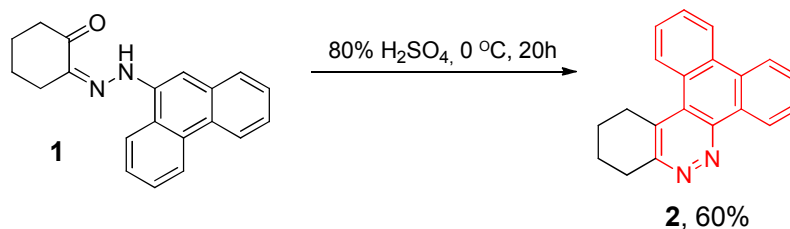


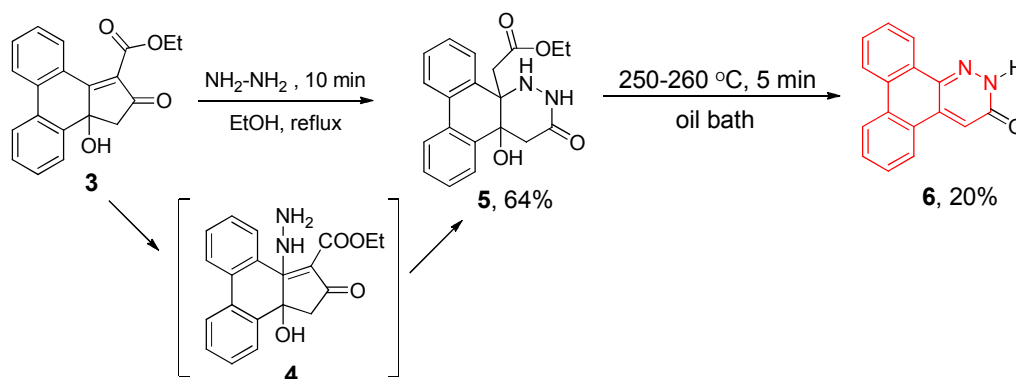
Figure 2. Structures of possible tetracyclic diazatriphenylenes and related thiophene-containing systems bearing the pyridazine ring.

A simple protocol for the synthesis of unsymmetrical cinnoline polycyclic systems has been developed through sulfuric acid promoted intramolecular cyclizations of 1-arylhydrazones derived from cyclohexan-1,2-dione and 4-methyl cyclohexane-1,2-dione.⁵⁴ In particular, 7,8,9,10-tetrahydrotribenzo[*c,f,h*]cinnoline (**2**) was prepared by cyclization of 2-[2-(phenanthren-9-yl)hydrazone]cyclohexanone (**1**) in 80% H₂SO₄ at 0 °C (Scheme 1).



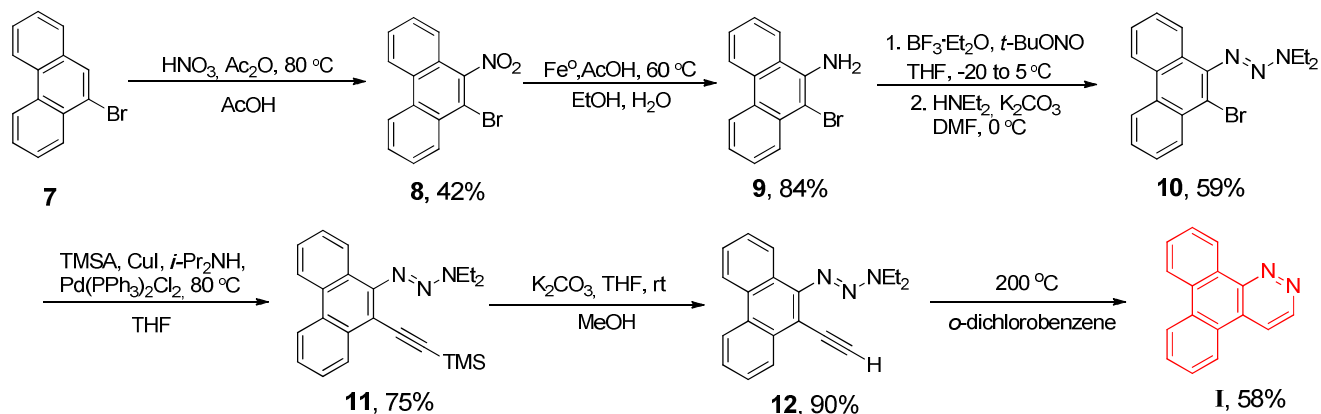
Scheme 1. Synthesis of the dibenzo[*f,h*]cinnoline ring system (**1**) through intramolecular cyclization of cyclohexane-1,2-dione 1-arylhyazone.

Another approach to the dibenzo[*f,h*]cinnoline ring system (**1**) was suggested by Cort *et al.*⁵⁵ The reaction of ethyl 3a-hydroxy-2-oxo-3,3a-dihydro-2*H*-cyclopenta[*l*]phenanthrene-1-carboxylate (**3**) with hydrazine proceeded *via* rearrangement of the intermediate (**4**), leading to ethyl 4a-hydroxy-3-oxo-2,3,4,4a-tetrahydro-1*H*-1,2-diazatriphenylen-12*b*-yl)acetate (**5**). The thermal degradation of compound (**5**) on melting at *ca.* 250 °C (oil bath) resulted in the formation of dibenzo[*f,h*]cinnoline-3(2*H*)-one (**6**) in 20% yield (Scheme 2).



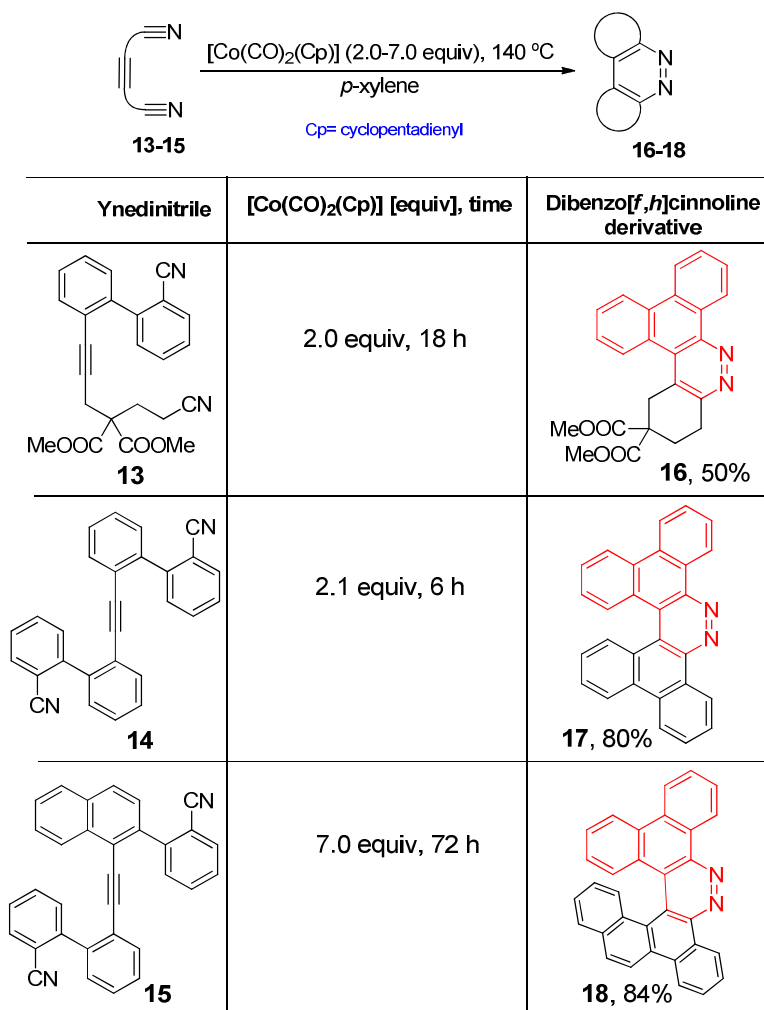
Scheme 2. Synthesis of dibenzo[*f,h*]cinnoline (**6**) from cyclopenta[*l*]phenanthrene (**3**).

A similar route to the parent dibenzo[*f,h*]cinnoline (**1**) through thermolysis of triazene (**12**) in 58% yield (Scheme 3) has been demonstrated by Young *et al.*⁵⁶ The starting triazene (**12**) was obtained, as shown in Scheme 3. Nitration of commercially available 9-bromophenanthrene (**7**) afforded **8**, which was subsequently reduced with iron powder in the presence of acetic acid to give bromoaniline (**9**). Diazotization of **9** with BF₃·Et₂O and *t*-BuONO followed by quenching with HNEt₂ furnished the formation of triazene (**10**). The Sonogashira cross-coupling reaction of **10** with trimethylsilylacetylene (TMSA) afforded the protected acetylene compound **11**, which was then transformed into give the desired terminal acetylene **12** in 14% overall yield, taking into account all five steps (Scheme 3).



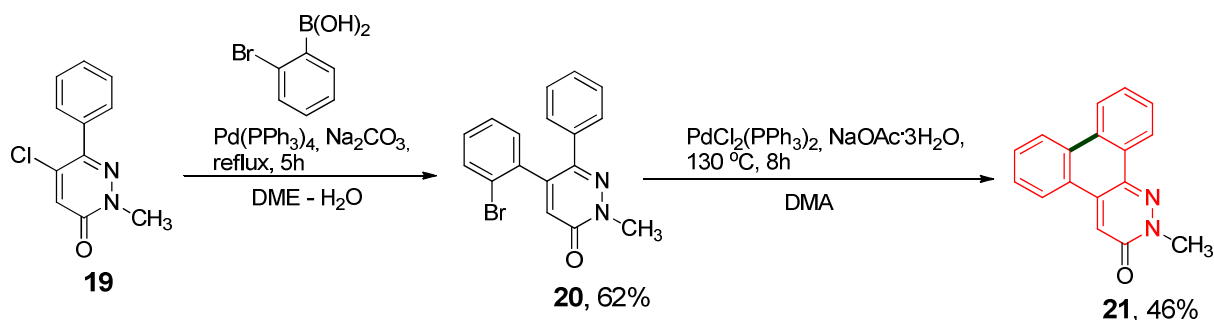
Scheme 3. Synthesis of the parent dibenzo[*f,h*]cinnoline (I).

Cobalt-mediated [2+2+2] cycloisomerisation of ynedinitriles **13-15**, developed by Chercheja *et al*,⁵⁷ appears to be a novel, facile, and straight forward synthesis of dibenzo[*f,h*]cinnolines **16-18** (Scheme 4).



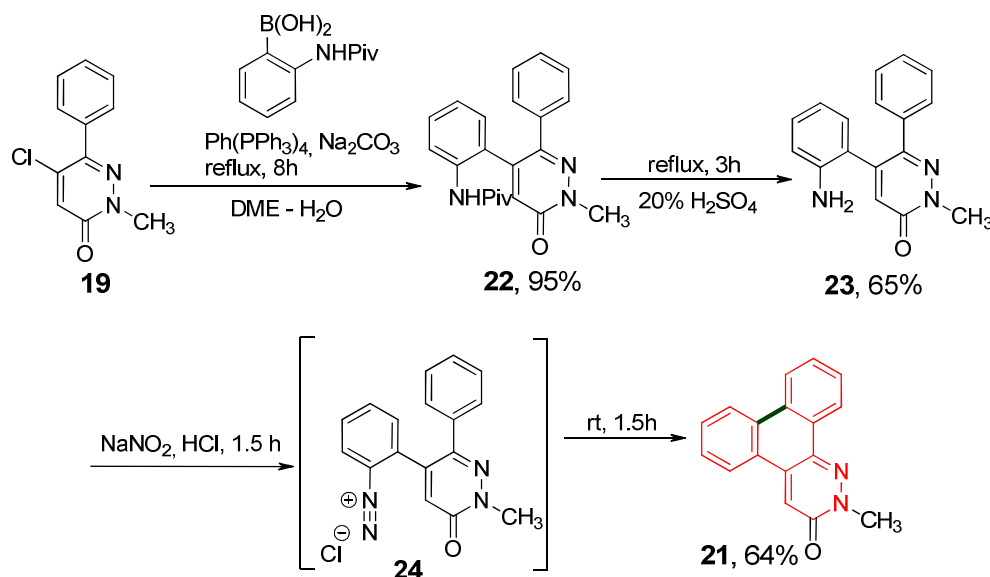
Scheme 4. Cobalt-mediated [2+2+2] cycloisomerisation of ynedinitriles **13-15** into dibenzo[*f,h*]cinnoline derivatives **16-18**.

The formation of 2-methyldibenzo[*f,h*]cinnolin-3(2*H*)-one (**21**) via the palladium-catalyzed intramolecular arylation of 2-methyl-5-(2-bromophenyl)-6-phenylpyridazin-3(2*H*)-one (**20**) was investigated by Tapolcsányi *et al.*⁵⁸ (Scheme 5)



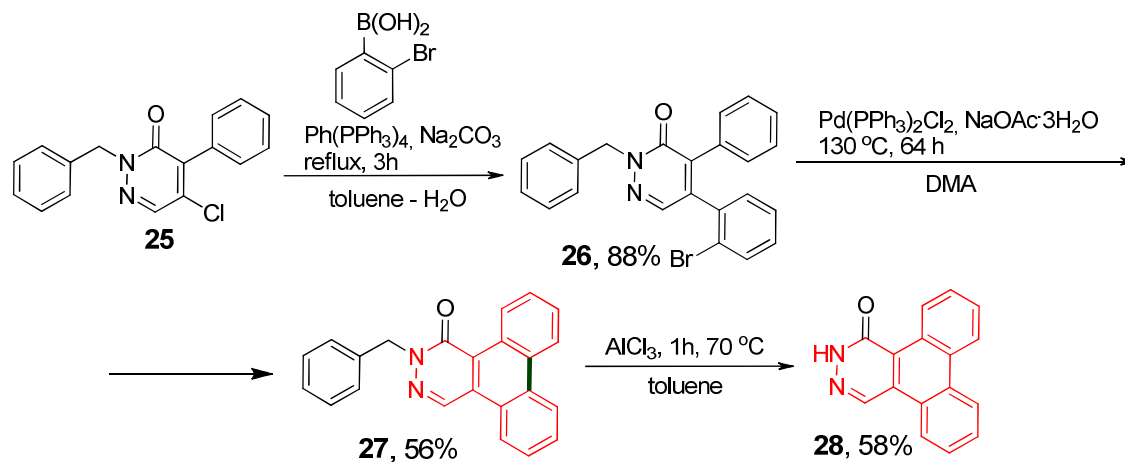
Scheme 5. Synthesis of dibenzo[*f,h*]cinnolinone (**21**) via palladium-catalyzed intramolecular arylation.

The moderate yields of the target product **21** obtained for the palladium-catalyzed cyclodehydrobromination of **20** prompted the same group to seek alternative pathways to 1,2-diaza-analogues of triphenylene. They proposed an alternative approach to 2-methyldibenzo[*f,h*]cinnolin-3(2*H*)-one (**21**), providing a higher yield of the latter compound *via* the Pschorr type ring closure reaction, caused by decomposition of the intermediate diazonium salt (**24**) (Scheme 6).⁵⁸



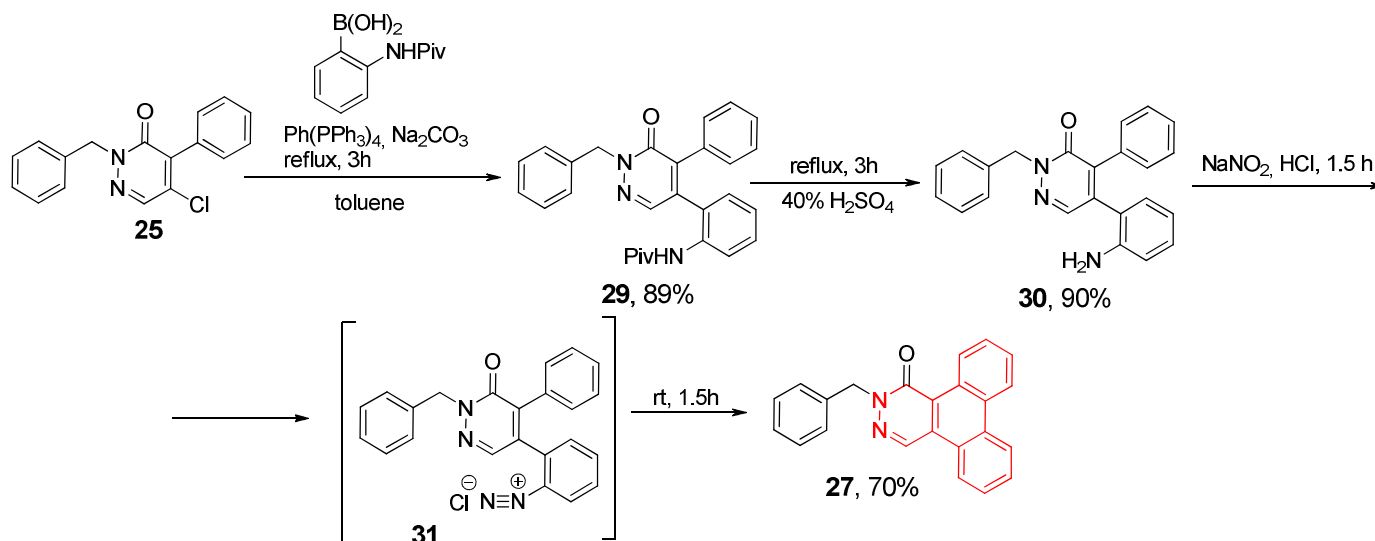
Scheme 6. Synthesis of dibenzo[*f,h*]cinnoline (**21**) via the Pschorr type ring closure reaction.

Cyclodehydrohalogenation of 2-benzyl-5-(2-bromophenyl)-4-phenylpyridazin-3(2*H*)-one (**26**) has been carried out under similar reaction conditions, as used for the synthesis of **21** (Scheme 7).⁵⁸ In this case, only 56% of 2-benzyl-5-(2-bromophenyl)-4-phenylpyridazin-3(2*H*)-one (**27**) was obtained after 64 hours, while 10% of the starting material (**26**) was recovered. Deprotection of **27** with AlCl_3 has been established to proceed smoothly, thus giving unsubstituted dibenzo[*f,h*]phthalazin-1(2*H*)-one (**28**) in good yield.



Scheme 7. Synthesis of dibenzo[*f,h*]phthalazine (**28**) (structural type II) via the palladium-catalyzed intramolecular arylation.

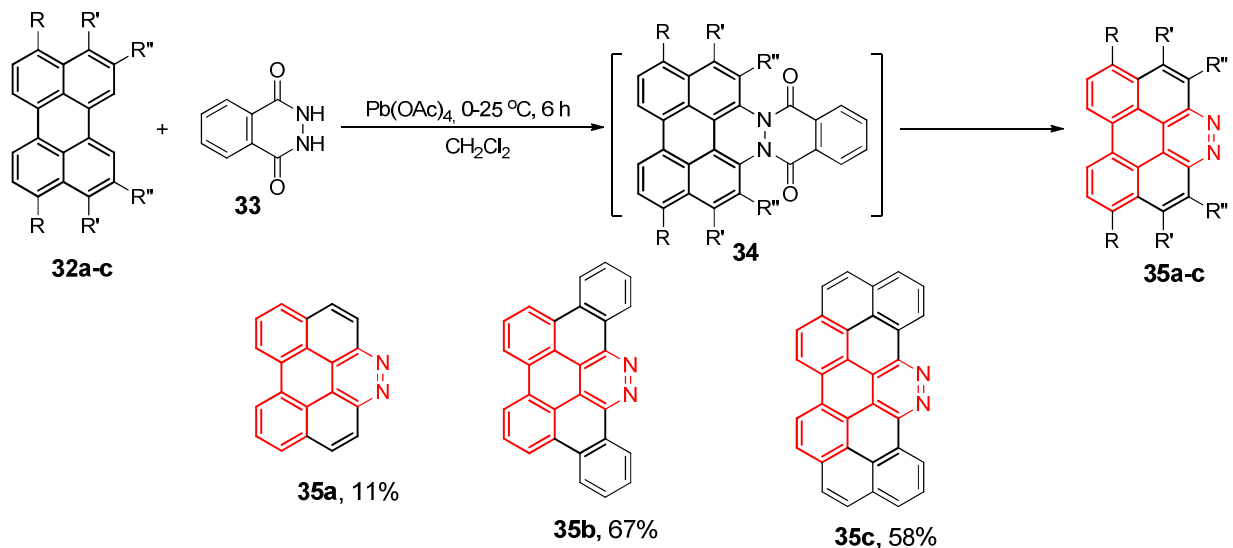
Analogously, 2-benzyl-dibenzo[*f,h*]phthalazin-1(2*H*)-one (**27**) was prepared from 5-(2-aminophenyl)-2-benzyl-4-phenylpyridazin-3(2*H*)-one (**30**) via the Pschorr type ring closure, caused by decomposition of the corresponding diazonium salt (**31**) at room temperature (Scheme 8).



Scheme 8. Synthesis of dibenzo[*f,h*]phthalazine (**27**) (structural type II) via the Pschorr type ring closure.

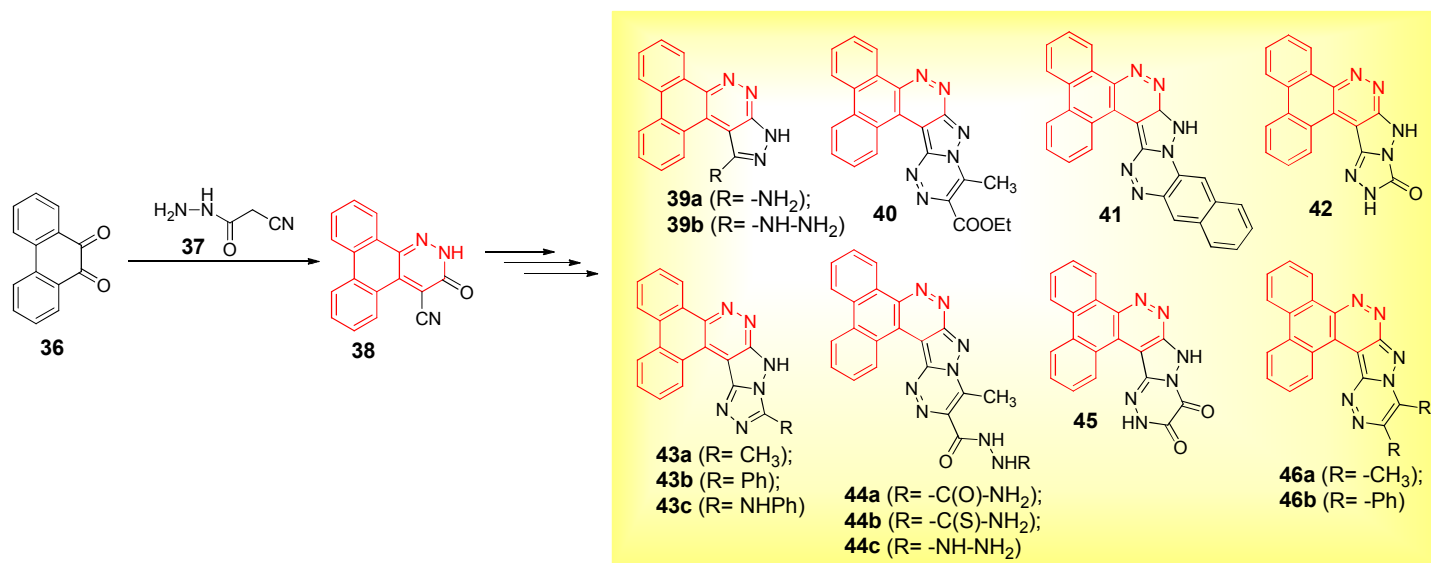
In fact, the diazotization / Pschorr type ring closure of **30** is certainly a superior method for the preparation of **27**, affording the target product in 70% yield (56% overall yield from **25**) within 3 hours of the reaction time. It should be compared with 56% yield of the same product (49% overall yield from **25**) reached for 64 hours of the intramolecular Pd-catalyzed arylation.

The intermolecular Diels-Alder reaction is a more traditional method for the formation of dibenzo[*f,h*]phthalazine (II) skeleton. In particular, the reaction of perylenes (**32a-c**) with an excess of 2,3-dihydrophthalazin-1,4-dione (**33**) in CH_2Cl_2 in the presence of lead (IV) acetate (taken in an amount which is equimolecular to **33**) at $0-25^\circ\text{C}$ affords benzo[4,10]anthra[1,9,8-*cdef*]cinnolines **35a-c** in 11-67% yields (Scheme 9).⁵⁹



Scheme 9. Synthesis of dibenzo[*f,h*]phthalazines **35a-c** (structural type II) via the intermolecular Diels-Alder reaction.

Classic carbanion chemistry has been exploited for the preparation of dibenzo[*f,h*]cinnoline derivatives: a base-promoted condensation of 2-cyanoacetohydrazide (**37**) with 9,10-phenanthrenequinone (**36**) has resulted in the formation of 3-oxo-2,3-dihydro-1,2-diazatriphenylene-4-carbonitrile (**38**) (Scheme 10).⁶⁰ It is noteworthy that compound **36** has been used as the starting material for the synthesis of a wide range of biologically active azolo-annulated dibenzo[*f,h*]cinnolines **39-46**, exhibiting anti-inflammatory, analgesic, antimicrobial and anticancer activities (Scheme 10).^{60,61}



Scheme 10. Examples of biologically active compounds in the series of dibenzo[*f,h*]cinnolines (I).

3. Synthesis of Tetracyclic Systems, Analogues of 1,3-Diazatriphenylenes

There are 9 tetracyclic structures (**XVIII-XXVI**) bearing 1,3-diazine fragments (see Figure 3). However, only four types of derivatives, viz. dibenzo[*f,h*]quinazolines (**XVIII**), benzo[*f*]thieno[3,2-*h*]quinazolines (**XIX**), dithieno[2,3-

f:3',2'-*h*]quinazolines (**XXIII**) and dithieno[3,2-*f*:3',2'-*h*]quinazolines (**XXVI**) have so far been described in the literature. Dibenzo[*f,h*]quinazolines (**XVIII**) have been considered as the basic structures for phosphorescent or electroluminescent host and/or hole transport materials to be used in organic electroluminescent devices.^{53,62-82}

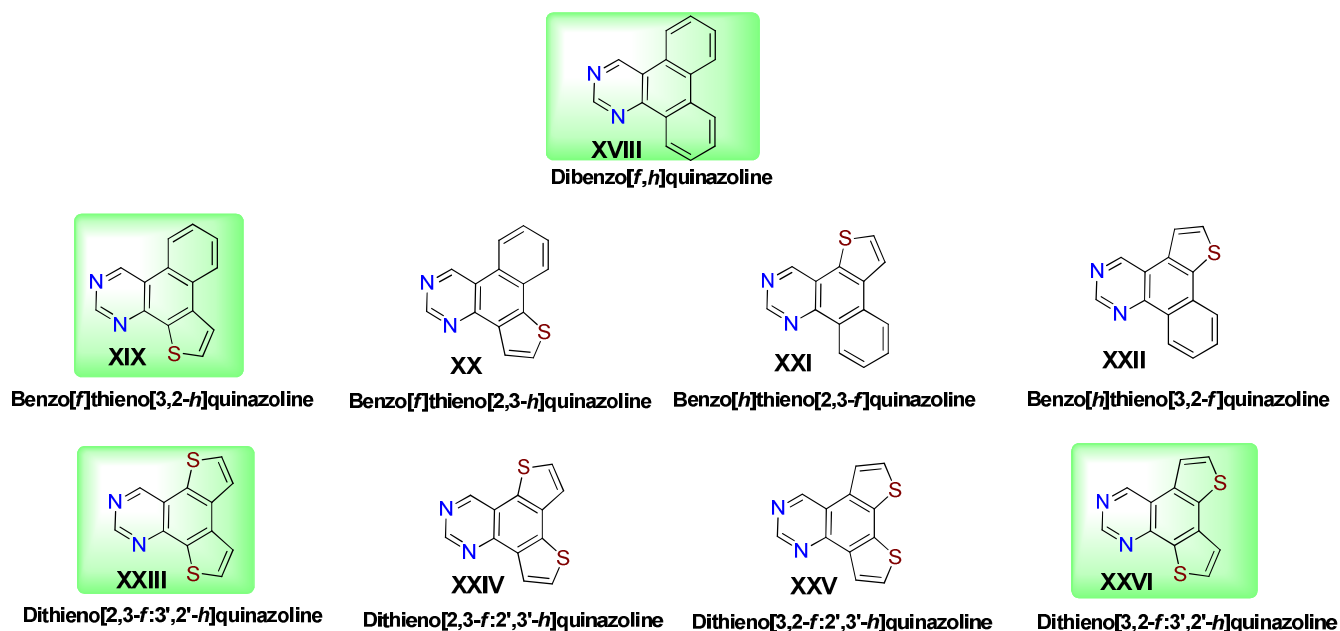
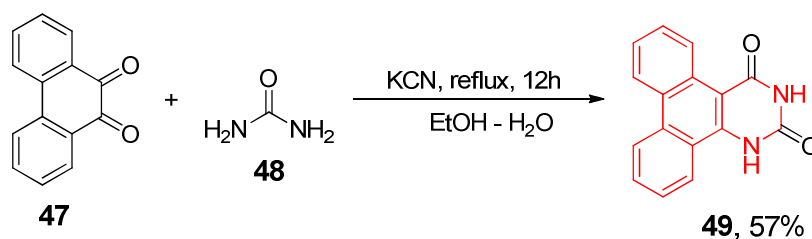


Figure 3. Structures of possible tetracyclic systems, as analogues of 1,3-diazatriphenylene.

Although many synthetic approaches are exploited to obtain dibenzo[*f,h*]quinazolines (**XVIII**), most of the practically important syntheses can be classified into two types. The first type syntheses of **XVIII** are based on closure of the 1,3-diazine ring, while the second type of the syntheses of **XVIII** involves construction of the triphenylene framework on the basis of the 1,3-diazine scaffold.

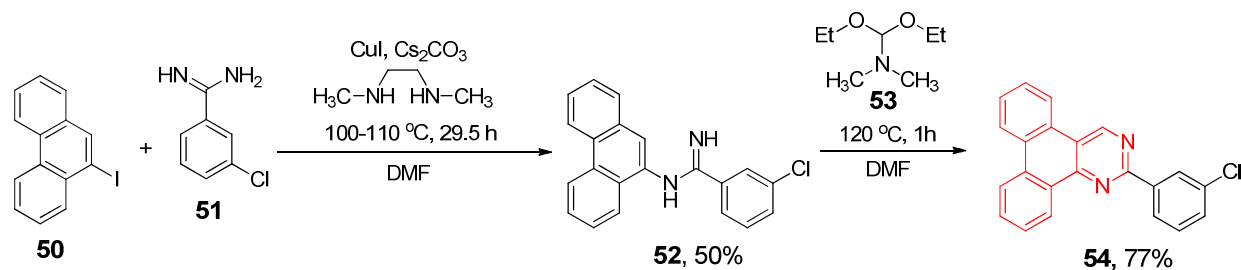
Various cyclocondensations are related with the first type of the synthesis of dibenzo[*f,h*]quinazolines (**XVIII**). Thus, Mahmoodi *et al.*⁸³ have demonstrated a simple cyclocondensation of phenanthren-9,10-dione (**47**) with urea (**48**), proceeding in an alkaline ethanol solution, and affording dibenzo[*f,h*]quinazolin-2,4(1*H*,3*H*)-dione (**49**) in good yield (Scheme 11).



Scheme 11. Synthesis of dibenzo[*f,h*]quinazolin-2,4(1*H*,3*H*)-dione (**49**) through the cyclocondensation of phenanthren-9,10-dione (**47**) with urea (**48**).

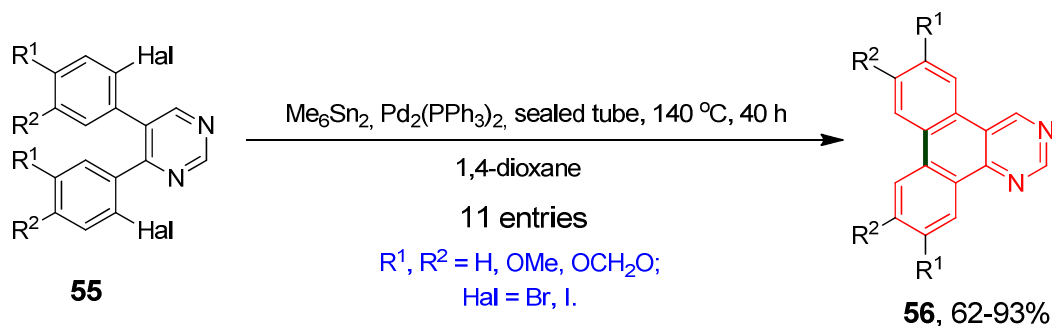
Another two-step pathway to dibenzo[*f,h*]quinazoline (**XVIII**) skeleton has been proposed by Hara *et al.*⁷⁸ At the first step, 9-iodophenanthrene (**50**) reacts with 3-chlorobenzamidine hydrochloride (**51**) at 100-110 °C in dimethylformamide in the presence of CuI, Cs₂CO₃ and *N,N'*-dimethylethylenediamine to afford *N*-

(phenanthren-9-yl)-3-chlorobenzamidine (**52**). At the final step, the compound **52** reacts with an excess of diethyl acetal (**53**) in DMF at 120 °C for 1 hour to give 2-(3-chlorophenyl)dibenzo[*f,h*]quinazoline (**54**) in 39% overall yield (Scheme 12).



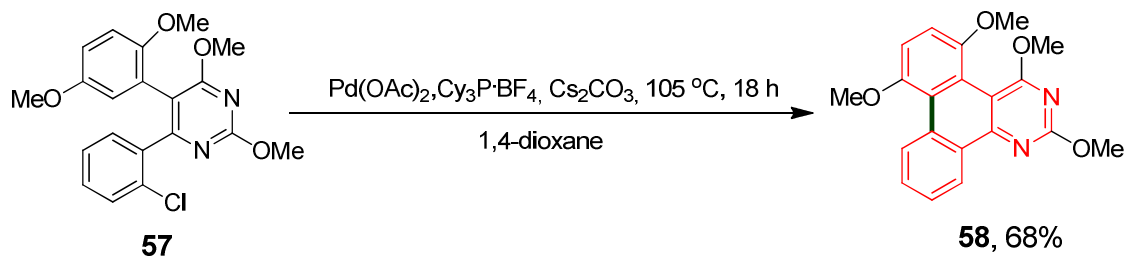
Scheme 12. Synthesis of dibenzo[*f,h*]quinazoline (**XVIII**) skeleton via condensation of *N*-(phenanthren-9-yl)-3-chlorobenzamidine (**52**) with diethyl acetal (**53**).

The second principal pathway to obtain dibenzo[*f,h*]quinazolines (**XVIII**) involves the assembly of polyaromatic framework on the basis of the pyrimidine scaffold, and this approach is well-documented in literature. In particular, Olivera *et al.*^{84,85} have demonstrated a straightforward synthetic approach to 6,7,10,11-tetrasubstituted dibenzo[*f,h*]quinazolines (**56**) via the intramolecular Stille-Kelly stannylation / coupling of *o,o'*-dihalogenated 4,5-diarylpyrimidines (**55**) (Scheme 13).



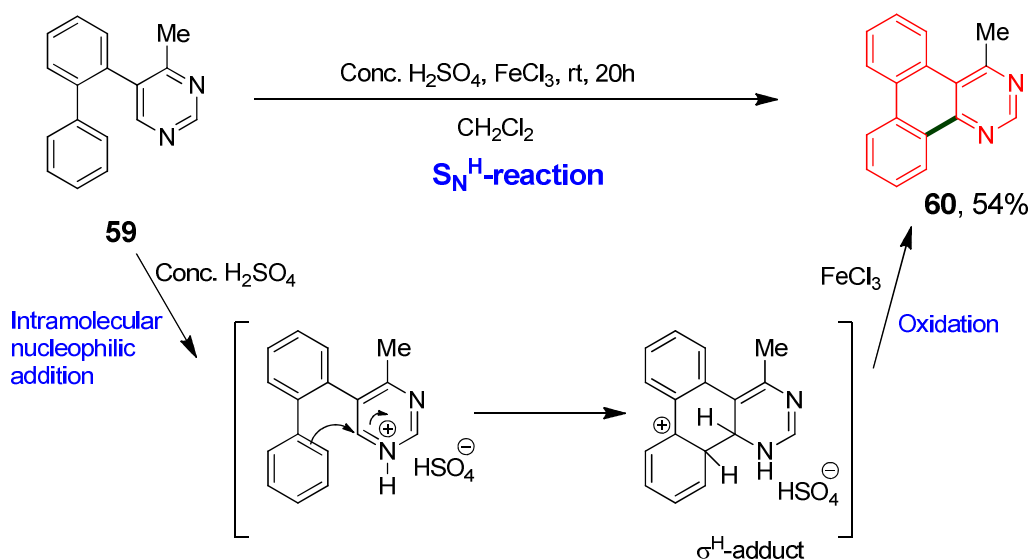
Scheme 13. Synthesis of dibenzo[*f,h*]quinazolines (**56**) via the intramolecular Stille-Kelly stannylation / coupling of *o,o'*-dihalogenated 4,5-diarylpyrimidines.

2,4,5,8-Tetramethoxydibenzo[*f,h*]quinazoline (**58**) has been prepared in 68% yield through the intramolecular C-H arylation of the corresponding chloride **57** in the presence of palladium(II) acetate and tri(cyclohexyl)phosphine, as an effective transition-metal catalyst, and cesium carbonate, as a base (Scheme 14).⁸⁶



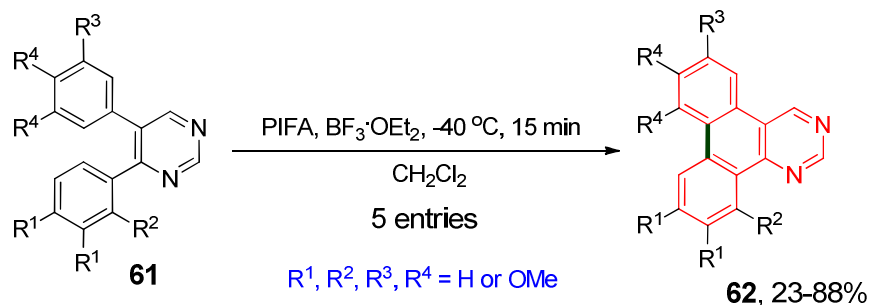
Scheme 14. Synthesis of the dibenzo[*f,h*]quinazoline (**XVIII**) skeleton via the Pd-catalyzed intramolecular C-H arylation of *o*-chloro substituted 4,5-diphenylpyrimidine (**57**).

Intramolecular version of nucleophilic aromatic substitution of hydrogen (the S_N^H reaction) has been used to synthesize dibenzo[*f,h*]quinazoline derivative (**60**) from 5-([1,1'-biphenyl]-2-yl) substituted pyrimidine (**59**), by using concentrated sulfuric acid as a catalyst and iron(III) chloride, as an oxidant (Scheme 15).⁷⁹ For a better understanding of the S_N^H reactions, see the recently published review⁸⁷ and references cited therein.



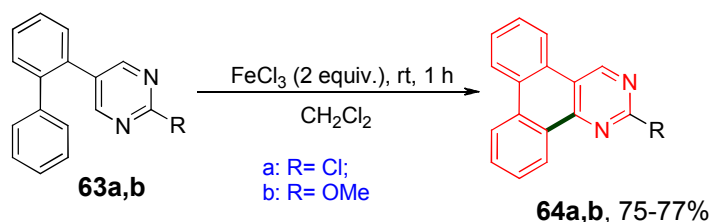
Scheme 15. Synthesis of dibenzo[*f,h*]quinazoline (**XVIII**) skeleton from 5-(1,1'-biphenyl-2-yl) substituted pyrimidine (**59**) via intramolecular S_N^H reaction.

Also oxidative cyclodehydrogenation (the Scholl reaction) appears to be a versatile tool for the construction of 1,3-diaza-analogues of triphenylenes. It requires a Lewis acid and oxidant, and is supposed to proceed through either the radical-cation (electron transfer) or arenium cation (proton transfer) intermediates.^{88,89} A variety of oxidants, including Fe(III), I(III), Tl(III), Ru(IV) and V(V), and their effects on the oxidative cyclodehydrogenation reaction, have been elucidated.⁸⁵ In particular, Olivera *et al.*^{85,90} have observed that phenyliodine(III) bis(trifluoroacetate) (PIFA) is the most suitable oxidant for the intramolecular reaction of non-halogenated 4,5-diarylpyrimidines (**61**) into the corresponding methoxy substituted dibenzo[*f,h*]quinazolines (**62**) in 23-88% yields (Scheme 16).

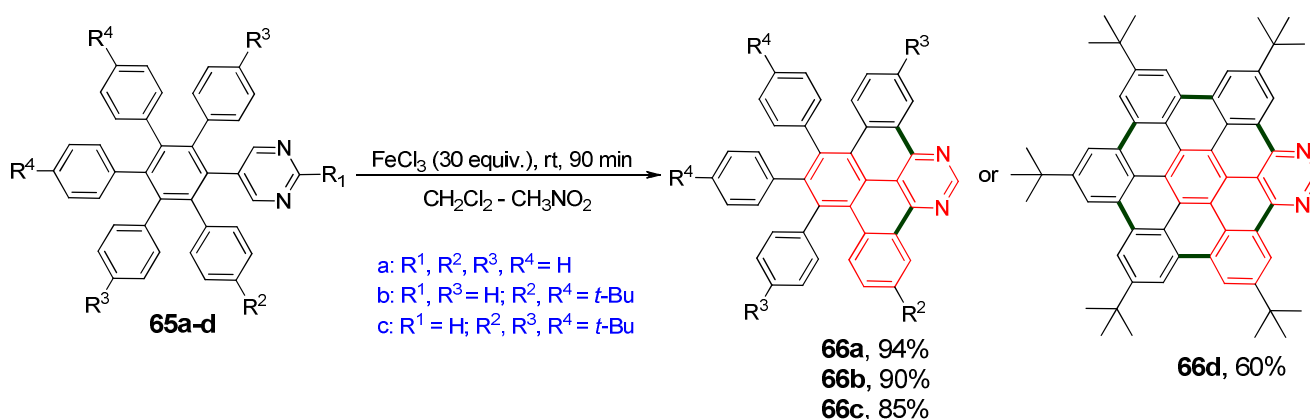


Scheme 16. Synthesis of substituted dibenzo[*f,h*]quinazolines (**62**) via the oxidative cyclodehydrogenation of 4,5-diphenylpyrimidines (**61**).

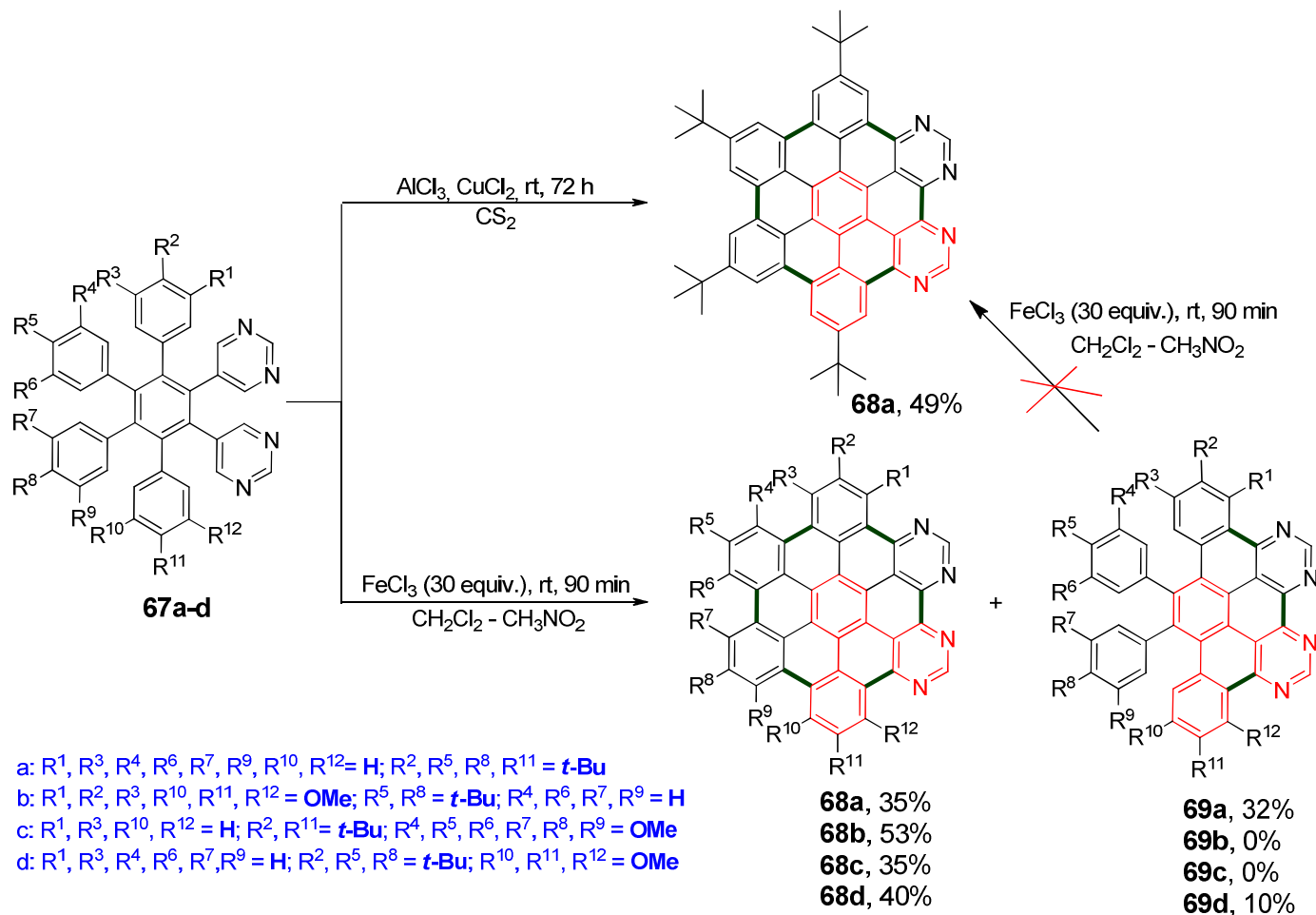
On the contrary, iron(III) chloride proved to be an appropriate oxidant for the intramolecular oxidative cyclodehydrogenation of 5-(1,1'-biphenyl-2-yl) substituted pyrimidines (**63**) and compounds (**65** and **67**), bearing a similar structural motif, to prepare 2-substituted dibenzo[*f,h*]quinazolines⁵² (**64**) (Scheme 17), as well as nitrogen-doped nanographenes⁹¹⁻⁹⁵ (**66**, **68** and **69**) (Schemes 18 and 19). It is remarkable that, whereas the Scholl cyclodehydrogenation of 1,2-dipyrimidyl-3,4,5,6-tetra(4-*t*-butylphenyl)benzene (**67**) by action of $\text{AlCl}_3/\text{CuCl}_2$ in CS_2 results in the formation of heterosuperbenzene **68a**, while use of a milder catalytic system ($\text{FeCl}_3/\text{nitromethane}/\text{dichloromethane}$) affords a mixture of **68a** (35%) and of "half-cyclized" **69a** (32%).^{92,94} It has been found that neither treatment of **69a** with FeCl_3 , nor use of $\text{AlCl}_3/\text{CuCl}_2$, results in the formation of **68a**, thus indicating that the partially cyclodehydrogenated compound **69** is apparently not an intermediate in the formation of heterosuperbenzene **68** in this reaction.



Scheme 17. Synthesis of substituted dibenzo[*f,h*]quinazolines (**64a,b**) from 5-([1,1'-biphenyl]-2-yl)-substituted pyrimidines (**63**) via the intramolecular oxidative cyclodehydrogenation.



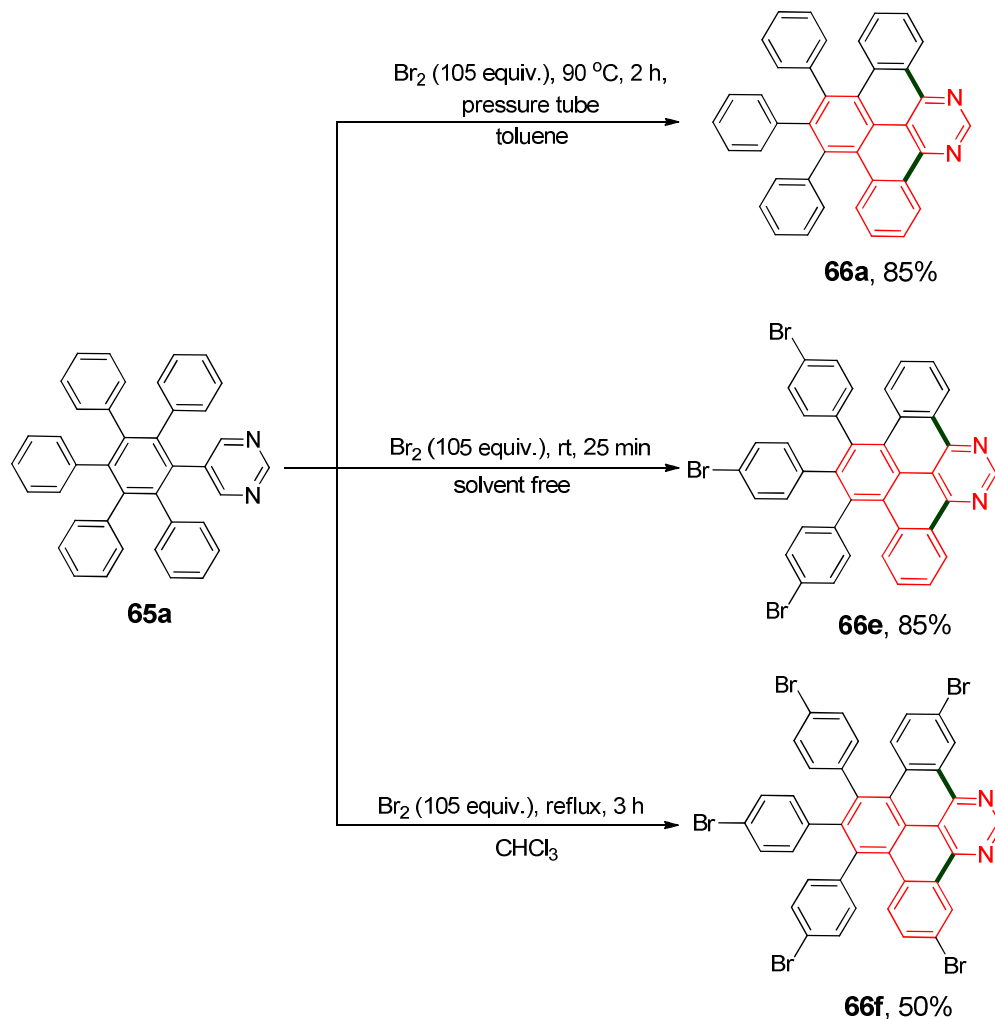
Scheme 18. Synthesis of heterosuperbenzenes **66** from pyrimidyl substituted pentaphenylbenzenes **65** via Scholl cyclodehydrogenation.



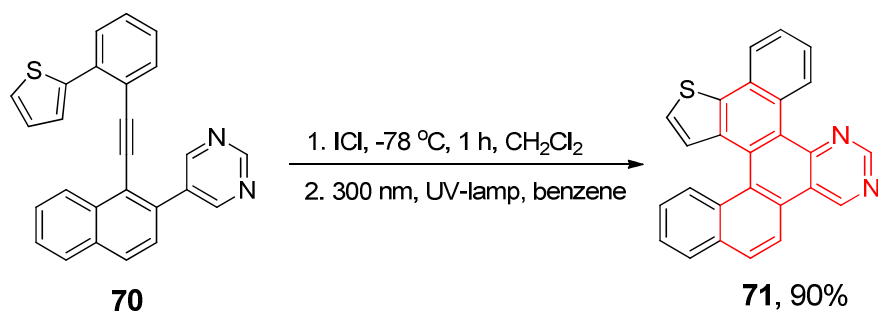
Scheme 19. Synthesis of heterosuperbenzenes (**68** and **69**) from 1,2-dipyrimidyl-3,4,5,6-tetraarylbzenes **67** via Scholl cyclodehydrogenation.

Also, Draper *et al.*⁹⁶ have demonstrated that use of elemental bromine in the reaction with diazopolyphenylenes results in the intramolecular bond formation with the pyrimidine ring, and the reaction is accompanied by bromination of the phenyl substituents to give products **66a,e,f**, which can be controlled by the reaction conditions (Scheme 20).

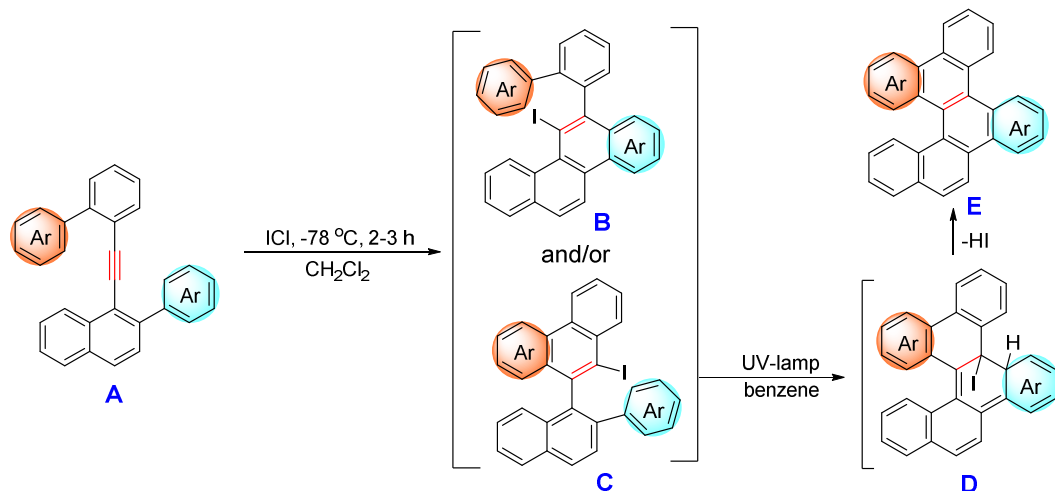
Recently, Mohamed *et al.*⁹⁷ have proposed a novel versatile method for the synthesis of fused functionalized helicenes, affording, for instance, naphtho[2,1-*f*]thieno[3',2':3,4]naphtho[2,1-*h*]quinazoline (**71**) in a high yield (Scheme 21). The first core ring of the helicene (**E**) is assembled by treatment of bis(biaryl)-acetylene (**A**) with 1.1 equiv of ICl in dichloromethane at -78 °C for 1 hour. The iodonium-induced carbocyclization affords either substituted 6-aryl-5-iodochrysene (**B**), or 9-iodo-10-arylphenanthrene (**C**), or a mixture of both. A convenience of this convergent synthetic strategy is that the subsequent photochemical cyclodehydroiodination step is supposed to convert both structural isomers (**C** or **B**) into the same final helical product (**E**), as shown in Scheme 22.



Scheme 20. Synthesis of 8,9,10-triphenyltribenzo[*e,gh,j*]perimidines **66a,e,f** from pyrimidyl substituted pentaphenylbenzene **65a** via intramolecular oxidative cyclodehydrogenation by action of elemental bromine.

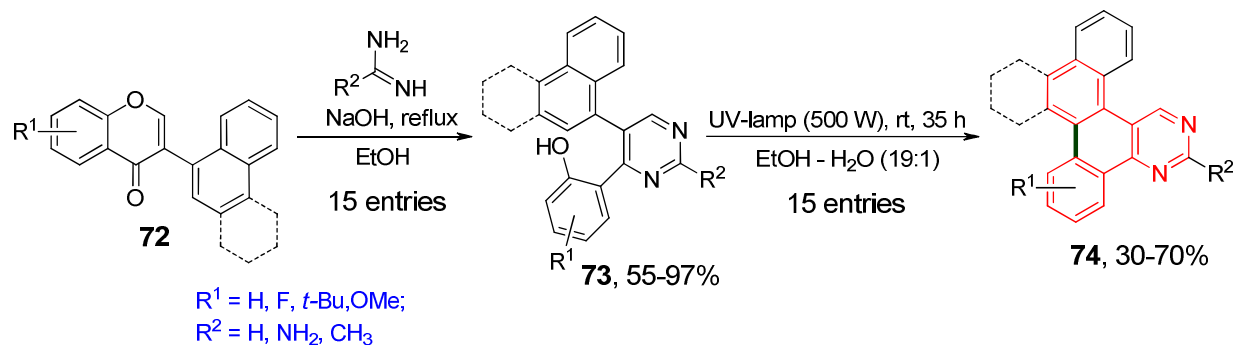


Scheme 21. Synthesis of dibenzo[*f,h*]quinazoline **71** (structural type XVIII) through the iodonium-induced carbocyclization with the subsequent light-induced cyclodehydroiodination.



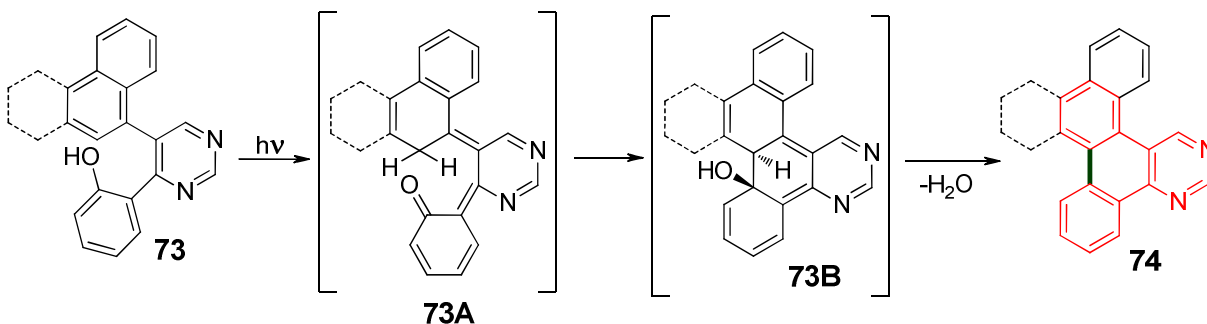
Scheme 22. A mechanism proposed for the synthesis of fused functionalized helicenes through the iodonium-induced carbocyclization of bis(biaryl)acetylenes with subsequent light-induced cyclodehydroiodination.

Furthermore, Zhang *et al.*⁹⁸ have described a simple and efficient method for the synthesis of benzo[*h*]-naphtho[1,2-*f*]quinazolines (**74**) and benzo[*h*]phenanthren[9,10-*f*]quinazolines (**74**) from intermediate 4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidines (**73**) and 4-(2-hydroxyphenyl)-5-(phenanthren-1-yl)pyrimidines (**73**) through the intramolecular photo-induced dehydration, proceeding in EtOH-H₂O (19:1) solution under an argon atmosphere for 35 h (Scheme 23). The corresponding intermediates **73** have been obtained in 55-97% yields by condensation of substituted 3-aryl-chromones (**72**) with formamidine acetate, acetamidine hydrochloride or guanidine hydrochloride in ethanol at 78 °C (Scheme 23).



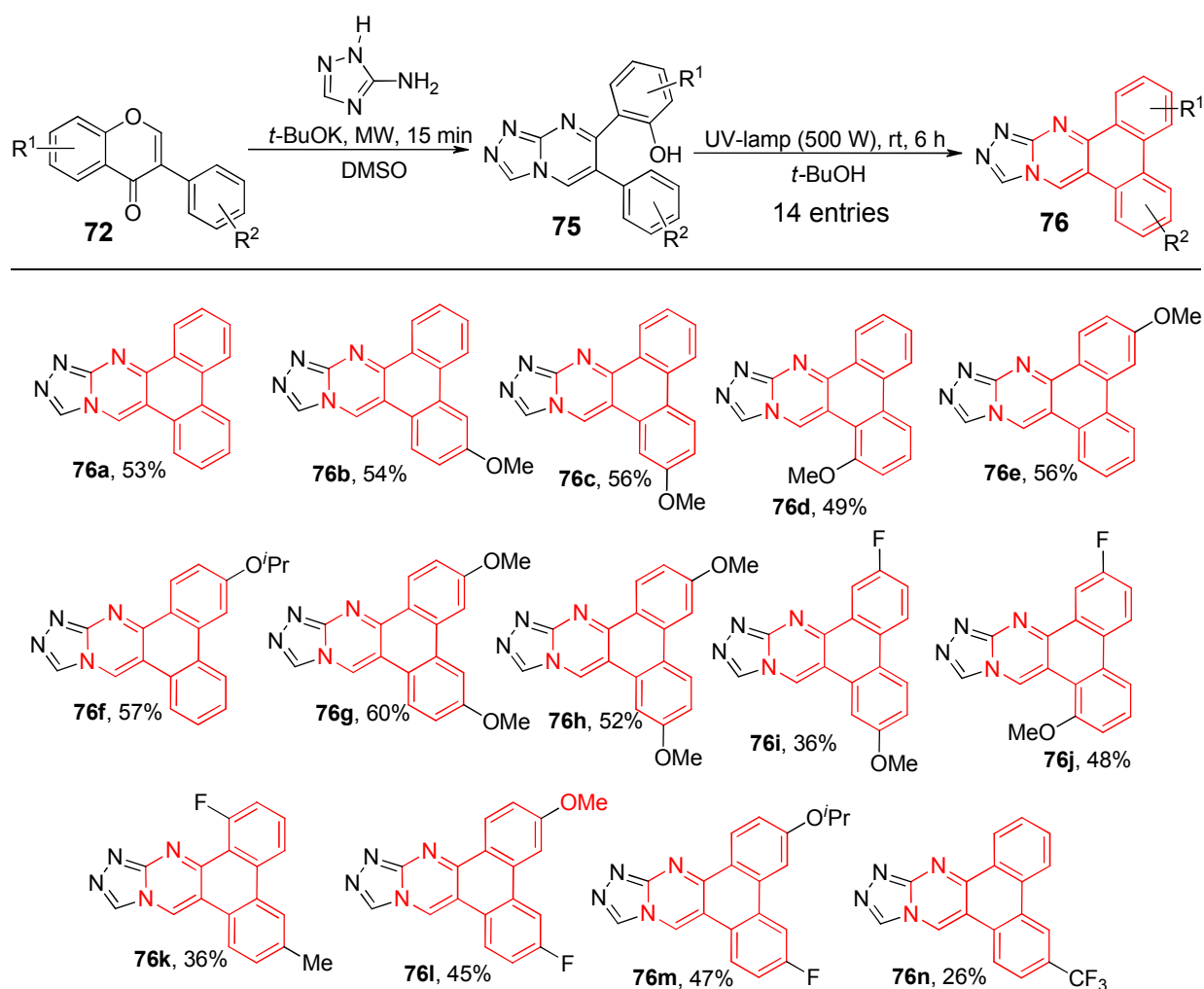
Scheme 23. Synthesis of dibenzo[*f,h*]quinazoline (**XVIII**) skeleton via the photoinduced dehydration.

A reasonable mechanism for the synthesis of polycyclic benzoquinazolines **74** has been formulated (Scheme 24).⁹⁸ Being irradiated with the UV-light, compound **72** in the excited state is transformed to the keto form **72A** by means of the intramolecular proton transfer. The intermediate **72B** is then formed under UV irradiation, followed by dehydration into the target product **74**.



Scheme 24. A plausible mechanism for the photocyclization reaction.

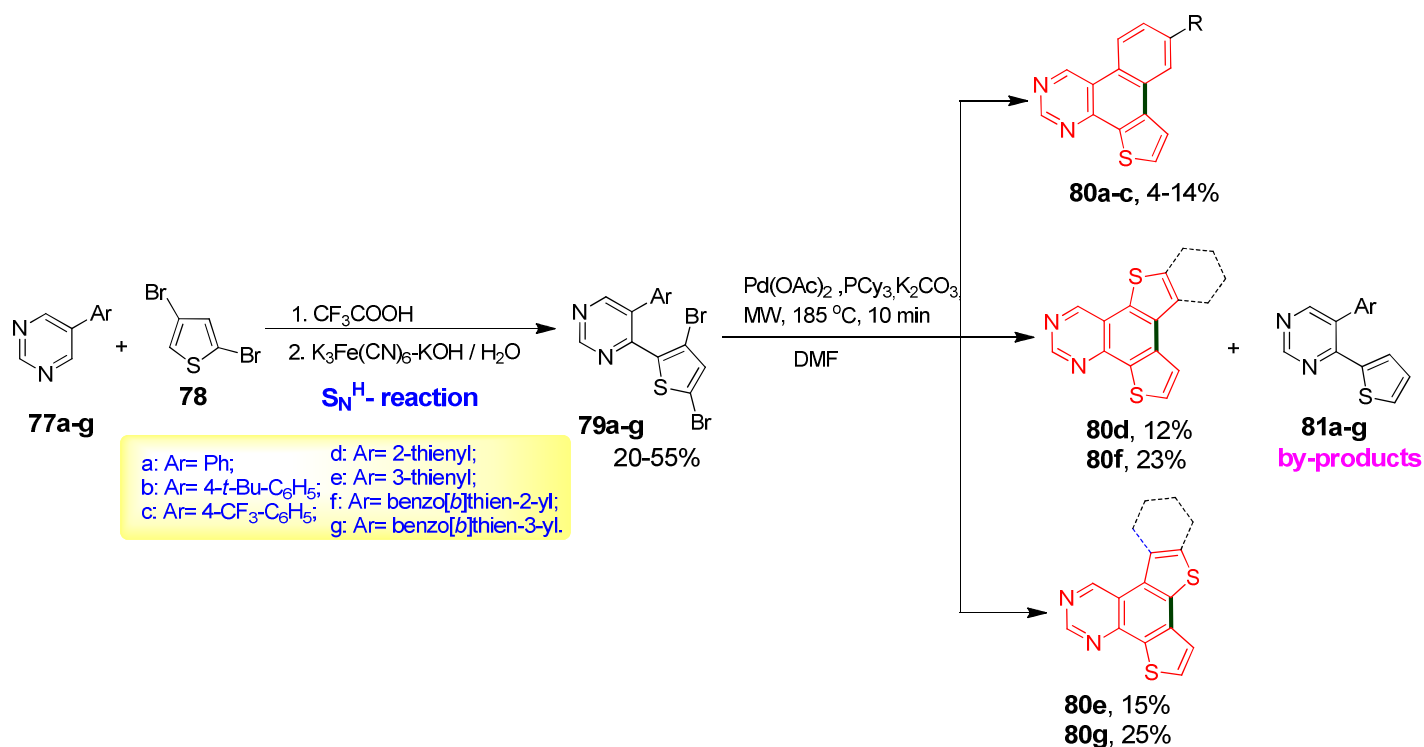
The same procedure has been used for the synthesis of a wide range of dibenzo[*f,h*][1,2,4]triazolo[3,4-*b*]-quinazolines (**76**), which are of interest as compounds exhibiting distinct fluorescent properties (Scheme 25).⁹⁹



Scheme 25. Synthesis of dibenzo[*f,h*][1,2,4]triazolo[3,4-*b*]quinazolines (**76a-n**) through a two-step reaction pathway; overall yields of product **76** from **72** are given.

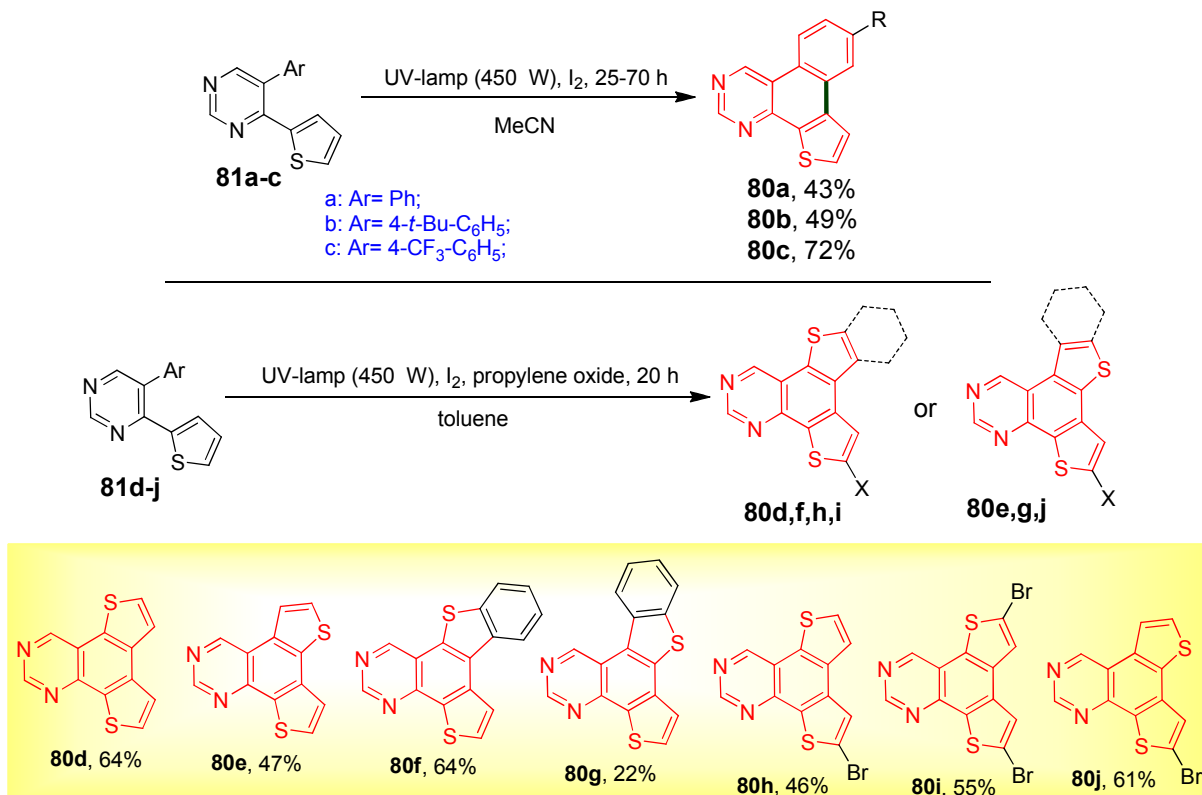
Only a few papers dealing with the synthesis of benzo[*f*]thieno[3,2-*h*]quinazolines (**XIX**), dithieno[2,3-*f*:3',2'-*h*]quinazolines (**XXIII**) and dithieno[3,2-*f*:3',2'-*h*]quinazolines (**XXVI**) are available in the

literature.¹⁰⁰⁻¹⁰² In particular, a simple synthetic route to compounds **XIX**, **XXIII** and **XXVI** has been suggested using palladium-catalyzed intramolecular cyclization of 4-(3,5-dibromothiophen-2-yl)-5-(hetero)arylpyrimidines (**79a-g**), proceeding in DMF at 185 °C under microwave irradiation for 10 min (Scheme 26).¹⁰⁰ Unfortunately, the desired products **80a-g** were obtained in low yield due to a side reaction, affording 5-aryl-4-(thien-2-yl)pyrimidines (**81a-c**) in 20-37% yields. The starting pyrimidines (**79a-g**) were obtained as shown in Scheme 26. The nucleophilic displacement of hydrogen (the S_N^H -reaction)⁸⁷ in 5-(hetero)arylpyrimidines (**77a-g**) by action of 2,4-dibromothiophene (**78**) proceeds smoothly in CF_3COOH , followed by oxidation of the intermediates into 4-(3,5-dibromothiophen-2-yl)-5-(hetero)arylpyrimidines (**79a-g**).

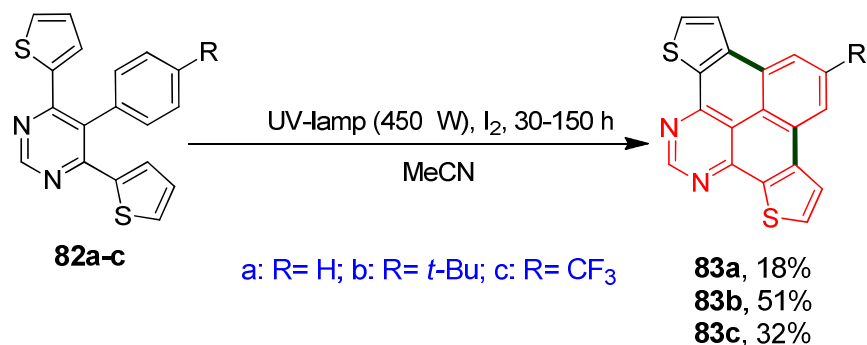


Scheme 26. Synthesis of benzo[*f*]thieno[3,2-*h*]quinazoline (**80a-c**), dithieno[2,3-*f*:3',2'-*h*]quinazoline (**80d,f**) and dithieno[3,2-*f*:3',2'-*h*]quinazoline (**80e,g**) derivatives via Pd-catalyzed intramolecular cyclization of **79a-g** under microwave irradiation.

Poor yields of the target products **80** obtained for palladium-catalyzed intramolecular arylation of **79a-g** prompted the authors to develop a convenient protocol for the syntheses of benzo[*f*]thieno[3,2-*h*]quinazolines (**80a-c**), dithieno[2,3-*f*:3',2'-*h*]quinazolines (**80d,f,h,i**) and dithieno[3,2-*f*:3',2'-*h*]quinazolines (**80e,g,j**) by using the oxidative photocyclization of the corresponding 5-aryl-4-(thiophen-2-yl)pyrimidines (**81a-c**) and 4,5-dithienyl substituted pyrimidines (**81d-j**) (Scheme 27).^{101,102} It is noteworthy that 8-substituted benzo[*gh*]dithieno[2,3-*e*:3',2'-*j*]perimidines (**82a-c**) have been obtained from 5-(4-*R*-phenyl)-4,6-dithiophen-2-ylpyrimidines (**83a-c**) in good yields by exploiting the same procedure (Scheme 28).



Scheme 27. Synthesis of benzo[*f*]thieno[3,2-*h*]quinazolines (**80a-c**), dithieno[2,3-*f*:3',2'-*h*]quinazolines (**80d,f,h,i**) and dithieno[3,2-*f*:3',2'-*h*]quinazolines (**80e,g,j**) via the oxidative photocyclization of appropriate 4,5-di(hetero)aryl substituted pyrimidines (**81a-j**).



Scheme 28. Synthesis of 8-substituted benzo[*gh*]dithieno[2,3-*e*:3',2'-*j*]perimidines (**83a-c**) by the oxidative photocyclization of 5-(4-substituted-phenyl)-4,6-dithiophen-2-yl-pyrimidines (**82a-c**).

4. Synthesis of Heteropolycyclic Systems, Analogues of 1,4-Diazatriphenylenes

There are 6 tetracyclic aromatic structures (**XXII-XXXII**), bearing the 1,4-diazine fragment (see Figure 4). Surprisingly, only dithieno[2,3-*f*:2',3'-*h*]quinoxalines (**XXXII**) have not so far been described in the literature.

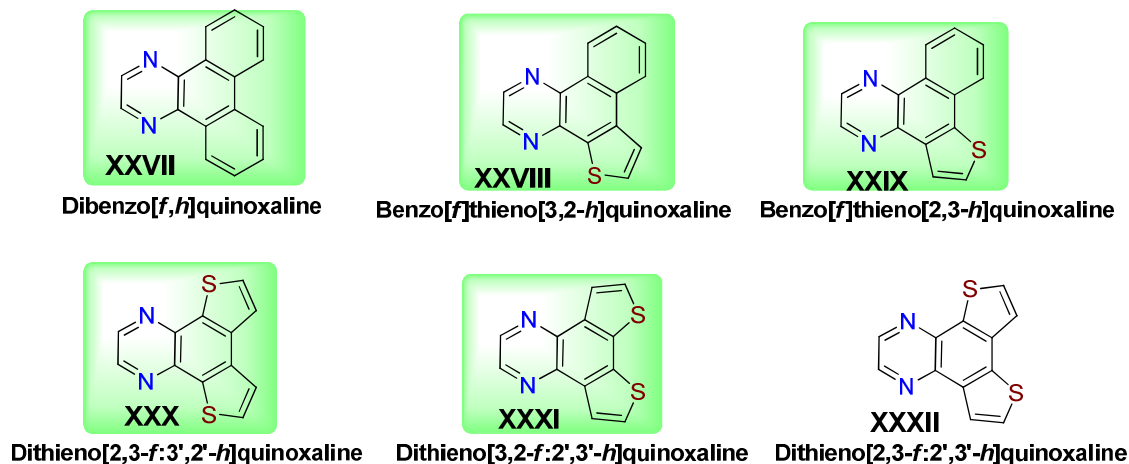
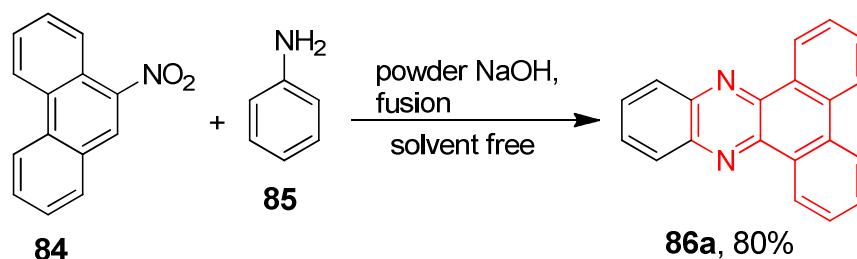


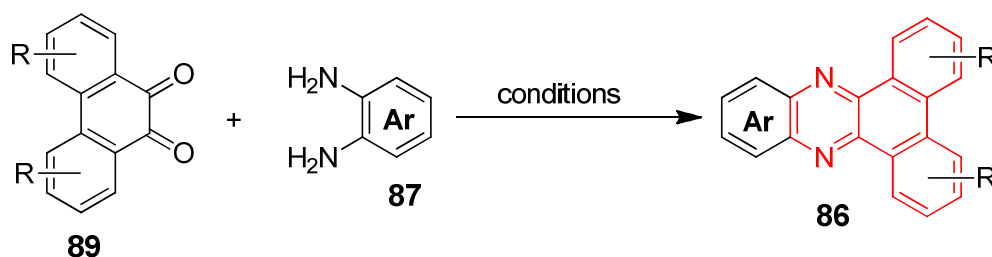
Figure 4. The structures of tetracyclic aromatic systems bearing the pyrazine ring.

For the first time the synthesis of dibenzo[*f,h*]quinoxaline (**XXVII**) derivatives, *e.g.* dibenzo[*a,c*]phenazine (**86a**), has been carried out by condensation of 9-nitrophenanthrene (**84**) with aniline (**85**) in the presence of powdered NaOH at 170-180 °C (Scheme 29).¹⁰³



Scheme 29. The synthesis of dibenzo[*f,h*]quinoxaline **86a** by the reaction of 9-nitrophenanthrene (**84**) and aniline (**85**).

A variety of methods have been developed to prepare dibenzo[*f,h*]quinoxalines (**XXVII**), including the most widely used condensation of 1,2-diamines, such as *o*-phenylenediamine (**87**) and ethylenediamine (**88**) derivatives, with substituted phenanthrene-9,10-diones (**89**) (Schemes 30 and 31). The reaction conditions for condensations leading to dibenzo[*a,c*]phenazines (**86**)¹⁰⁴⁻¹⁵⁹ and dibenzo[*f,h*]quinoxalines (**90**)^{152,153,160-163} are summarized in Tables 1 and 2.



Scheme 30. Synthesis of dibenzo[*a,c*]phenazines (**86**) by condensation of *o*-phenylenediamines (**87**) with substituted phenanthrene-9,10-diones (**89**).

Table 1. Selected examples of condensation of *o*-phenylenediamines (**87**) with phenanthrene-9,10-diones (**89**)

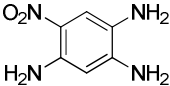
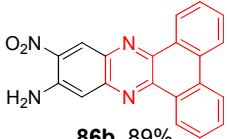
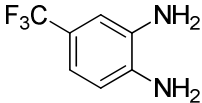
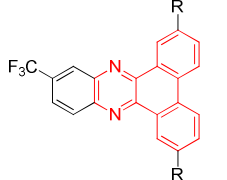
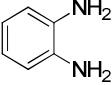
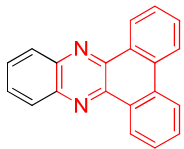
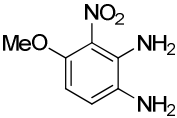
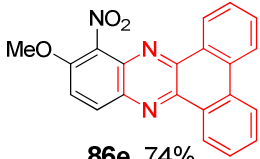
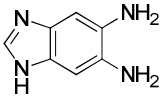
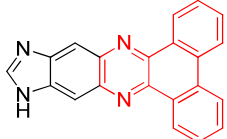
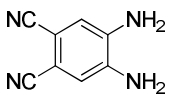
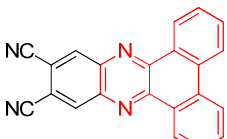
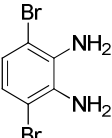
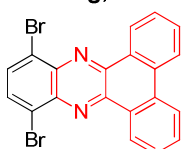
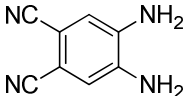
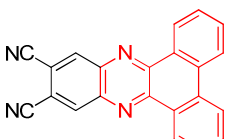
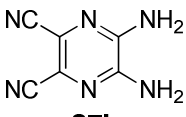
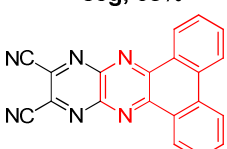
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
1	 87b	EtOH - CH ₃ COOH (3:10), reflux, 20 min.	 86b , 89%	104
2	 87c	Fusion	 86c (R= H), 88% 86d (R= NO ₂), 88%	105
3	 87a	EtOH, reflux with catalytic amount HCl, 2 h.	 86a , 88%	106
4	 87d	EtOH - 5M HCl solution (50:1), reflux, 40 min.	 86e , 74%	107
5	 87e	EtOH, EtONa, reflux.	 86f , 75%	108
6	 87f	CH ₃ COOH, reflux.	 86g , 79%	109
7	 87g	EtOH - CH ₃ COOH (20:1), reflux, 2 h.	 86h , 80%	110
8	 87f	DMF, reflux, 4 h.	 86g , 63%	111
9	 87h	pyridine, reflux, 15 h.	 86i , 94%	112

Table 1. Continued

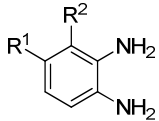
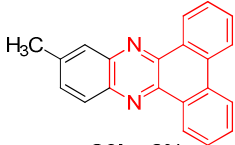
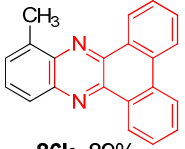
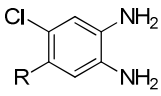
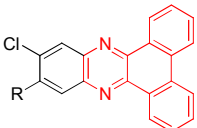
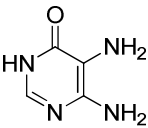
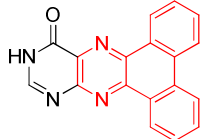
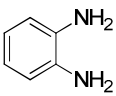
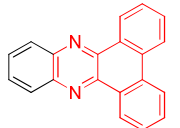
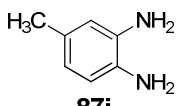
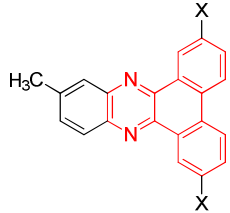
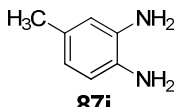
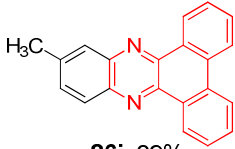
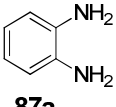
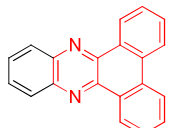
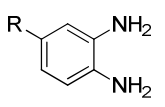
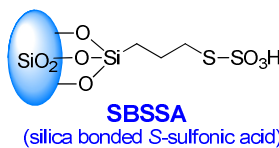
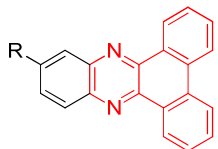
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
10	 87i (R ¹ = CH ₃ , R ² = H) 87j (R ¹ = H, R ² = CH ₃)	CHCl ₃ - CF ₃ COOH (298:1), reflux, 6 h. CHCl ₃ , reflux, 29 h.	 86j , 46%  86k , 89%	113
11	 87k (R= H) 87l (R= Cl)	glacial CH ₃ COOH, reflux, 5 h.	 86l (R= H), 85% 86m (R= Cl), 83%	114
12	 87m	CH ₃ COOH, CH ₃ COONa, 150 °C, 2 h.	 86n , 60%	115
13	 87a	TMSCN (2.4 equiv.), 0.8 GPa, 30 °C, 24 h.	 86a , 98%	116
14	 87i	toluene, reflux, 1 h.	 86o (X= H), 64% 86p (X= Br), 67%	117
15	 87i	CH ₃ COOH, reflux, 3 h.	 86j , 89%	118
16	 87a	M(HSO ₄) _n [M= K, Na, Ca, Mg, Al] (5 mol %), EtOH, rt, 3 min.	 86a , 96-98%	119
17	 87a (R= H) 87i (R= CH ₃)	EtOH - H ₂ O (70:30), SBSSA (3.4 mol %), rt, 5 min. 	 86a (R= H), 94% 86j (R= CH ₃), 92%	120

Table 1. Continued

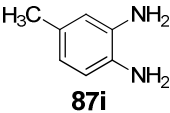
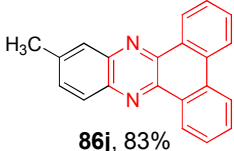
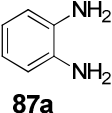
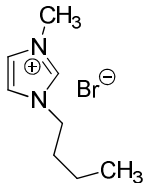
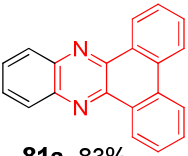
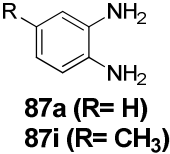
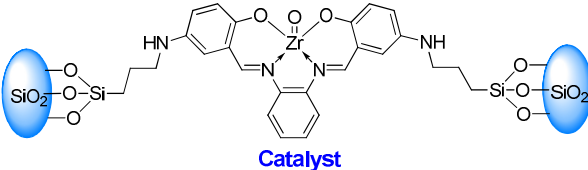
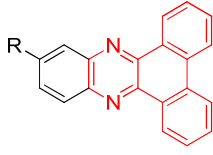
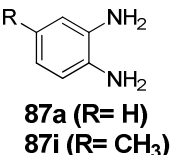
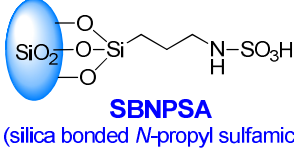
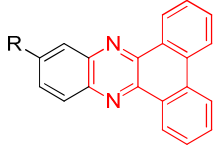
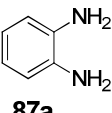
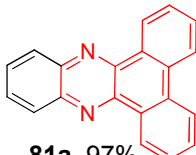
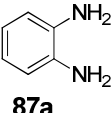
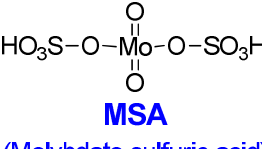
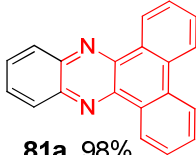
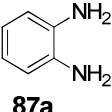
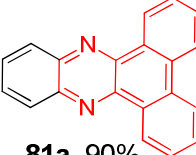
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
18		EtOH - conc. HCl, (20:1), reflux, 4 h. [bmim]Br (1.5 equiv.), MW (500 W), 130 °C, 30 min.	 86j, 83%	121
19		 [bmim]Br (Ionic liquid 1-butyl-3-methylimidazolium bromide)	 81a, 83%	122
20		EtOH, catalyst (10 wt.%), rt, 1.7-2.0 h.  Catalyst	 81a (R=H), 89% 81j (R=CH ₃), 87%	123
21		EtOH, SBNPSA (3.4 mol %), rt, 5 min.  SBNPSA (silica bonded N-propyl sulfamic acid)	 81a (R=H), 93% 81j (R=CH ₃), 90%	124
22		Polyethylene glycol (PEG-600) - H ₂ O (1:1), rt, 5 min. EtOH, MSA (5 mol %), rt, 8 min.	 81a, 97%	125
23		 MSA (Molybdate sulfuric acid)	 81a, 98%	126
24		Glycerol - H ₂ O (5 :2), 90 °C, 4h.	 81a, 90%	127

Table 1. Continued

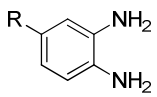
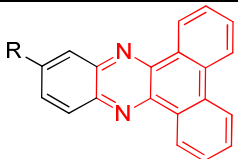
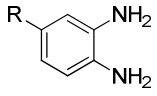
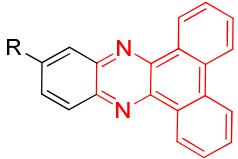
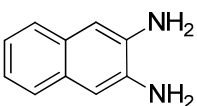
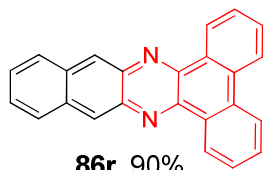
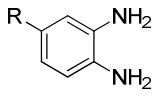
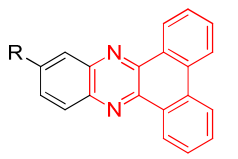
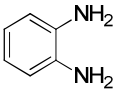
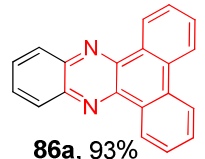
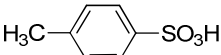
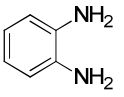
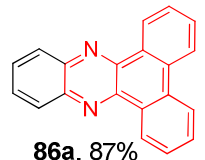
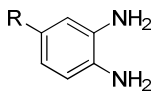
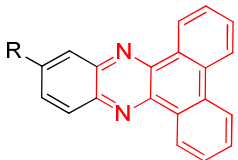
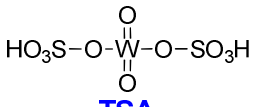
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
25	 87a (R= H) 87i (R= CH₃)	EtOH, MgSO ₄ ·7H ₂ O (20 mol %), rt, 15 min.	 81a (R= H), 90% 81j (R= CH₃), 92%	128
26	 87a (R= H) 87i (R= CH₃)	1,2-Dichloroethane, nano-TiO ₂ (2.5 mol %), rt, 20-25 min.	 81a (R= H), 90% 81j (R= CH₃), 91%	129
27	 87n	EtOH, reflux, 2 h.	 86r, 90%	130
28	 87a (R= H) 87i (R= CH₃)	Ball-milling, solvent free, rt, 4 h.	 86a (R= H), >99% 86j (R= CH₃), 95%	131
29	 87a	H ₂ O, PTSA (5 mol %), NaPTSA (40 wt.%), rt, 7 min.	 86a, 93%	132
		 PTSA		
30	 87a	Solvent free, nano-SiO ₂ (0.6 g to 1 mmol 87a), grinding, rt, 10 min.	 86a, 87%	133
31	 87a (R= H) 87i (R= CH₃)	Solvent free, TSA (5 mol %), grinding, rt, 20-22 min.	 86a (R= H), 91% 86j (R= CH₃), 90%	134
		 TSA (Tungstate sulfuric acid)		

Table 1. Continued

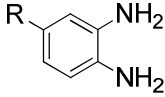
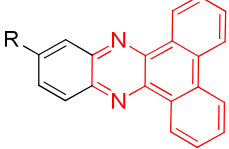
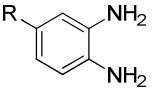
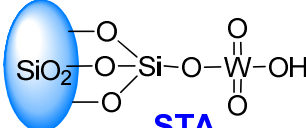
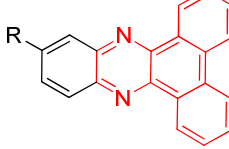
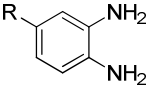
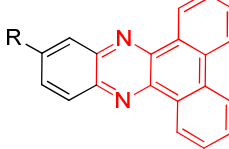
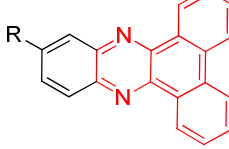
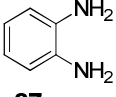
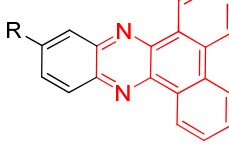
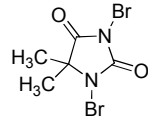
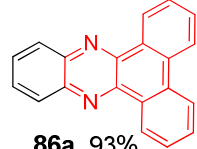
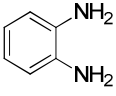
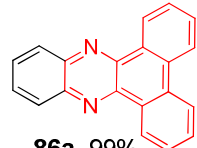
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
32	 87a (R= H) 87i (R= CH₃) 87k (R= Cl)	EtOH, LiCl (10 mol %), rt, 8-42 min.	 86a (R= H), 95% 86j (R= CH₃), 95% 86l (R= Cl), 84%	135
33	 87a (R= H) 87i (R= CH₃)	Solvent free, STA (2 mol %), grinding, rt, 5 min.  STA (Silica tungstic acid)	 86a (R= H), 90% 86j (R= CH₃), 90%	136
34	 87a (R= H) 87i (R= CH₃)	EtOH, CrCl ₂ ·6H ₂ O (10 mg to 1.1 mmol 87a,i), r.t., 9 min.	 86a (R= H), 96% 86j (R= CH₃), 94%	137
		EtOH, PbBr ₂ (10 mg to 1.1 mmol 87a,i), r.t., 16 min.	 86a (R= H), 96% 86j (R= CH₃), 95%	
35	 87a	EtOH, CuSO ₄ ·5H ₂ O (10 mg to 1.1 mmol 87a,i), r.t., 32 min.	 86a (R= H), 92% 86j (R= CH₃), 90%	138
		Solvent free, DBH (6 mol %), oil bath, 110 °C, 30 min.  DBH (1,3-Dibromo-5,5-dimethylhydantoin)	 86a, 93%	
36	 87a	EtOH-H ₂ O (7:3), PhOH (20 mol %), rt, 2 min.	 86a, 99%	139

Table 1. Continued

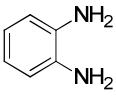
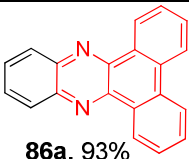
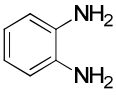
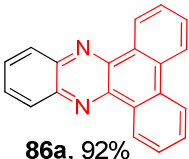
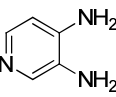
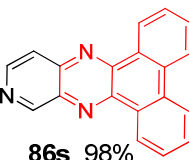
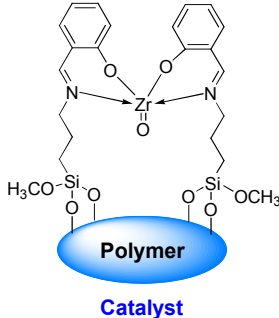
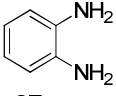
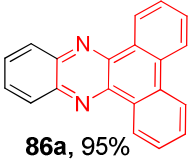
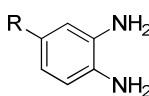
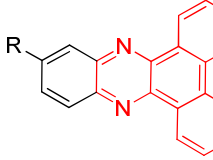
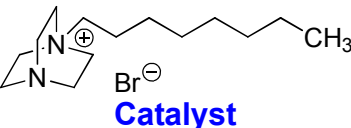
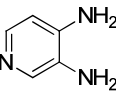
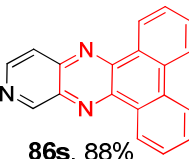
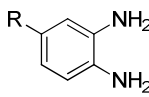
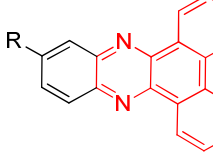
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
37	 87a	EtOH, graphite (2 equiv.), rt, 30 min.	 86a , 93%	140
38	 87a	CH ₃ CN – H ₂ O (1:1), rice husk (0.35 mol %), 50 °C, 20 min.	 86a , 92%	141
39	 87o	H ₂ O, catalyst (10 mg to 1.0 mmol 87o), reflux, 2 h.	 86s , 98%	142
		 Catalyst		
40	 87a	EtOH, nano-MoO ₃ (2 mol %), 25 °C for 2 min. and 60 °C for 5 min.	 86a , 95%	143
41	 87a (R= H) 87i (R= CH₃)	H ₂ O, catalyst (1 equiv.), rt for 10 min. and 70 °C for 35-38 min..	 86a (R= H) , 90% 86j (R= CH₃) , 85%	144
		 Catalyst		
42	 87o	EtOH, FeCl ₃ (20 mmol %), reflux, 80 min.	 86s , 88%	145
43	 87a (R= H) 87i (R= CH₃)	EtOH, PbCl ₂ (20 mol %), rt, 10 min.	 86a (R= H) , 95% 86j (R= CH₃) , 95%	146

Table 1. Continued

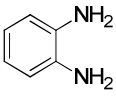
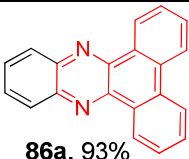
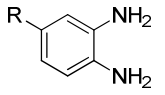
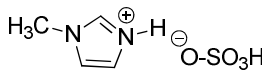
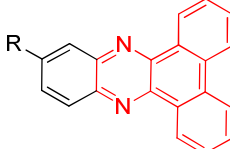
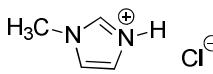
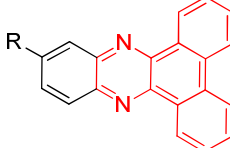
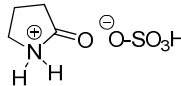
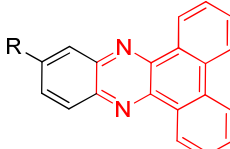
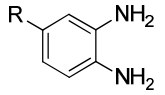
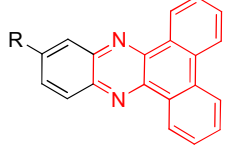
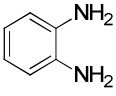
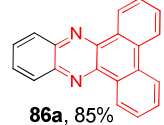
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.	
44	 87a	Solvent free, nano-ZnO (1.1 mol %), rt, 20 min.	 86a , 93%	147	
45	 87a (R= H) 87i (R= CH ₃)	H ₂ O, ionic liquid [Hmim]HSO ₄ (10 mol %), rt, 3 min.	 [Hmim]HSO₄ (1-Hydrogen-3-methylimidazolium hydrogen sulfate)	 86a (R= H), 95% 86j (R= CH ₃), 97%	148
		H ₂ O, ionic liquid [Hmim]Cl (10 mol %), rt, 7-10 min.	 [Hmim]Cl (1-Hydrogen-3-methylimidazolium chloride)	 86a (R= H), 92% 86j (R= CH ₃), 90%	
		H ₂ O, ionic liquid [Hnhp]HSO ₄ (10 mol %), rt, 7 min.	 [Hnhp]HSO₄ (2-Pyrrolidonium hydrogen sulfate)	 86a (R= H), 94% 86j (R= CH ₃), 90%	
46	 87i (R= CH ₃) 87p (R= NO ₂)	EtOH – H ₂ O (3:2), Zr(OTf) ₄ (10 mol %), rt, 20-30 min.	 86j (R= CH ₃), 95% 86t (R= NO ₂), 96%	149	
47	 87a	EtOH, nano-ZrO ₂ (3.2 mol %), 60 °C, 7 min.	 86a , 85%	150	

Table 1. Continued

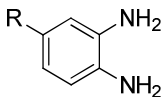
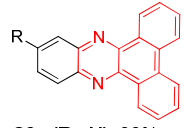
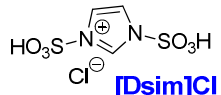
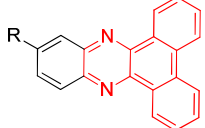
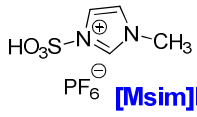
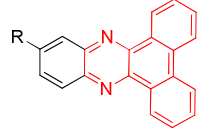

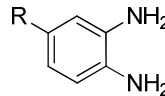
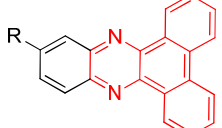
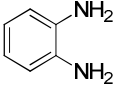
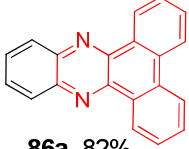
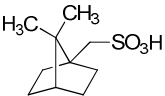
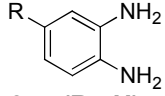
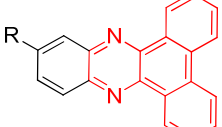
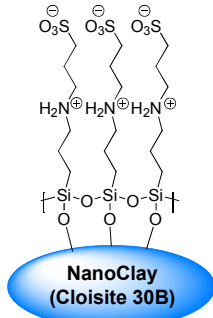
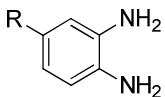
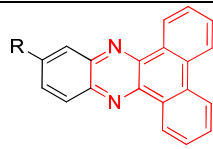
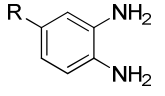
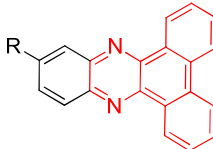
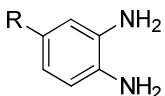
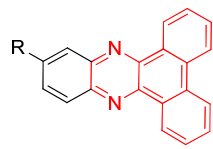

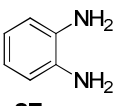
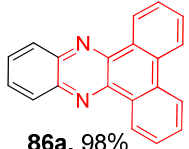
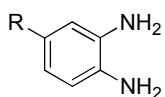
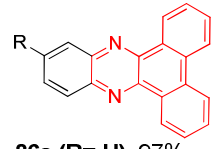
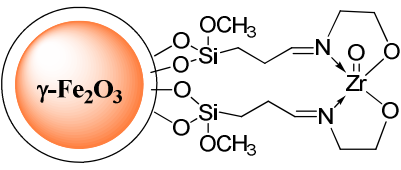
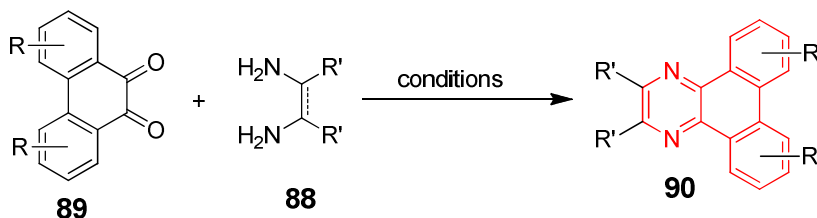
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.	
48	 87a (R= H) 87i (R= CH₃) 87p (R= NO₂)	Solvent free, ionic liquid [Dsim]Cl (10 mol%), 110 °C, 2-20 min.	 86a (R= H), 99% 86j (R= CH₃), 96% 86t (R= NO₂), 94%	151	
		 [Dsim]Cl (1,3-Disulfonic acid imidazolium chloride)	Solvent free, ionic liquid [Msim]PF ₆ (10 mol%), 110 °C, 3-20 min.		 86a (R= H), 96% 86j (R= CH₃), 93% 86t (R= NO₂), 90%
		 [Msim]PF₆ (3-Methyl-1-sulfonic acid imidazolium hexafluorophosphate)	Solvent free, ionic liquid [Msim]BF ₄ (10 mol%), 110 °C, 3-35 min.		 86a (R= H), 97% 86j (R= CH₃), 95% 86t (R= NO₂), 89%
		 [Msim]BF₄ (3-Methyl-1-sulfonic acid imidazolium tetrafluoroborate)			
49	 87a (R= H) 87k (R= Cl) 87p (R= NO₂)	5 M aqueous NaCl solution, 95 °C, 0.5-3 h.	 86a (R= H), 92% 86l (R= Cl), 92% 86t (R= NO₂), 83%	152	
50	 87a	EtOH – H ₂ O (1:3), DL-camphorsulfonic acid (5 mol%), rt, 20 min.	 86a, 82%	153	
		 DL-camphorsulfonic acid			
51	 87a (R= H) 87p (R= NO₂)	EtOH, sulfonated nanoClay (5 mol%), rt, 15-25 min.	 86a (R= H), 99% 86t (R= NO₂), 90%	154	
		 NanoClay (Cloisite 30B) Sulfonated nanoClay			

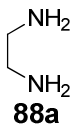
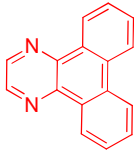
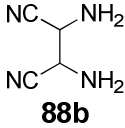
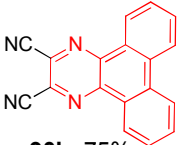
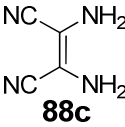
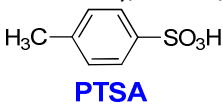
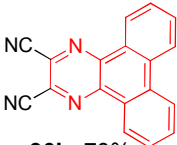
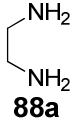
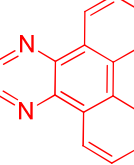
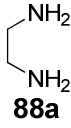
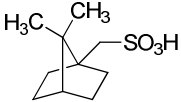
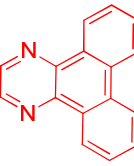
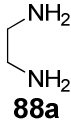
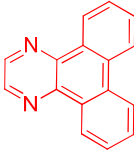
Table 1. Continued

Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
52	 87a (R= H) 87i (R= CH₃) 87p (R= NO₂)	EtOH – H ₂ O (7:3), phthalic acid (5 mol%), rt, 2-20 min.	 86a (R= H), 99% 86j (R= CH₃), 95% 86t (R= NO₂), 93%	155
53	 87a (R= H) 87i (R= CH₃)	H ₂ O, propylsulfonic acid functionalized nanozeolite clinoptilolite (10 mg to 1.0 mmol 87a,i), rt, 10-15 min.	 86a (R= H), 92% 86j (R= CH₃), 92%	156
54	 87a (R= H) 87i (R= CH₃) 87p (R= NO₂)	H ₂ O – CH ₃ COOH – DABCO (3:1:1), 80 °C, 20-40 min.	 86a (R= H), 90% 86j (R= CH₃), 82% 86t (R= NO₂), 82%	157
		 DABCO (1,4-Diazabicyclo[2.2.2]octane)		
55	 87a	Solvent free, sulfonated rice husk ash (15 mg to 1.0 mmol 87a), 80 °C, 10 min.	 86a, 98%	158
56	 87a (R= H) 87p (R= NO₂)	EtOH, nanoparticles (4 mg to 1.5 mmol 87a,p), 60 °C, 3-60 min.	 86a (R= H), 97% 86t (R= NO₂), 88%	159
		 Nanoparticles (A zirconium Schiff base complex immobilized on starch-coated maghemite nanoparticles)		

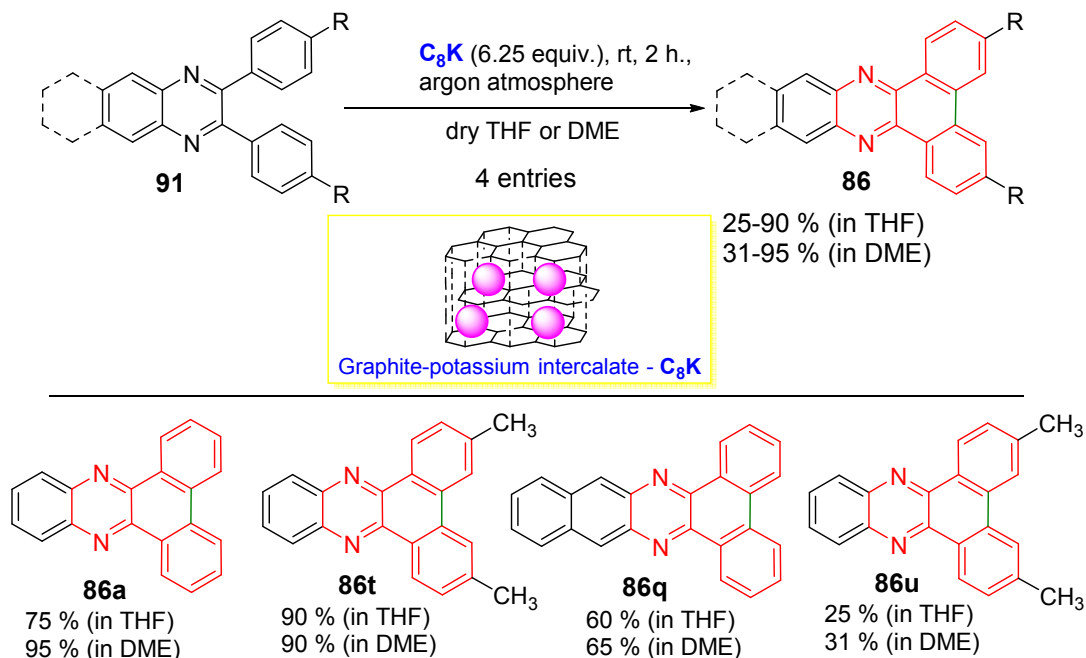


Scheme 31. Synthesis of dibenzo[*f,h*]quinoxaline (**90**) by condensation of ethylenediamines (**88**) with substituted phenanthren-9,10-diones (**89**).

Table 2. Selected examples of the condensation of ethylenediamines (**88**) with phenanthrene-9,10-dione (**89**)

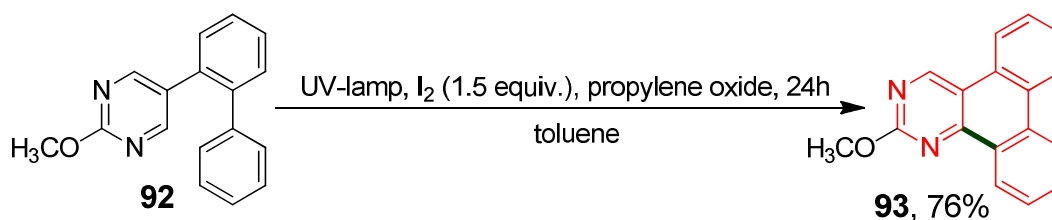
Entry	1,2-Diamine (88)	Conditions	Product (90) – Isolated yield	Ref.
1	 88a	EtOH – CH ₃ COOH (3:10), reflux, 20 min.	 90a , 78%	160
2	 88b	EtOH, reflux with catalytic amount CH ₃ COOH, 2 h.	 90b , 75%	161
3	 88c	EtOH, PTSA (0.26 mol %), reflux, 5 h.  PTSA	 90b , 70%	162
4	 88a	5 M aqueous NaCl solution, 95 °C, 1 h.	 90a , 82%	152
5	 88a	EtOH – H ₂ O (1:3), DL-camphorsulfonic acid (5 mol %), rt, 5 min.  DL-camphorsulfonic acid	 90a , 87%	153
6	 88a	1. Toluene, reflux, 24 h ; 2. Toluene, MnO ₂ (2.3 equiv.), reflux.	 90a , 86%	163

In addition to this well-known condensation reaction, Rabinovitz *et al.*^{164,165} have designed a new synthetic approach to dibenzo[*a,c*]phenazines (**86**), based on the reductive coupling reaction of 2,3-diphenyl substituted quinoxalines (**91a,q,t,u**), proceeding with graphite-potassium intercalate (**C₈K**) in dry tetrahydrofuran (THF) or dimethoxyethane (DME) at room temperature (Scheme 32). A plausible mechanism for the ring closure reaction has been described in the literature.^{165,166}



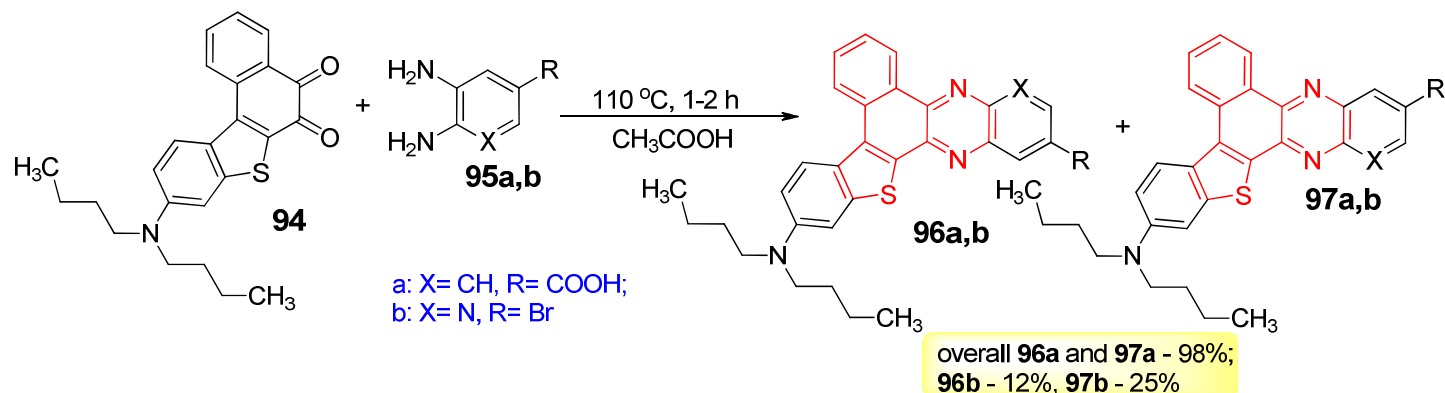
Scheme 32. Synthesis of dibenzo[α,c]phenazines (**86**) by the reductive coupling reaction of 2,3-diphenyl substituted quinoxalines (**91a,q,t,u**), proceeding with graphite-potassium intercalate (C_8K) in dry tetrahydrofuran (THF) or dimethoxyethane (DME).¹⁶⁵

Photocyclization is also an efficient synthetic tool for construction of dibenzo[f,h]quinoxalines (**XXVII**). For example, 2-methoxydibenzo[f,h]quinoxaline (**93**) has been obtained in a high yield by irradiating 2-(biphenyl-2-yl)-5-methoxy pyrazine (**92**) with UV-light in the presence of iodine, as oxidant, and propylene oxide, as an acid scavenger (Scheme 33).⁵²



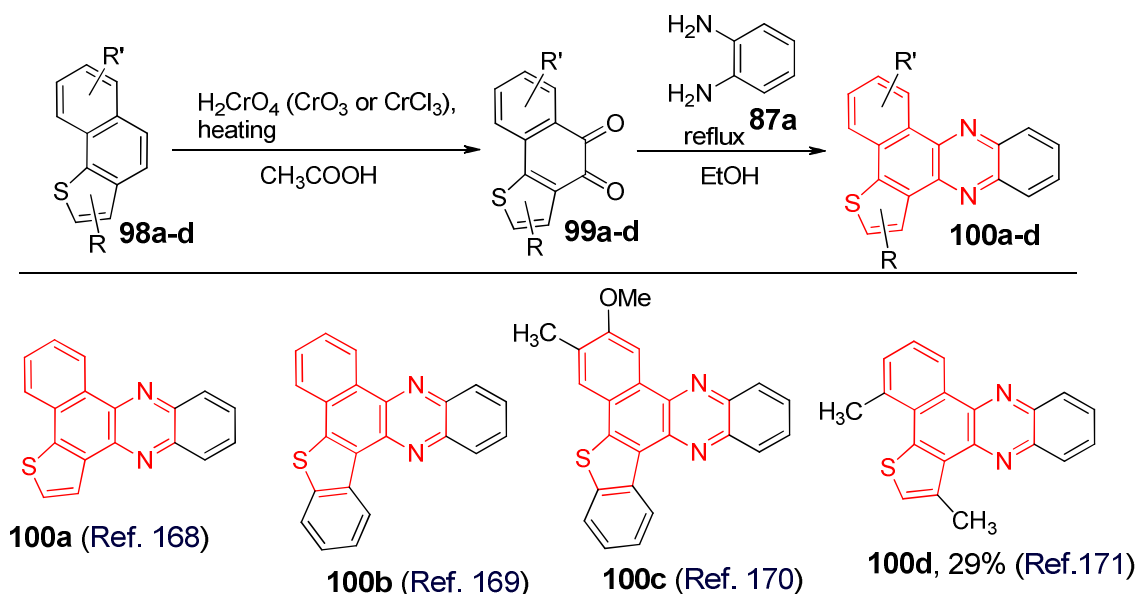
Scheme 33. Synthesis of 2-methoxydibenzo[f,h]quinoxaline (**93**) by the oxidative photocyclization of 2-(biphenyl-2-yl)-5-methoxy pyrazine (**92**).

There is only one publication¹⁶⁶ reporting the synthesis of benzo[f]thieno[3,2- h]quinoxalines (**XXVIII**). Benzo[f]thieno[3,2- h]quinoxalines (**96a,b** and **97a,b**) have been prepared in 37-98% overall yields by condensation of 9-dibutylaminobenzo[b]naphtho[1,2- d]thiophen-5,6-dione (**94**) with 3,4-diaminobenzoic acid (**95a**) or 2,3-diamino-5-bromopyridine (**95b**) in acetic acid at 110 °C (Scheme 34).¹⁶⁷



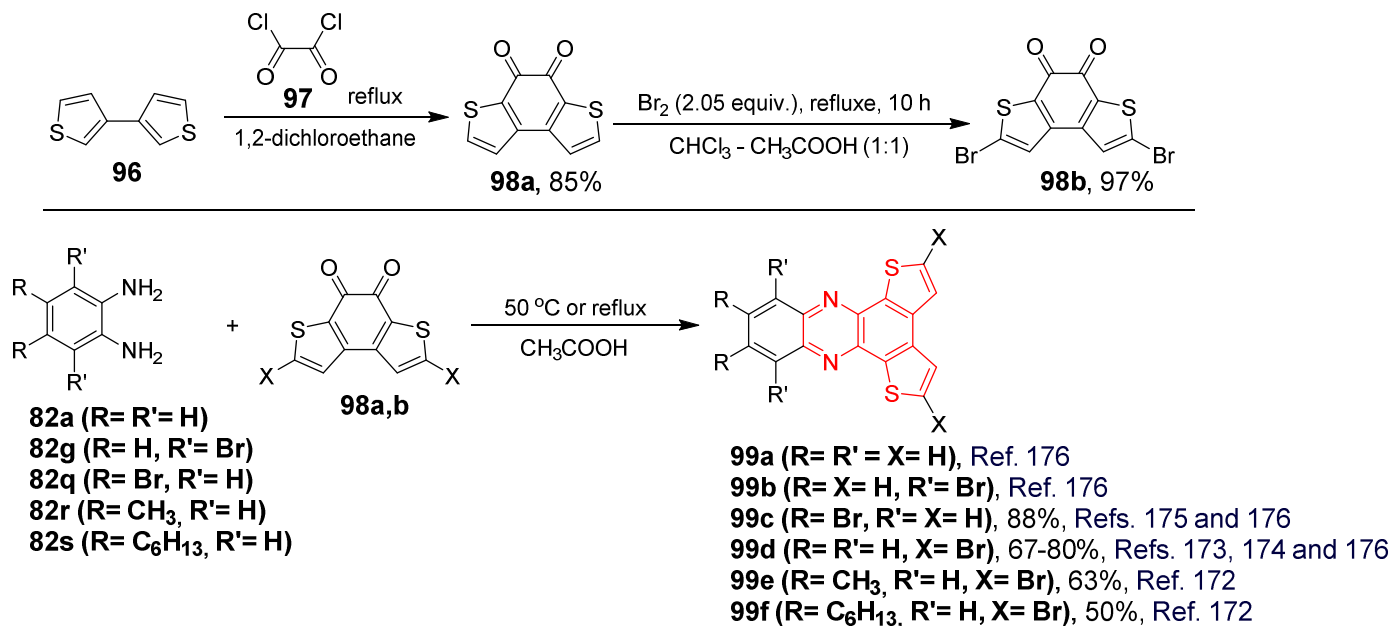
Scheme 34. Synthesis of benzo[*f*]thieno[3,2-*h*]quinoxalines (**96a,b** and **97a,b**) by condensation of 9-dibutylaminobenzo[*b*]naphtho[1,2-*d*]thiophene-5,6-dione (**94**) with 3,4-diaminobenzoic acid (**95a**) or 2,3-diamino-5-bromopyridine (**95b**).

Compounds of the benzo[*f*]thieno[2,3-*h*]quinoxaline (**XXIX**) series are also scarcely presented in the literature. There are only four references concerning the synthesis of **XXIX** skeleton.¹⁶⁸⁻¹⁷¹ The most common procedure for the synthesis of benzo[*f*]thieno[2,3-*h*]quinoxalines (**100a-d**) is oxidation of naphtho[1,2-*b*]thiophenes (**98a-d**) into the corresponding naphtho[1,2-*b*]thiophen-4,5-diones (**99a-d**) with chromic acid, followed by treatment with *o*-phenylenediamine (**87a**) (Scheme 35).



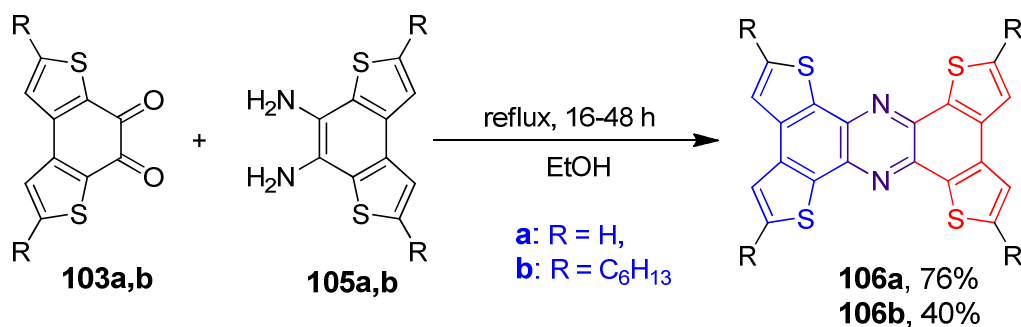
Scheme 35. Synthesis of benzo[*f*]thieno[2,3-*h*]quinoxaline derivatives (**100a-d**).

The dithieno[2,3-*f*:3':2'-*h*]quinoxaline (**XXX**) skeleton can be constructed by two general methods. The first synthetic protocol starts from 3,3'-bithiophene (**101**), which can be converted readily into benzo[1,2-*b*:4,-*b'*]dithiophene-4,5-dione (**103a**) through the ring-closing reaction with oxalyl dichloride (**102**), proceeding in refluxing 1,2-dichloroethane. Bromination of **103a** affords 2,7-dibromobenzo[1,2-*b*:4,3-*b'*]dithiophene-4,5-dione (**103b**) in a high yield. Condensation of the latter compound with substituted 1,2-phenylenediamine (**87**) results in the desired dithieno[2,3-*a*:3':2'-*c*]phenazine derivative (**104a-f**) (Scheme 36).¹⁷²⁻¹⁷⁶



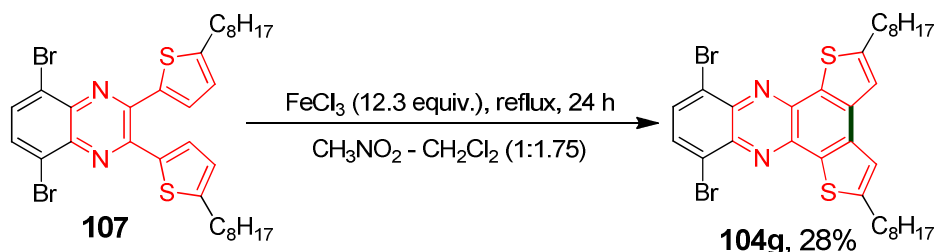
Scheme 36. Synthesis of dithieno[2,3-*a*:3',2'-*c*]phenazine derivatives (**104a-f**).

It is noteworthy that tetrathienophenazine derivatives (**106a,b**) containing two dithieno[2,3-*f*:3',2'-*h*]quinoxaline (**XXX**) skeletons have been obtained in a similar manner (Scheme 37).¹⁷⁷

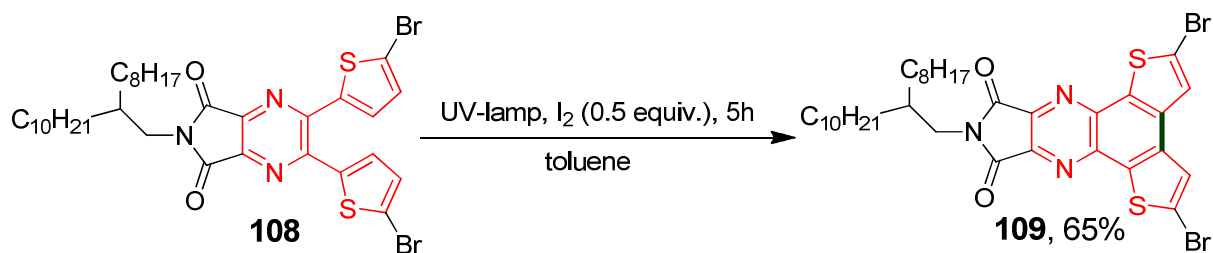


Scheme 37. Synthesis of 2,5,9,12-tetrastituted tetrathieno[2,3-*a*:3',2'-*c*:2''*''*:3''-*h*:3''':2''-*j*]phenazines (**106a,b**).

The second synthetic pathway to dithieno[2,3-*f*:3',2'-*h*]quinoxalines (**XXX**) involves the oxidative cyclodehydrogenation of 2,3-di(thiophen-2-yl)pyrazines (**107** or **108**) through the Scholl reaction, proceeding in the presence of iron(III) chloride, as an oxidant (Scheme 38),¹⁷⁸ or it can be based on the oxidative photocyclization in the presence of iodine, as oxidant (Scheme 39).¹⁷⁹

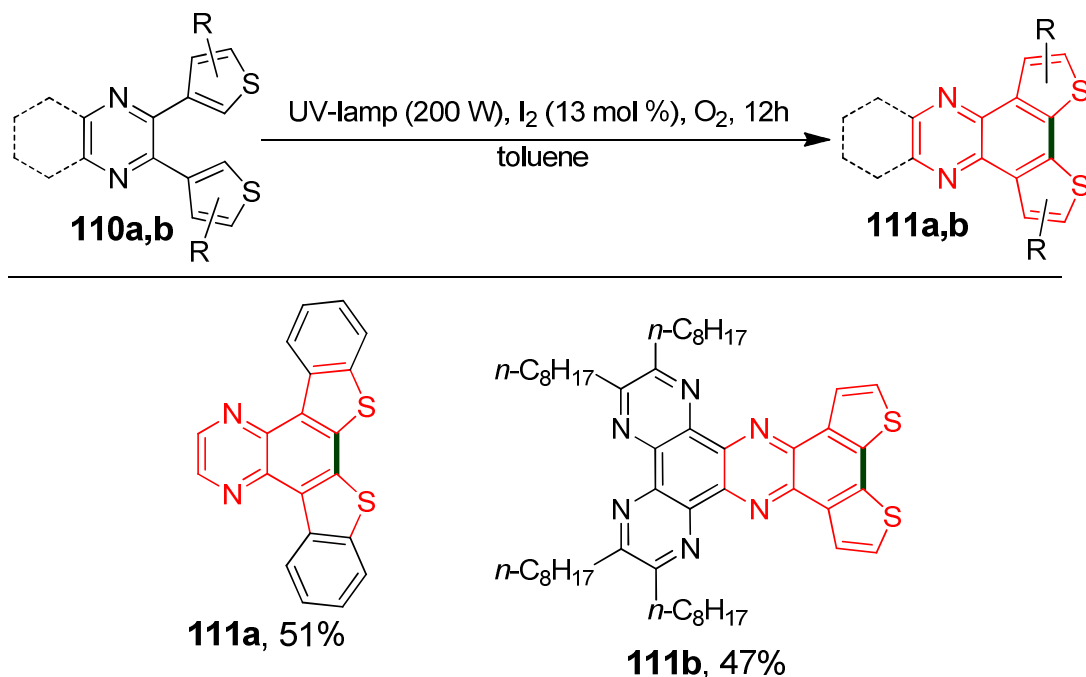


Scheme 38. Synthesis of dithieno[2,3-*f*:3',2'-*h*]quinoxaline (**XXX**) skeleton by using the Scholl reaction.



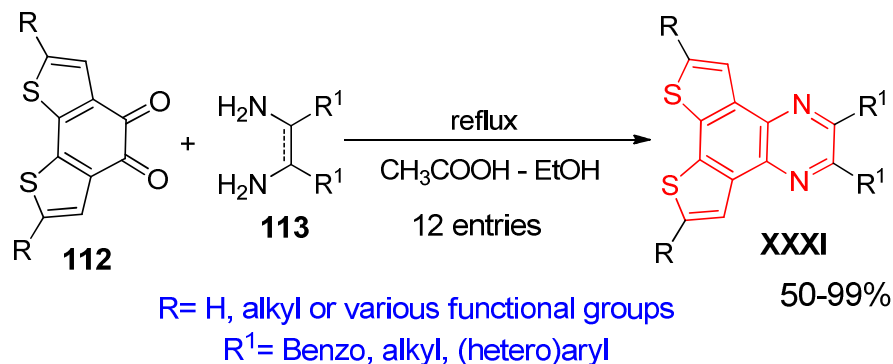
Scheme 39. Synthesis of dithieno[2,3-f:3',2'-h]quinoxaline (**XXX**) skeleton using oxidative photocyclization.

As for the synthesis of dithieno[3,2-f:2',3'-h]quinoxalines (**XXXI**) is concerned, there are only two examples showing how to obtain these structures via the oxidative photocyclization of the corresponding 2,3-di(thien-3-yl)pyrazine derivatives (**110a,b**). The reaction proceeds in the presence of iodine (as oxidant) on irradiation with a 200W mercury lamp with an additional bubbling of air through the reaction mixture for 12 hours. The target dithieno[3,2-f:2',3'-h]quinoxaline derivatives (**111a,b**) have been obtained in moderate yields (Scheme 40).^{180,181}

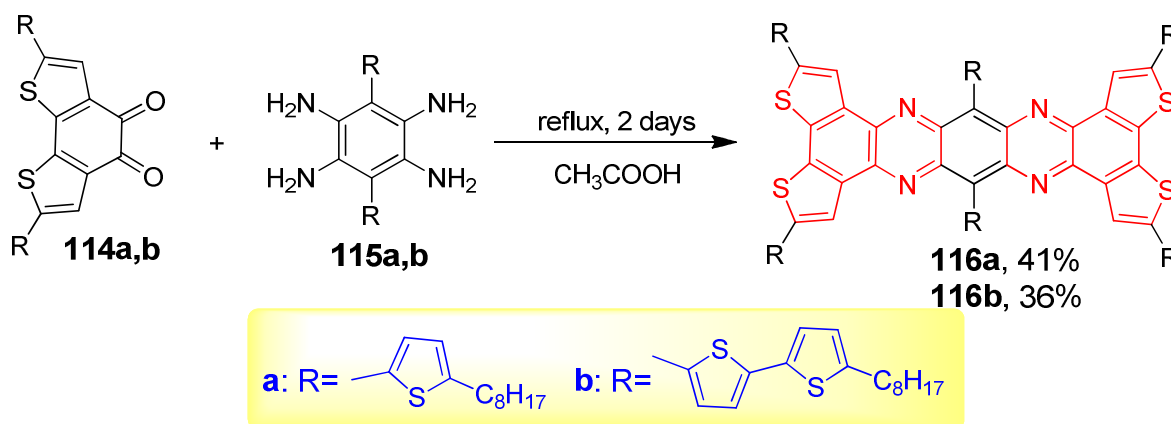


Scheme 40. Synthesis of dithieno[3,2-f:2',3'-h]quinoxalines (**111a,b**) through the oxidative photocyclization of the corresponding 2,3-di(thiophen-3-yl)pyrazine derivatives (**110a,b**).

A common approach to the synthesis of dithieno[3,2-f:2',3'-h]quinoxalines (**XXXI**) is condensation of 2,7-disubstituted benzo[1,2-b:6,5-b']dithiophen-4,5-dione (**112**) with various 1,2-diaminoalryl or 1,2-diamino(hetero)aryl (**113**), respectively, in ethanol/acetic acid or ethanol (Scheme 41).^{172,182-188} In particular, compounds **116a,b**, bearing two dithieno[3,2-f:2',3'-h]quinoxaline (**XXXI**) skeletons, have been obtained by reacting benzo[1,2-b:6,5-b']dithiophen-4,5-dione (**114a,b**) with 3,6-dithienyl substituted 1,2,4,5-tetraaminobenzenes (**115a,b**) (Scheme 42).¹⁸⁹ Notably, various methods for the preparation of unsubstituted and functionalized benzo[1,2-b:6,5-b']dithiophene-4,5-diones (**112**) have been described in the literature.^{186,190-192}

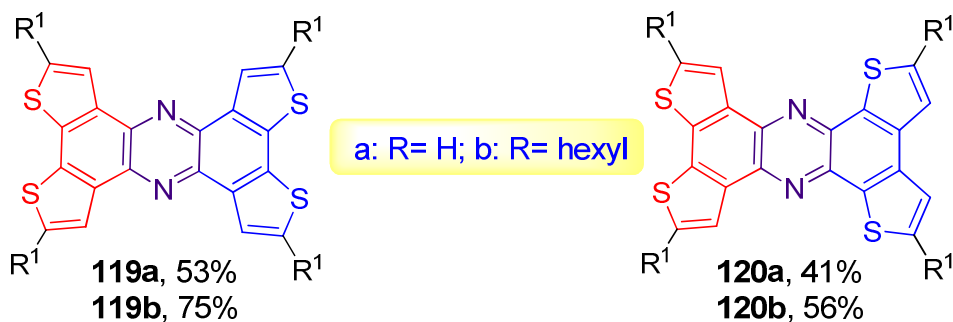
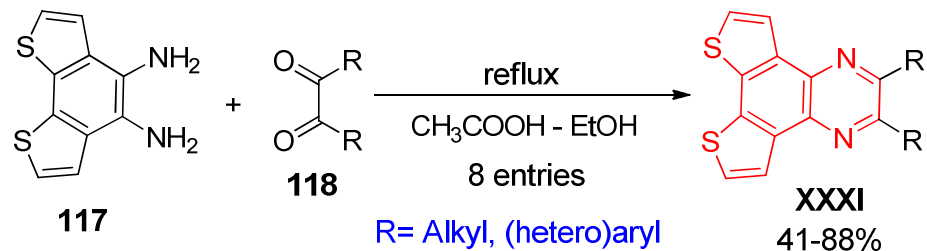


Scheme 41. Synthesis of dithieno[3,2-*f*:2',3'-*h*]quinoxalines (**XXXI**) by condensation of benzo[1,2-*b*:6,5-*b'*]dithiophen-4,5-dione (**112**) with 1,2-diamine derivative (**113**).



Scheme 42. Synthesis of 2,5,8,11,14,17-hexasubstituted dithieno[3',2':5,6;2'',3'':7,8]quinoxalino[2,3-*i*]dithieno[3,2-*a*:2',3'-*c*]phenazine derivatives (**116a,b**).

The skeleton of dithieno[3,2-*f*:2',3'-*h*]quinoxalines (**XXXI**) can also be obtained by using condensation of benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-diamine (**117**) with alkyl or (hetero)aryl 1,2-diones (**118**) (Scheme 43).¹⁹³⁻¹⁹⁵ Symmetrical tetrathieno[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazines (**119a,b**) and asymmetrical tetrathieno[2,3-*a*:3',2'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazines (**120a,b**) have been synthesized in the same manner.¹⁹⁵



Scheme 43. Synthesis of dithieno[3,2-*f*:2',3'-*h*]quinoxalines (**XXXI**) by condensation of benzo[1,2-*b*:6,5-*b'*]dithiophen-4,5-diamine (**117**) with 1,2-diones (**118**).

Many compounds in the series of dibenzo[*f,h*]quinoxalines (**XXVII**),^{53,112,113,117,121,130} benzo[*f*]thieno[3,2-*h*]quinoxalines (**XXVIII**),¹⁶⁷ dithieno[2,3-*f*:3',2'-*h*]quinoxalines (**XXX**)¹⁷³⁻¹⁷⁹ and dithieno[3,2-*f*:2',3'-*h*]quinoxalines (**XXXI**)^{177,178,180-184,189-192,195} have been found to be highly luminescent and/or prospective semiconductor materials, demonstrating their potential applications in organic electronics.

5. Conclusions

In this review article we have tried to present up-to-date literature data on the latest achievements in the chemistry of 1,2-, 1,3- and 1,4-diaza-analogues of triphenylene, phenanthro[9,10-*b*]thiophene and naphthothiophenes. In order to prepare 1,2- and 1,4-diaza derivatives of these polycyclic aromatic systems various types of condensation reactions appear to be appropriate ones, while the synthesis of 1,3-diaza compounds is usually realized via intramolecular cross-coupling reactions. It should be noted that from 32 possible diazaanalogues of triphenylene, phenanthro[9,10-*b*]thiophene and naphthothiophenes only 11 structures have so far been described in the literature. We believe that this review will be useful for organic chemists working in the field of polycyclic (hetero)aromatics and their metal complexes.

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