The Free Internet Journal
for Organic Chemistry

Archive for
Organic Chemistry

Review

Arkivoc **2017**, part i, 356-401

Diazatriphenylenes and their thiophene analogues: synthesis and applications

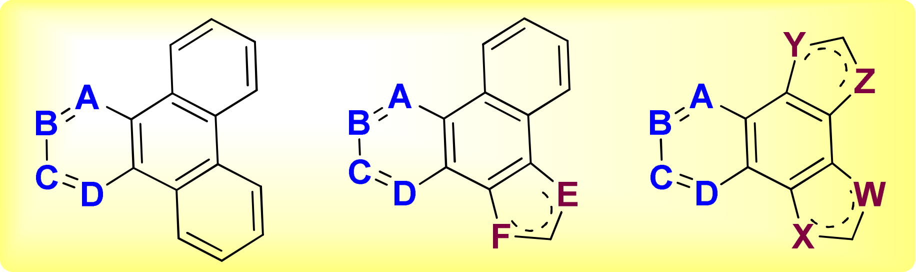
Egor V. Verbitskiy,[a,b,]* Gennady L. Rusinov,[a,b] and Valery N. Charushin [a,b]

[a] Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,
S. Kovalevskoy St. 22, Ekaterinburg 620 990, Russia
[b] Ural Federal University, Mira St. 19, Ekaterinburg 620 002, Russia
Email: Verbitsky@ios.uran.ru

Received 05-27-2017 **Accepted** 06-23-2017 **Published on line** 10-03-2017

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

DOI: https://doi.org/10.24820/ark.5550190.p010.190

Table of Contents

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 triphenylenes[20-37] 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*']dithiophenes[50]) (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).

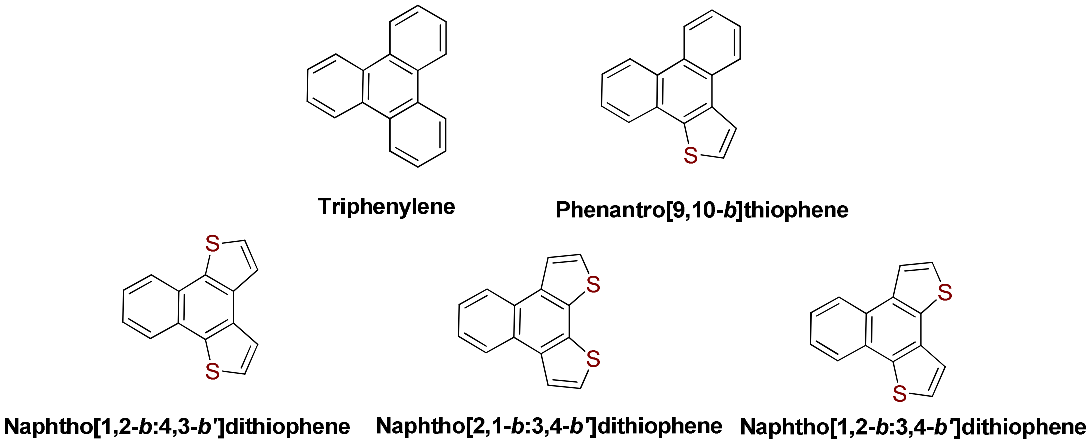


Figure 1. Structures of triphenylene, phenanthro[9,10-*b*]thiophene, naphthodithiophenes.

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]

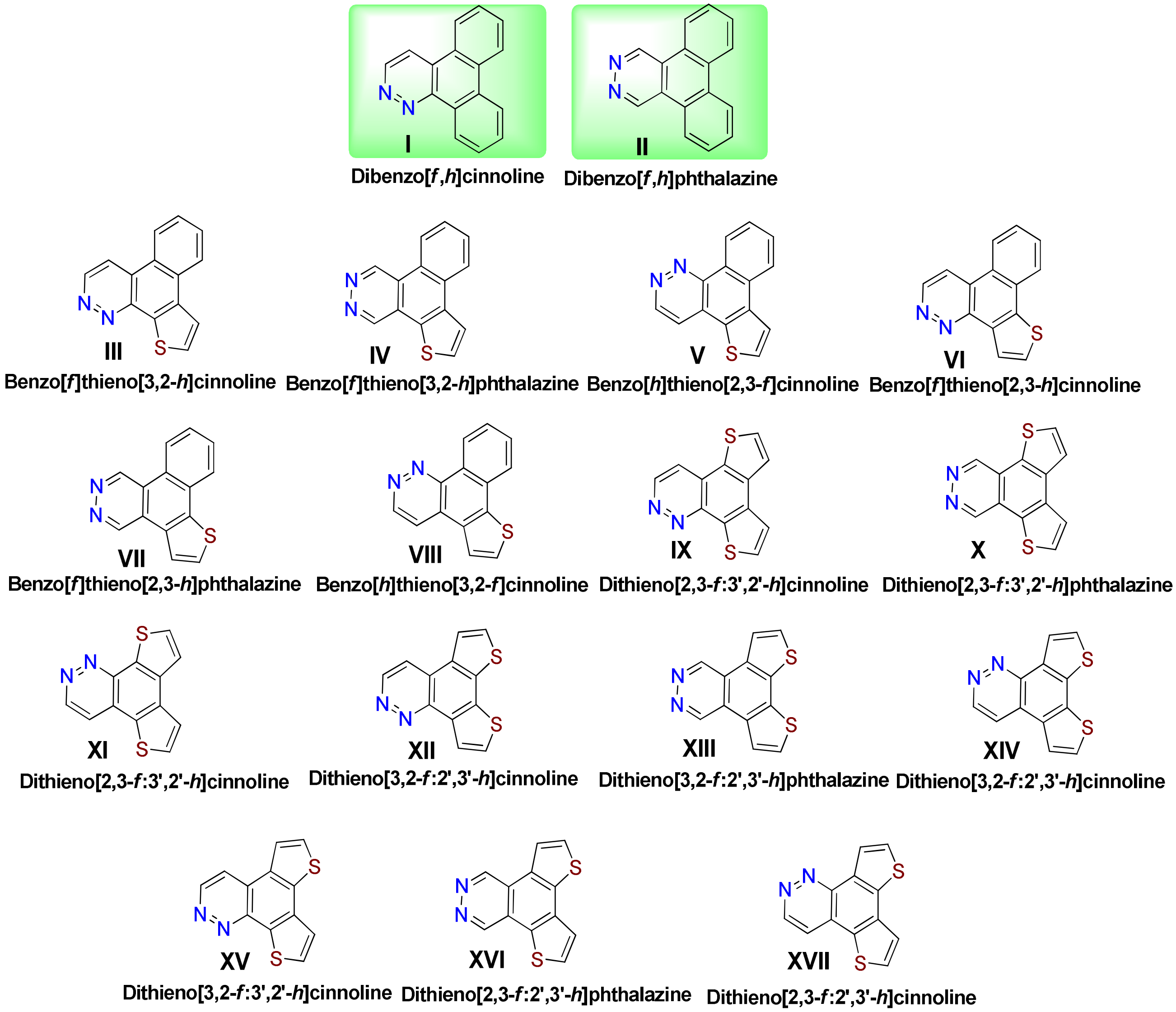
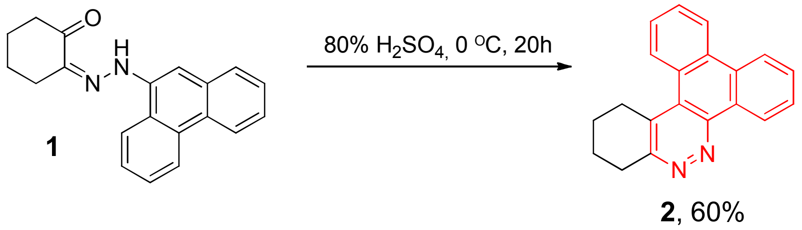


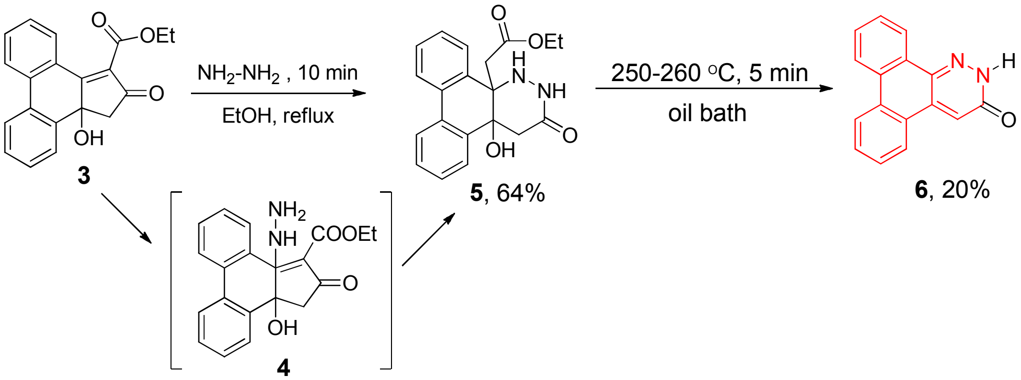
Figure 2. Structures of possible tetracyclic diazatriphenylenes and related thiophene-containing systems bearing the pyridazine ring.

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)hydrazono]cyclohexanone (**1**) in 80% H_2SO_4 at 0 ^{o}C (Scheme 1).



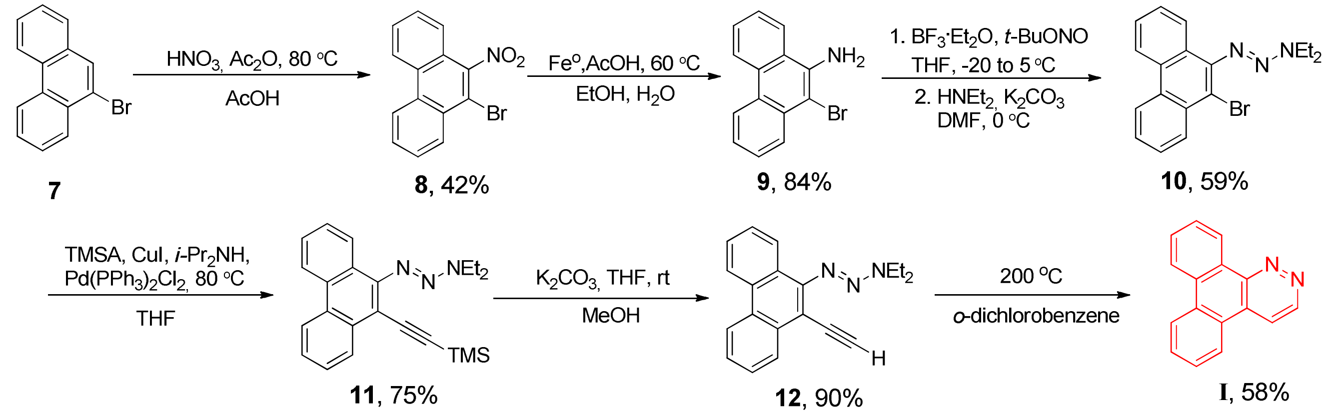
Scheme 1. Synthesis of the dibenzo[*f,h*]cinnoline ring system (**I**) through intramolecular cyclization of cyclohexane-1,2-dione 1-arylhydrazone.

Another approach to the dibenzo[*f,h*]cinnoline ring system (**I**) 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-12b-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).



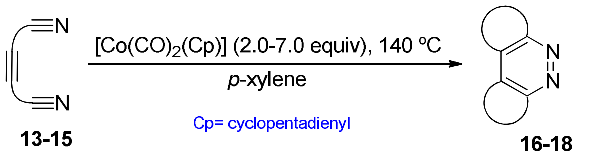
Scheme 2. Synthesis of dibenzo[*f,h*]cinnoline (**6**) from cyclopenta[*l*]phenanthrene (**3**).

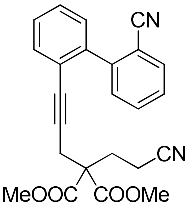
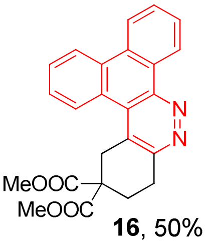
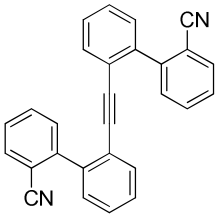
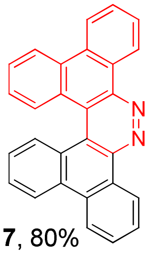
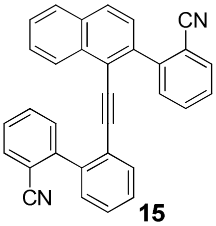
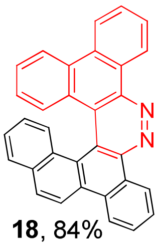
A similar route to the parent dibenzo[*f,h*]cinnoline (**I**) through thermolysis of triazene (**12**) in 58% yield (Scheme 3) has been demonstrated by Young *et al.*[56] The starting triazene (**12**) was obtained, as shown in Scheme 3. Nitration of commercially available 9-bromophenanthrene (**7**) afforded **8**, which was subsequently reduced with iron powder in the presence of acetic acid to give bromoaniline (**9**). Diazotization of **9** with $BF_3{\cdot}Et_2O$ and *t*-BuONO followed by quenching with $HNEt_2$ 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**).

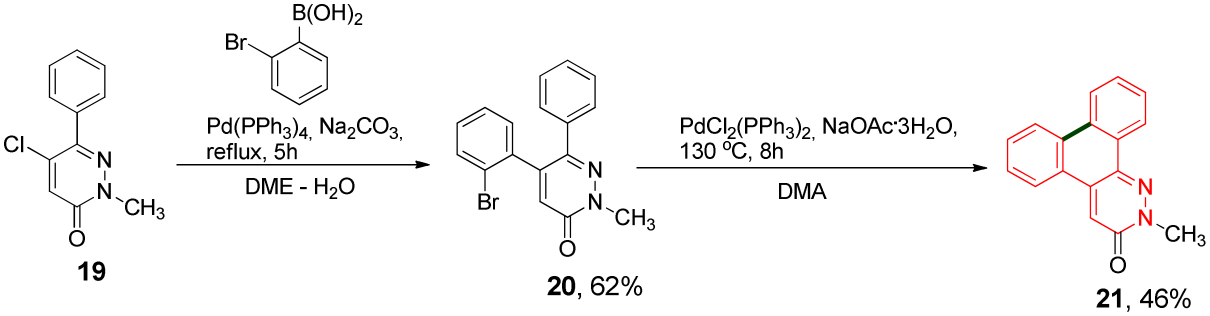
Cobalt-mediated [2+2+2] cycloisomerisation of ynedinitriles **13-15**, developed by Chercheja *et al*,[57] appears to be a novel, facile, and straight forward synthesis of dibenzo[*f,h*]cinnolines **16-18** (Scheme 4).



Ynedinitrile	[Co(CO)$_2$(Cp)] [equiv], time	Dibenzo[*f,h*]cinnoline derivative
 **13**	2.0 equiv, 18 h	 **16**, 50%
 **14**	2.1 equiv, 6 h	 **17**, 80%
 **15**	7.0 equiv, 72 h	 **18**, 84%

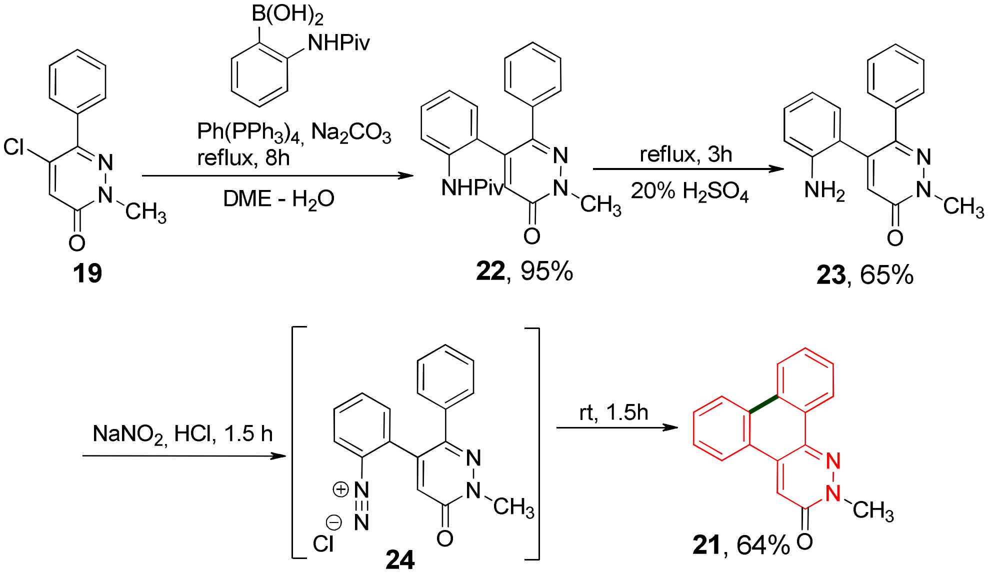
Scheme 4. Cobalt-mediated [2+2+2] cycloisomerisation of ynedinitriles **13-15** into dibenzo[*f,h*]cinnoline derivatives **16-18**.

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)



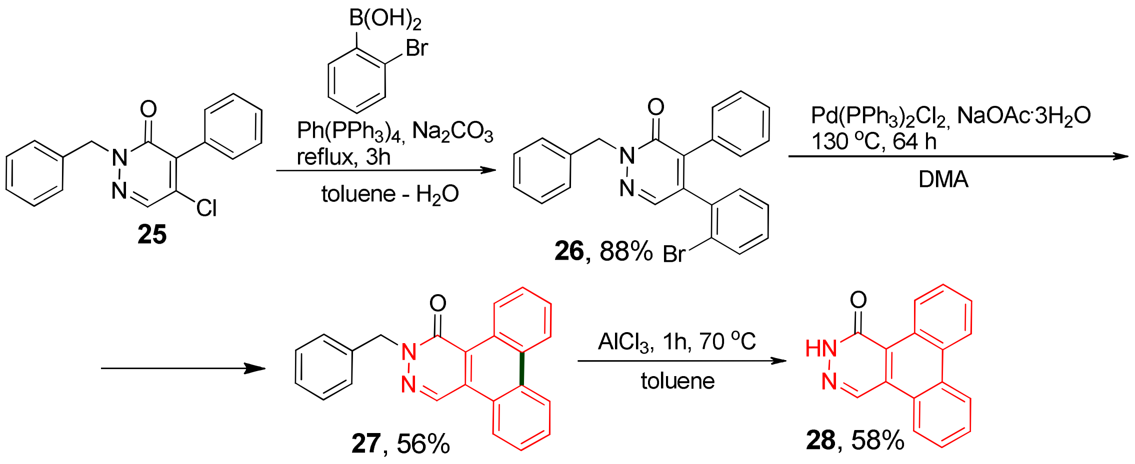
Scheme 5. Synthesis of dibenzo[*f,h*]cinnolinone (**21**) via palladium-catalyzed intramolecular arylation.

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]



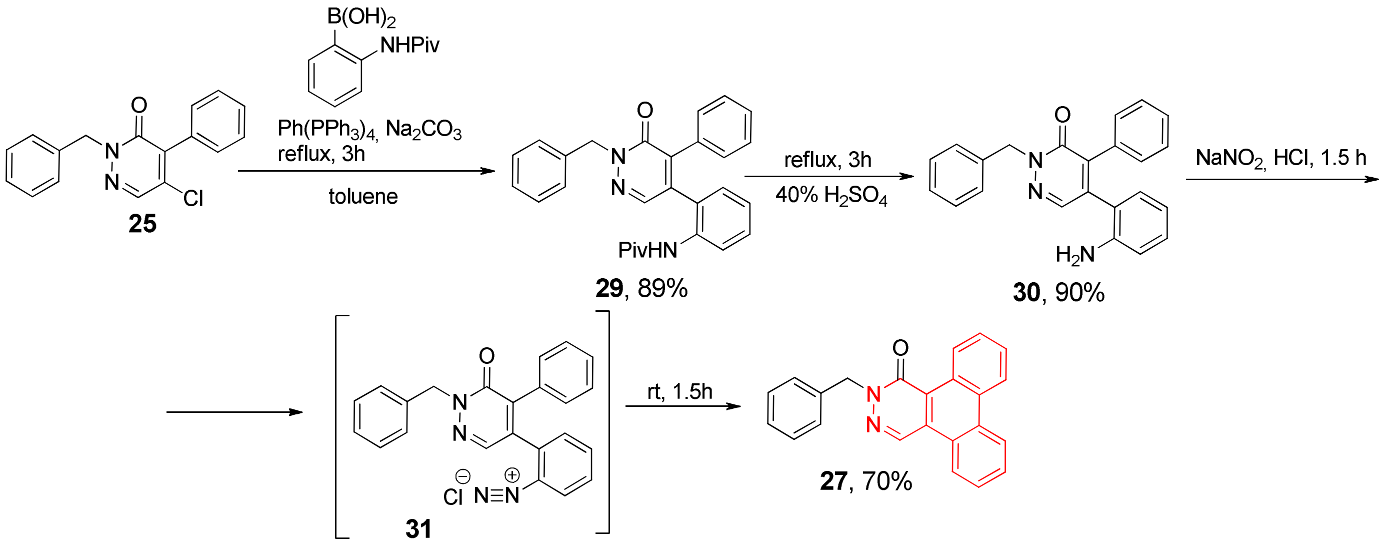
Scheme 6. Synthesis of dibenzo[*f,h*]cinnoline (**21**) via the Pschorr type ring closure reaction.

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-benzyldibenzo[*f,h*]phthalazin-1(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.

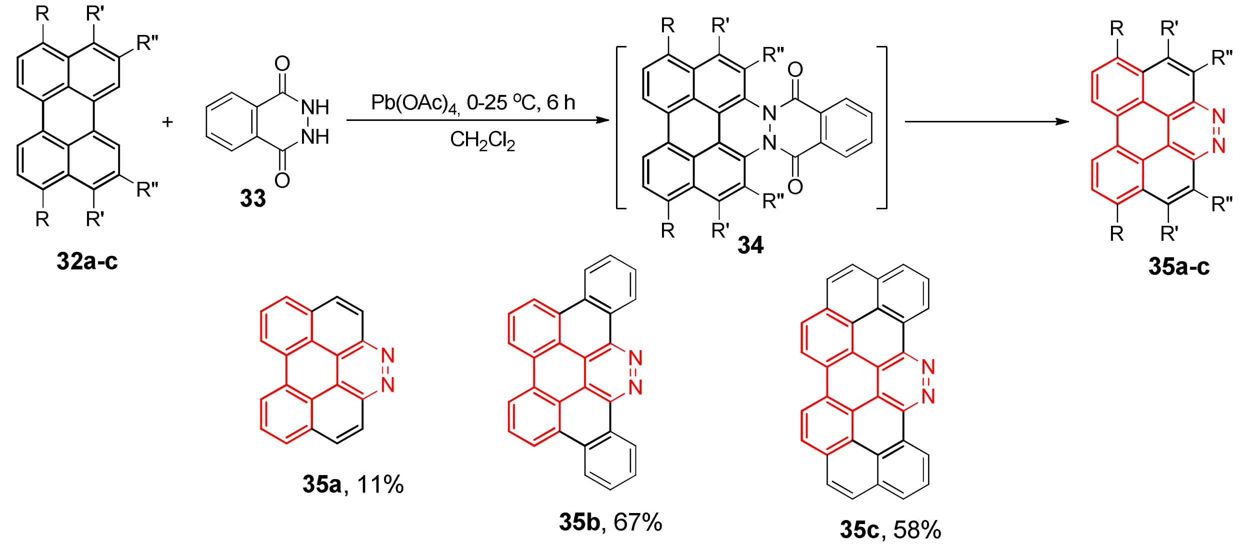
Analogously, 2-benzyldibenzo[*f,h*]phthalazin-1(2*H*)-one (**27**) was prepared from 5-(2-aminophenyl)-2-benzyl-4-phenylpyridazin-3(2*H*)-one (**30**) via the Pschorr type ring closure reaction, caused by decomposition of the corresponding diazonium salt (**31**) at room temperature (Scheme 8).



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

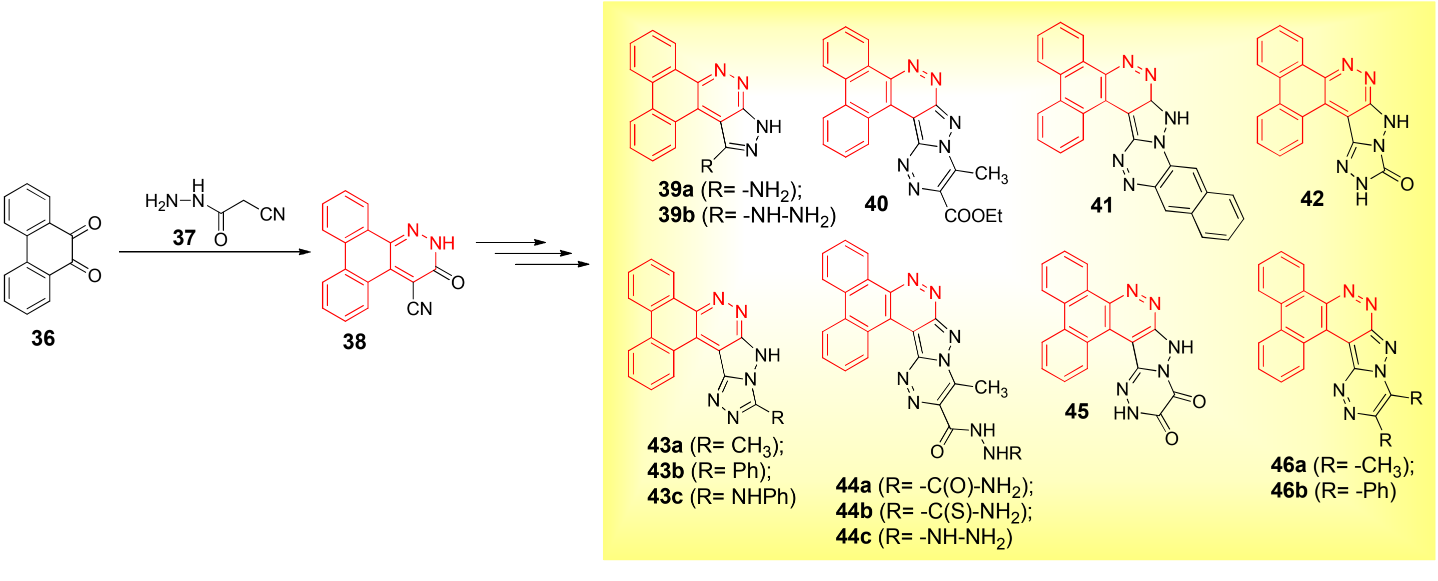
In fact, the diazotization / Pschorr type ring closure of **30** is certainly a superior method for the preparation of **27**, affording the target product in 70% yield (56% overall yield from **25**) within 3 hours of the reaction time. It should be compared with 56% yield of the same product (49% overall 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 ^{o}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]

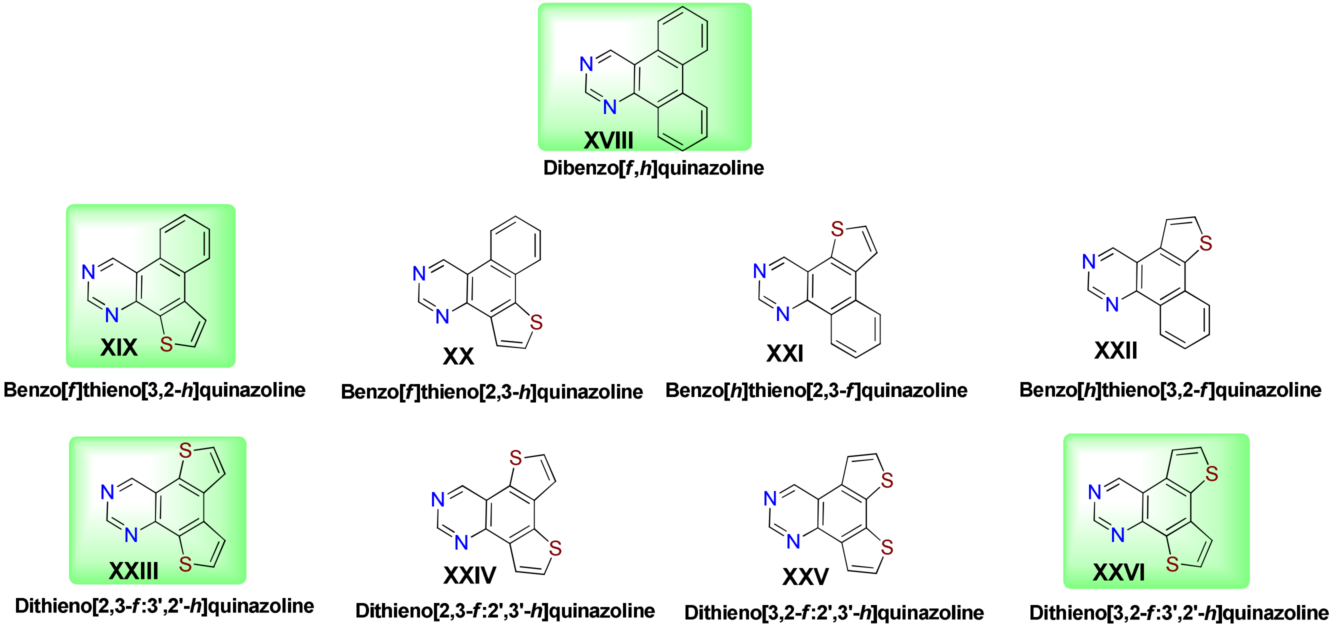
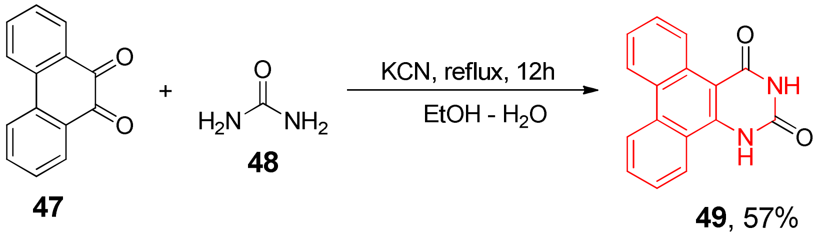


Figure 3. Structures of possible tetracyclic systems, as analogues of 1,3-diazatriphenylene.

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.

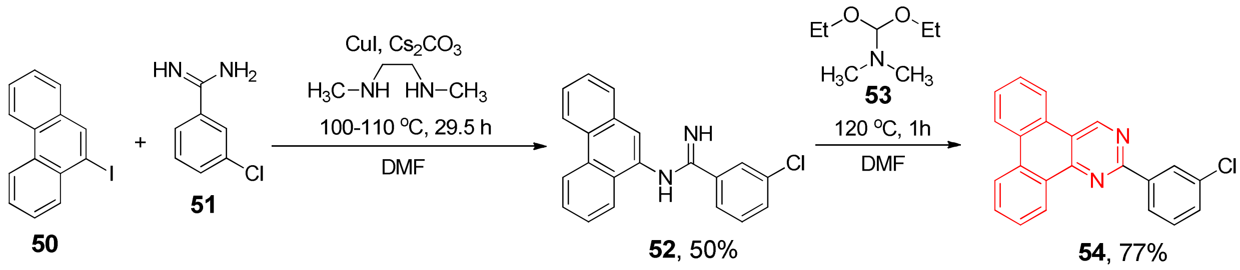
Various cyclocondensations are related with the first type of the synthesis of dibenzo[*f*,*h*]quinazolines (**XVIII**). Thus, Mahmoodi *et al.*[83] have demonstrated a simple cyclocondensation of phenanthren-9,10-dione (**47**) with urea (**48**), proceeding in an alkaline ethanol solution, and affording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

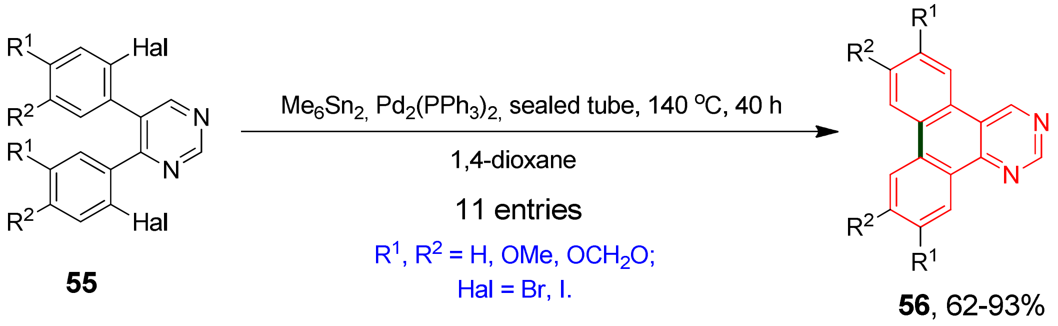
Another two-step pathway to dibenzo[*f*,*h*]quinazoline (**XVIII**) skeleton has been proposed by Hara *et al.*[78] At the fist step, 9-iodophenanthrene (**50**) reacts with 3-chlorobenzamidine hydrochloride (**51**) at 100-110 °C in dimethylformamide in the presence of CuI, Cs_2CO_3 and *N,N'*-dimethylethylenediamine 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).



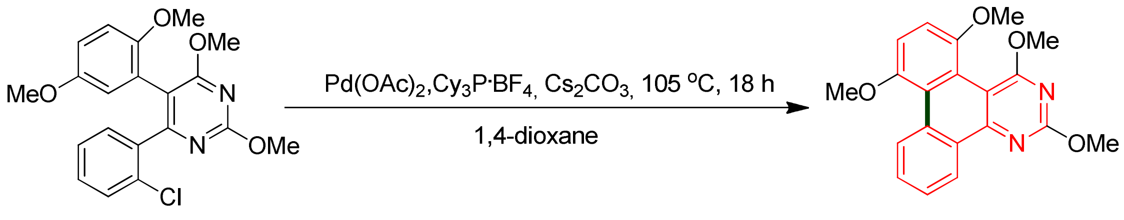
Scheme 12. Synthesis of dibenzo[*f*,*h*]quinazoline (**XVIII**) skeleton via condensation of *N*-(phenanthren-9-yl)-3-chlorobenzamidine (**52**) with diethyl acetal (**53**).

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.

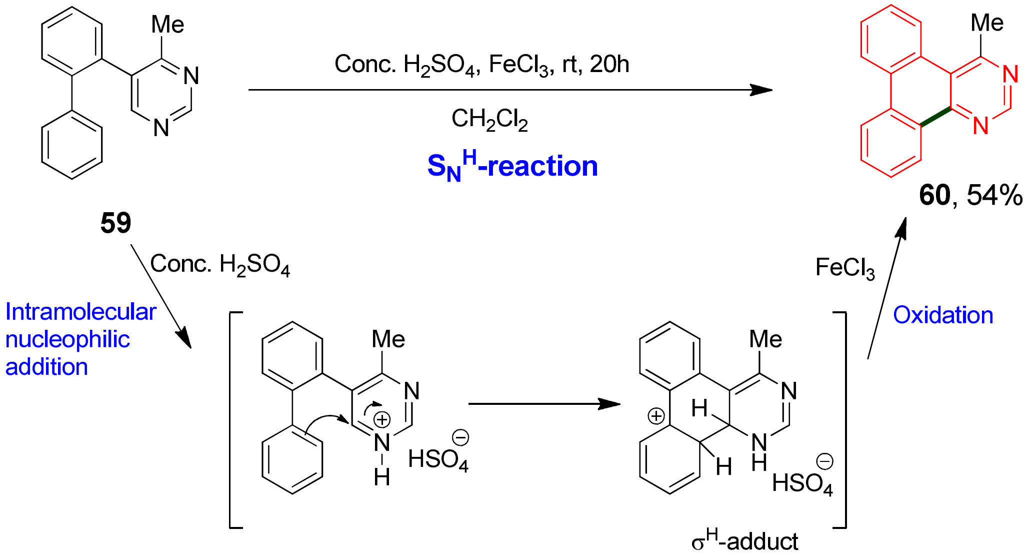
2,4,5,8-Tetramethoxydibenzo[*f*,*h*]quinazoline (**58**) has been prepared in 68% yield through the intramolecular C-H arylation of the corresponding chloride **57** in the presence of palladium(II) acetate and tri(cyclohexyl)phosphine, as an effective transition-metal catalyst, and cesium carbonate,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



57 **58**, 68%

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**).

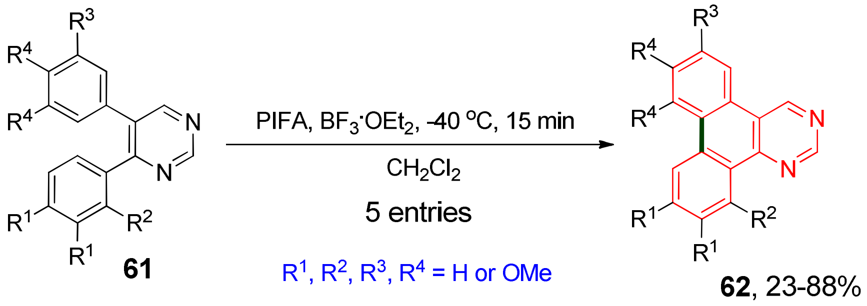
Intramolecular version of nucleophilic aromatic substitution of hydrogen (the S_N^H reaction) has been used to synthesize dibenzo[*f,h*]quinazoline derivative (**60**) from 5-([1,1′-biphenyl]-2-yl) substituted pyrimidine (**59**), by using concentrated sulfuric acid as a catalyst and iron(III) chloride, as an oxidant (Scheme 15).[79] For a better understanding of the S_N^H reactions, see the recently published review[87] and references cited therein.



59 **60**, 54%

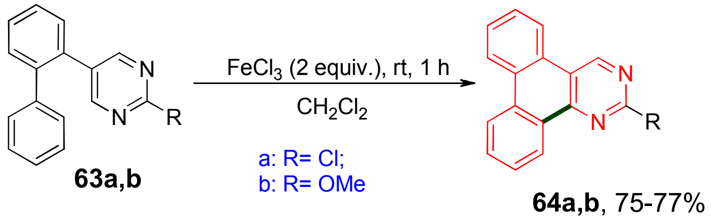
Scheme 15. Synthesis of dibenzo[*f,h*]quinazoline (**XVIII**) skeleton from 5-(1,1′-biphenyl-2-yl) substituted pyrimidine (**59**) via intramolecular S_N^H reaction.

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).

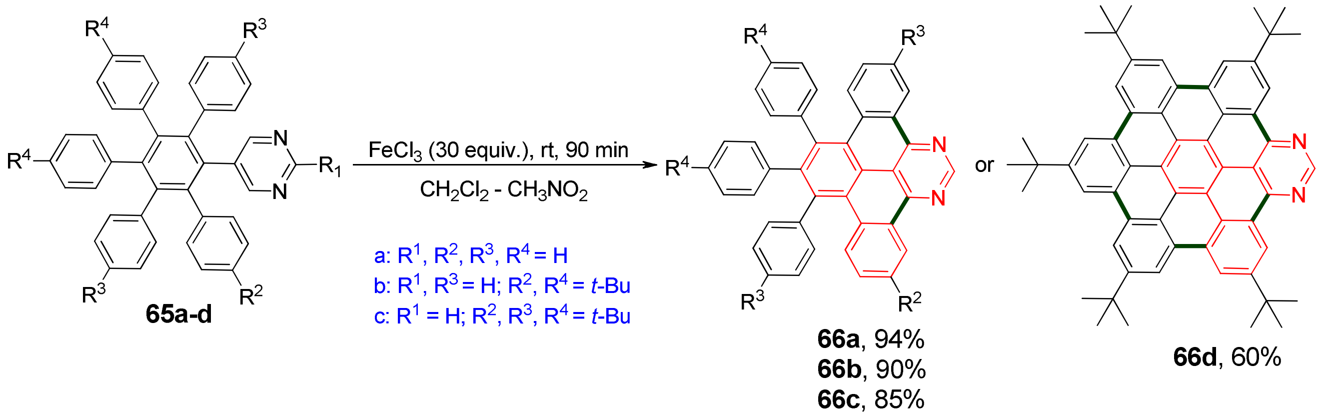


Scheme 16. Synthesis of substituted dibenzo[*f,h*]quinazolines (**62**) via the oxidative cyclodehydrogenation of 4,5-diphenylpyrimidines (**61**).

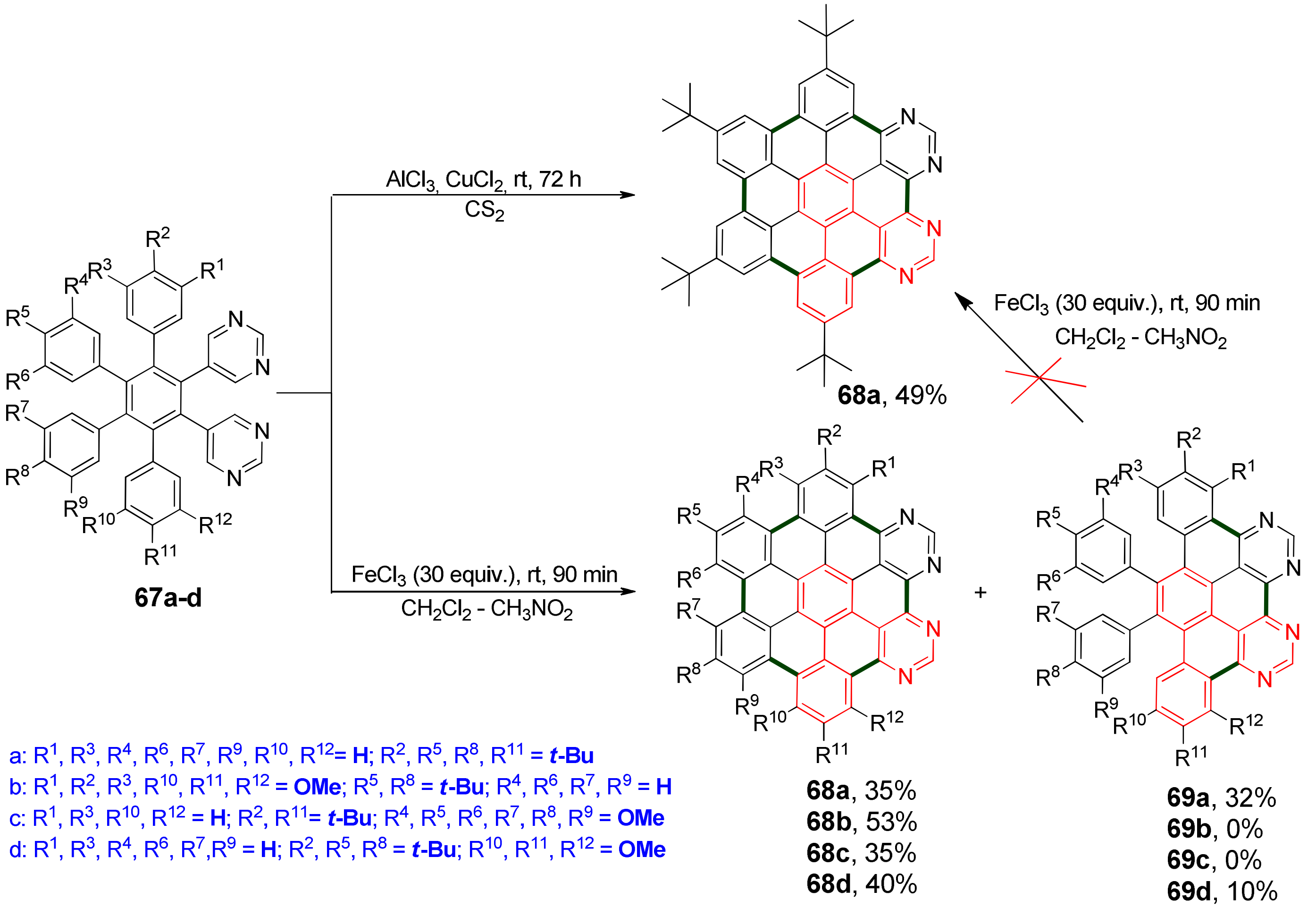
On the contrary, iron(III) chloride proved to be an appropriate oxidant for the intramolecular oxidative cyclodehydrogenation of 5-(1,1′-biphenyl-2-yl) substituted pyrimidines (**63**) and compounds (**65** and **67**), bearing a similar structural motif, to prepare 2-substituted dibenzo[*f,h*]quinazolines[52] (**64**) (Scheme 17), as well as nitrogen-doped nanographenes[91-95] (**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 $AlCl_3/CuCl_2$ in CS_2 results in the formation of heterosuperbenzene **68a**, while use of a milder catalytic system ($FeCl_3$/nitromethane/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 $AlCl_3/CuCl_2$, 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.



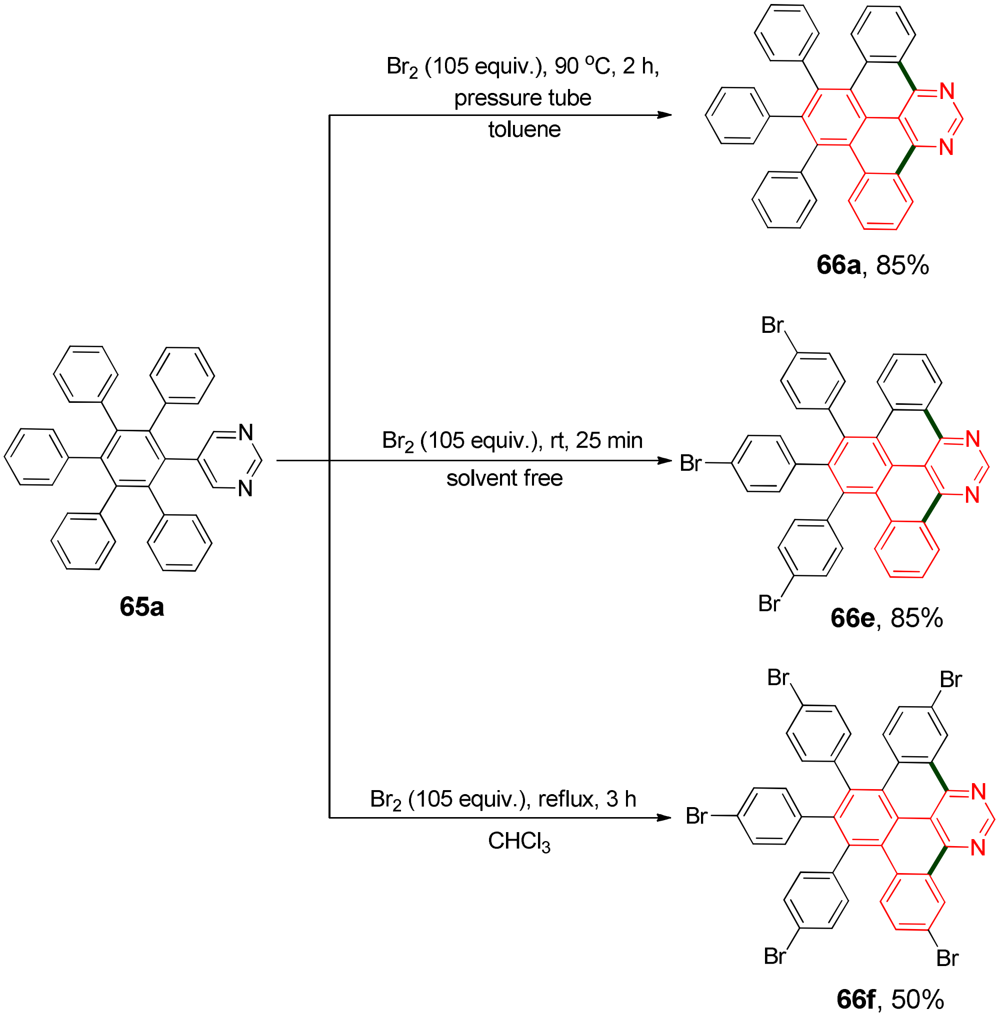
Scheme 18. Synthesis of heterosuperbenzenes **66** from pyrimidyl substituted pentaphenylbenzenes **65** via Scholl cyclodehydrogenation.



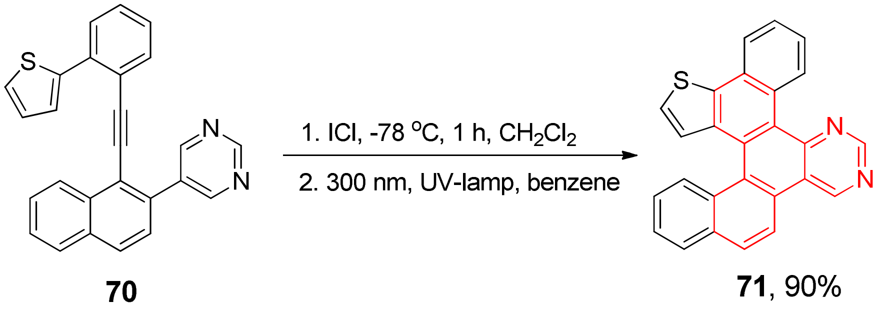
Scheme 19. Synthesis of heterosuperbenzenes (**68** and **69**) from 1,2-dipyrimidyl-3,4,5,6-tetraarylbenzenes **67** via Scholl cyclodehydrogenation.

Also, Draper *et al.*[96] have demonstrated that use of elemental bromine in the reaction with diaza-polyphenylenes 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).

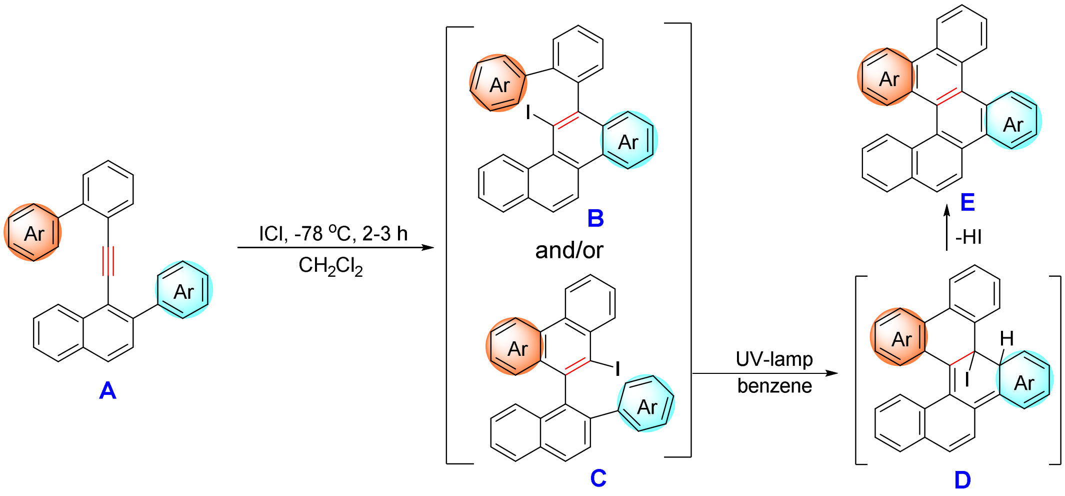
Recently, Mohamed *et al.*[97] have proposed a novel versatile method for the synthesis of fused functionalized helicenes, affording, for instance, naphtho[2,1-*f*]thieno[3′,2′:3,4]naphtho[2,1-*h*]quinazoline (**71**) in a high yield (Scheme 21). The first core ring of the helicene (**E**) is assembled 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.

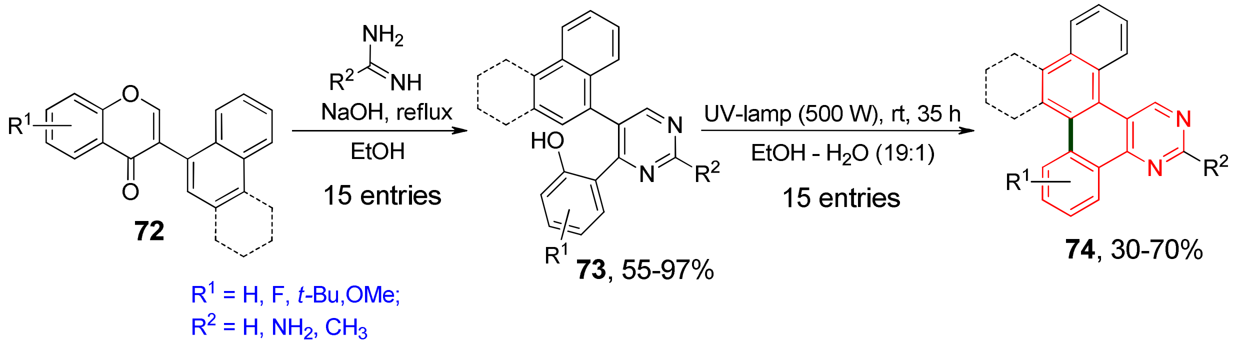


Scheme 21. Synthesis of dibenzo[*f,h*]quinazoline **71** (structural type **XVIII**) through the iodonium-induced carbocyclization with the subsequent light-induced cyclodehydroiodination.



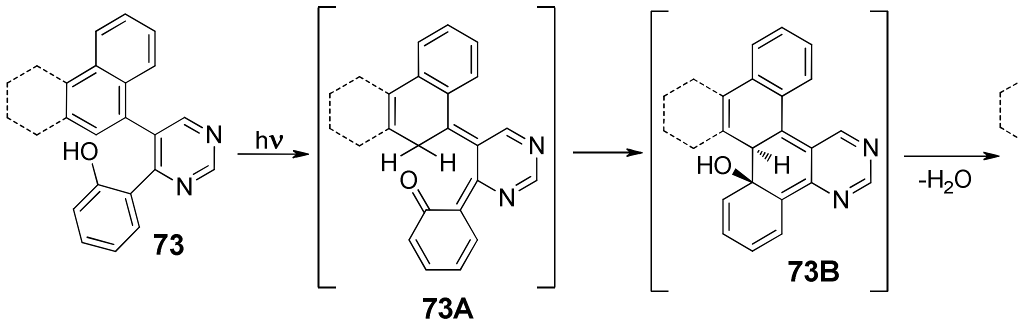
Scheme 22. A mechanism proposed for the synthesis of fused functionalized helicenes through the iodonium-induced carbocyclization of bis(biaryl)acetylenes with subsequent light-induced cyclodehydroiodination.

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*]quinazoines (**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-H_2O (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).



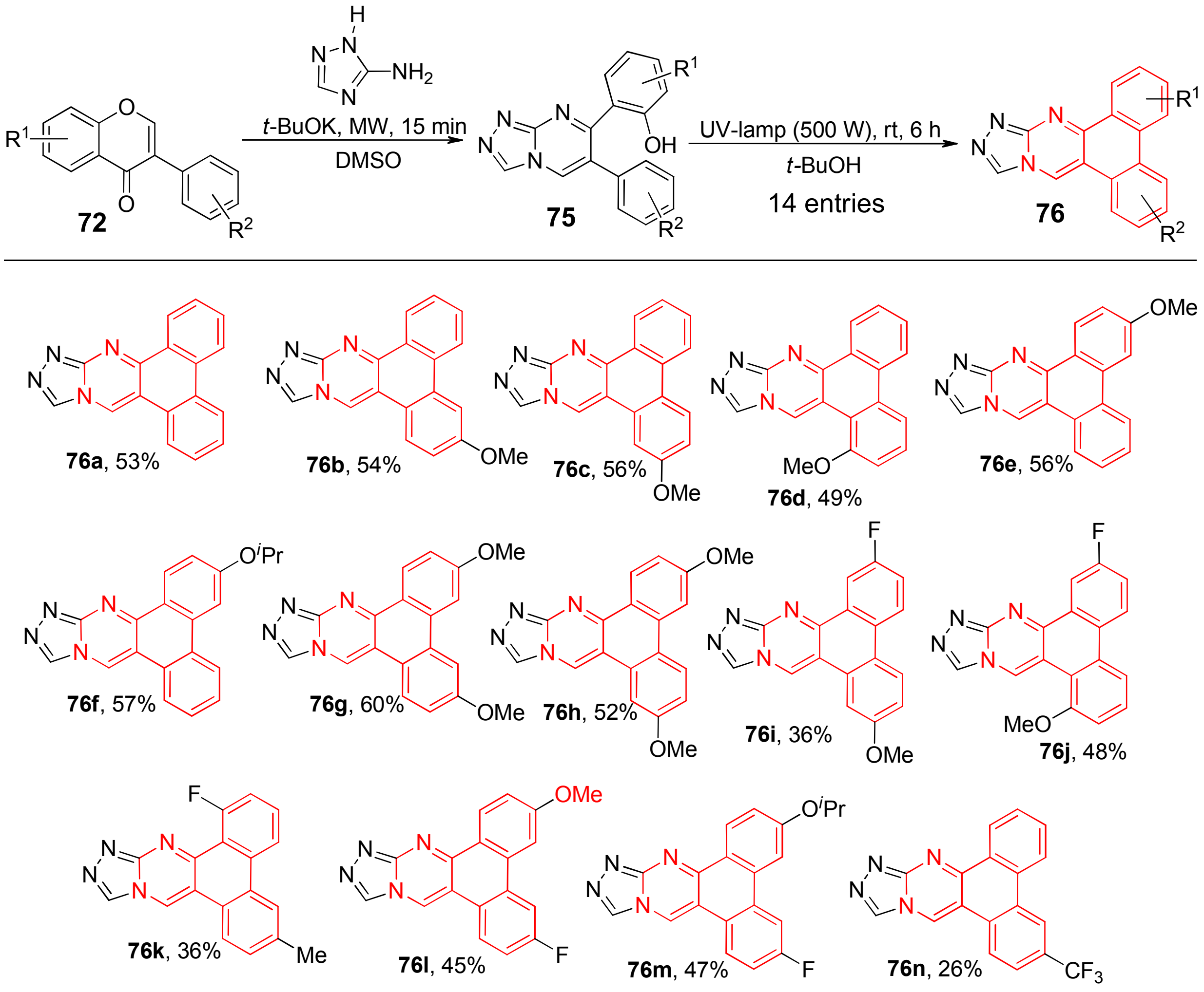
Scheme 23. Synthesis of dibenzo[*f,h*]quinazoline (**XVIII**) skeleton via the photoinduced dehydration.

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**.



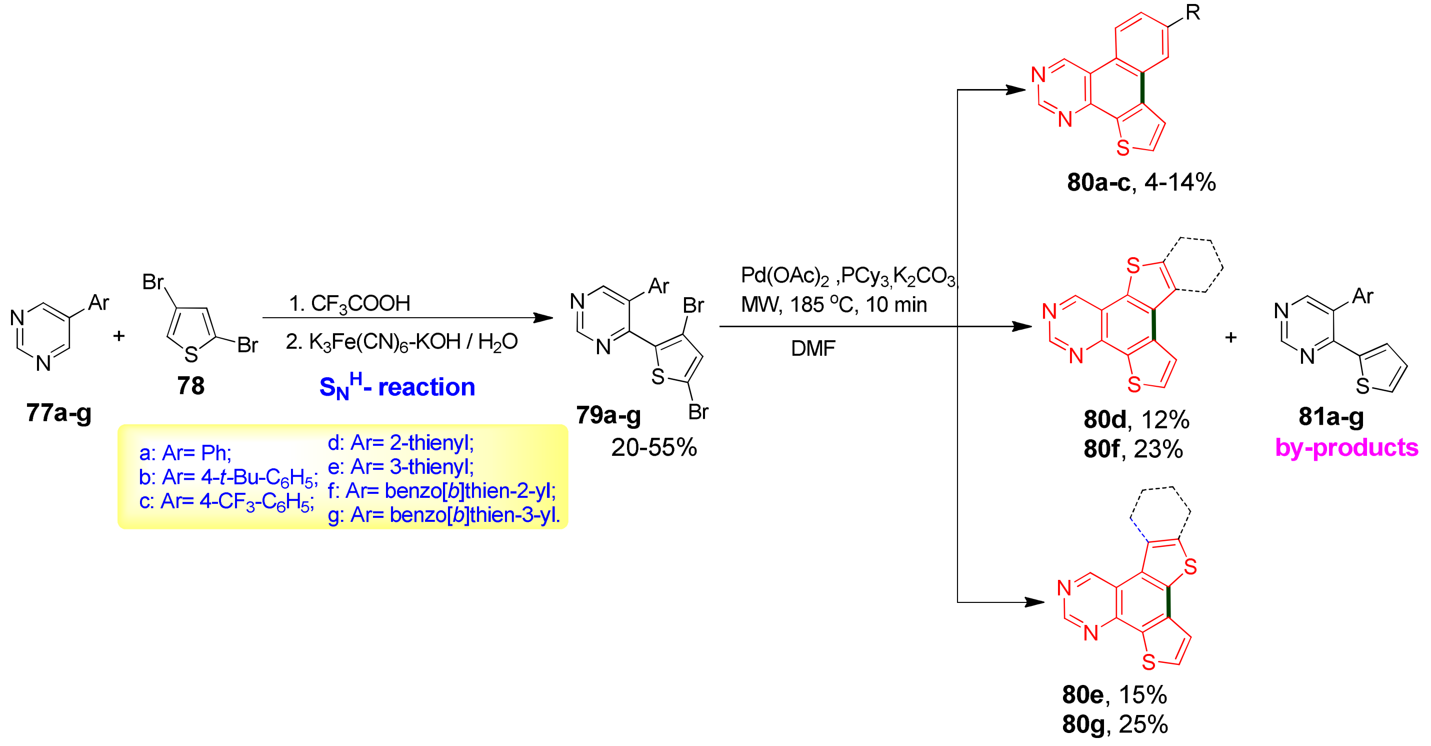
Scheme 24. A plausible mechanism for the photocyclization reaction.

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]



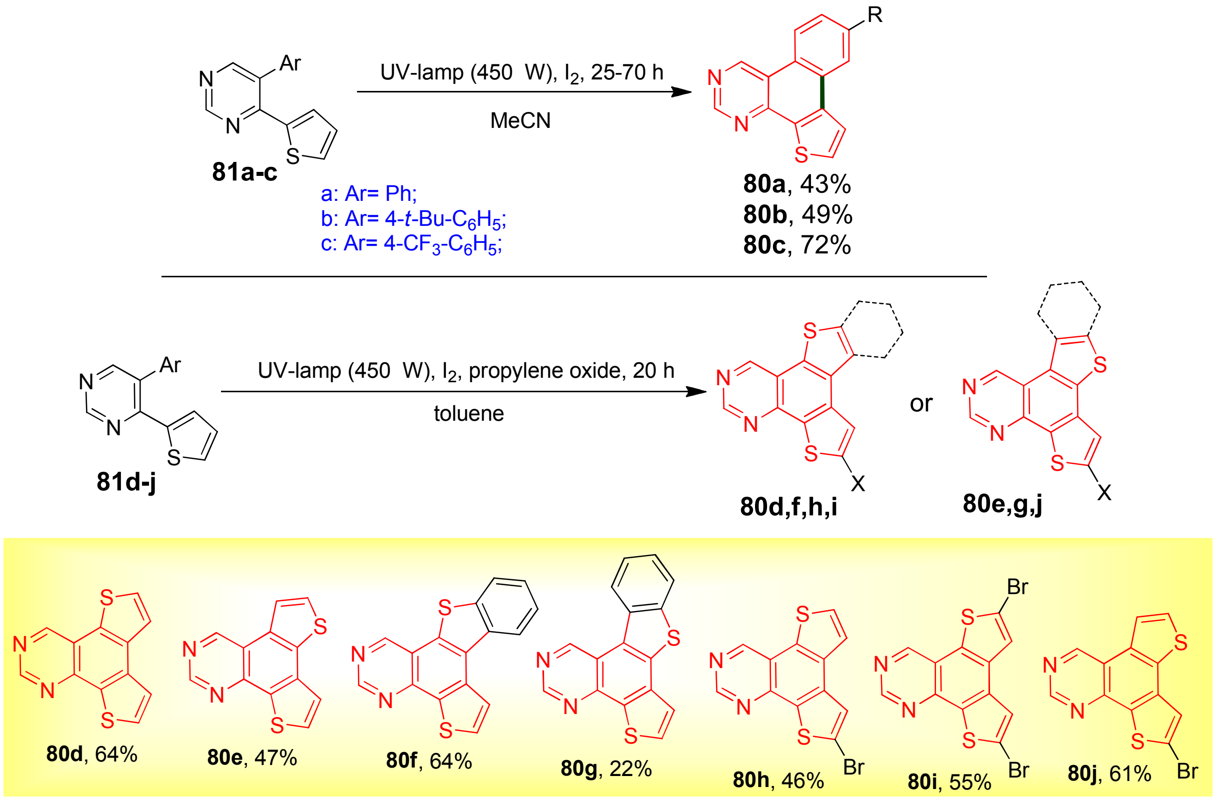
Scheme 25. Synthesis of dibenzo[*f,h*][1,2,4]triazolo[3,4-*b*]quinazolines (**76a-n**) through a two-step reaction pathway; overall yields of product **76** from **72** are given.

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)aryl-pyrimidines (**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-dibromothien-2-yl)-5-(hetero)arylpyrimidines (**79a-g**).

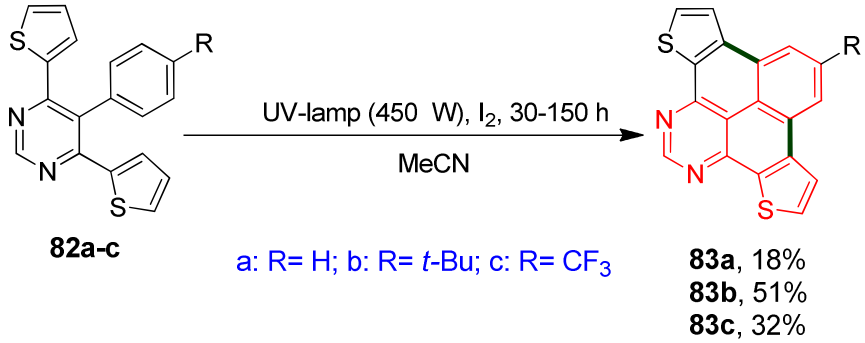


Scheme 26. Synthesis of benzo[*f*]thieno[3,2-*h*]quinazoline (**80a-c**), dithieno[2,3-*f*:3′,2′-*h*]quinazoline (**80d,f**) and dithieno[3,2-*f*:3′,2′-*h*]quinazoline (**80e,g**) derivatives via Pd-catalyzed intramolecular cyclization of **79a-g** under microwave irradiation.

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-yl-pyrimidines (**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(hetro)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.

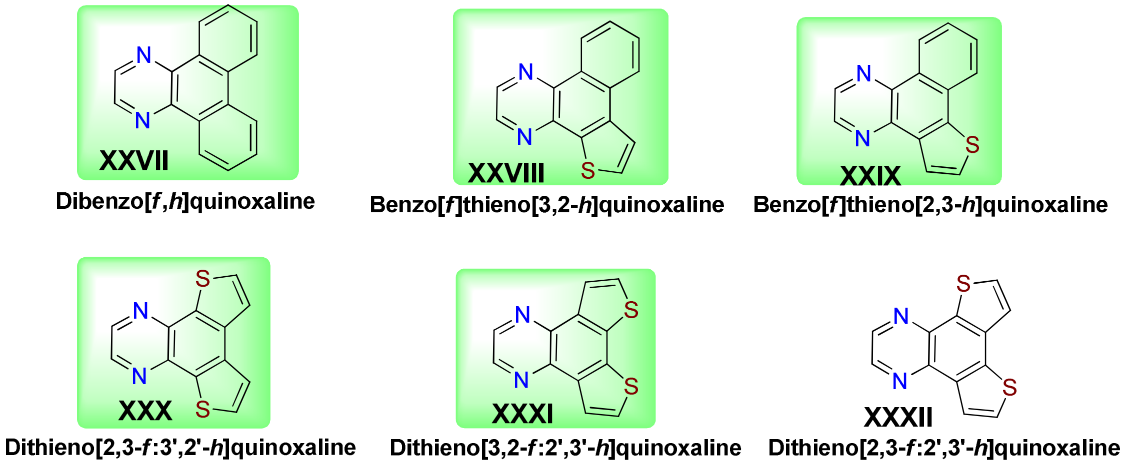
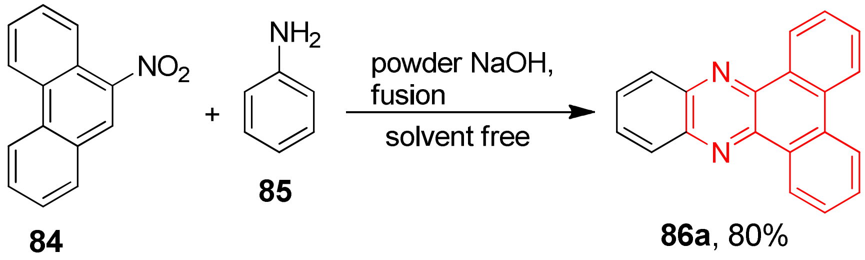


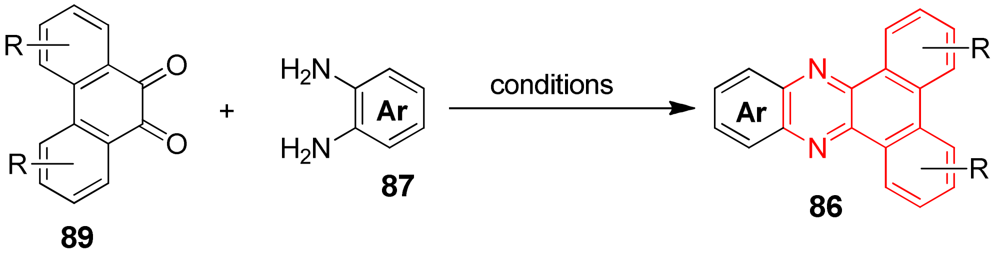
Figure 4. The structures of tetracyclic aromatic systems bearing the pyrazine ring.

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**)

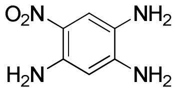
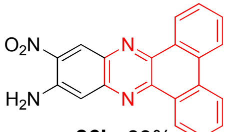
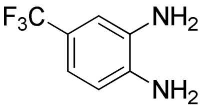
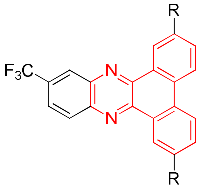
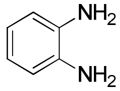
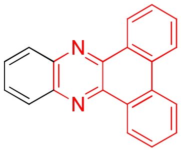
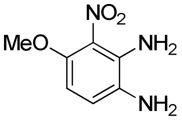
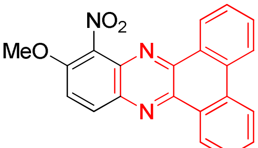
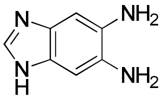
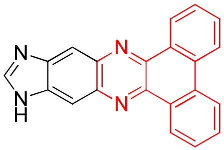
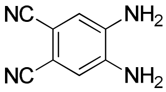
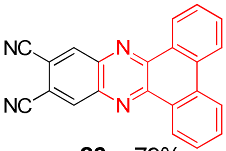
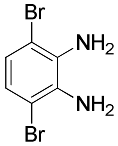
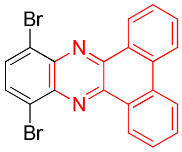
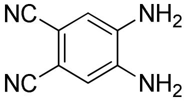
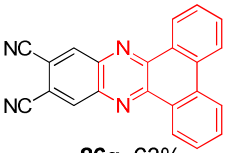
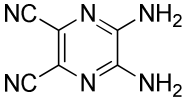
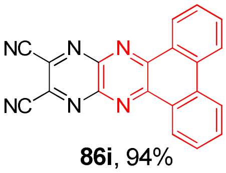
Entry	1,2-Diamine (**87**)	Conditions	Product (**86**)– Isolated yield	Ref.
1	 **87b**	EtOH - CH_3COOH (3:10), reflux, 20 min.	 **86b**, 89%	104
2	 **87c**	Fusion	 **86c (R= H)**, 88% **86d (R= NO$_2$)**, 88%	105
3	 **87a**	EtOH, reflux with catalytic amount HCl, 2 h.	 **86a**, 88%	106
4	 **87d**	EtOH - 5M HCl solution (50:1), reflux, 40 min.	 **86e**, 74%	107
5	 **87e**	EtOH, EtONa, reflux.	 **86f**, 75%	108
6	 **87f**	CH_3COOH, reflux.	 **86g**, 79%	109
7	 **87g**	EtOH - CH_3COOH (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

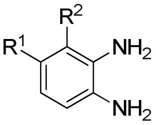
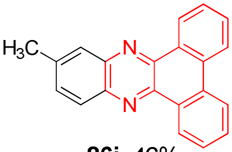
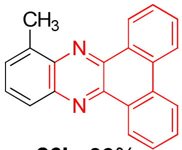
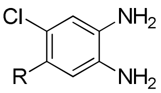
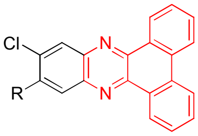
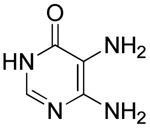
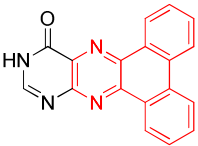
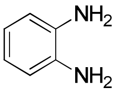
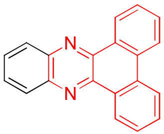
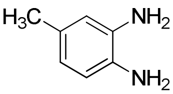
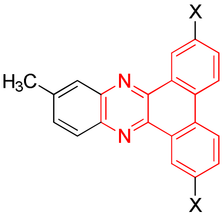
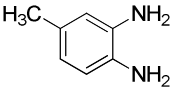
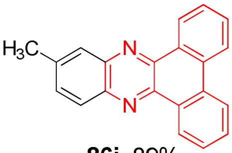
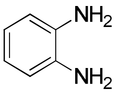
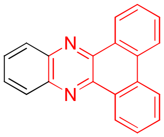
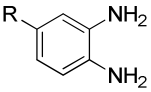
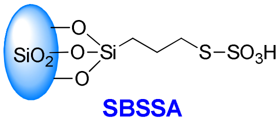
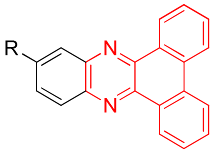
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
10	 **87i (R^1= CH$_3$, R^2= H)** **87j (R^1= H, R^2= CH$_3$)**	$CHCl_3$ - CF_3COOH (298:1), reflux, 6 h. $CHCl_3$, reflux, 29 h.	 **86j**, 46%  **86k**, 89%	113
11	 **87k (R= H)** **87l (R= Cl)**	glacial CH_3COOH, reflux, 5 h.	 **86l (R= H)**, 85% **86m (R= Cl)**, 83%	114
12	 **87m**	CH_3COOH, CH_3COONa, 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_3COOH, 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_2O (70:30), SBSSA (3.4 mol %), rt, 5 min.  **SBSSA** (silica bonded *S*-sulfonic acid)	 **86a (R= H)**, 94% **86j (R= CH$_3$)**, 92%	120

Table 1. Continued

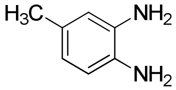
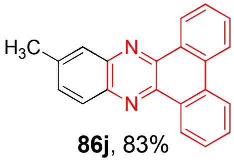
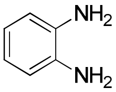
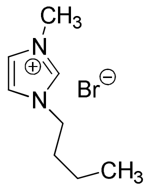
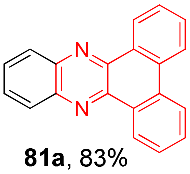
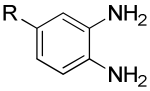
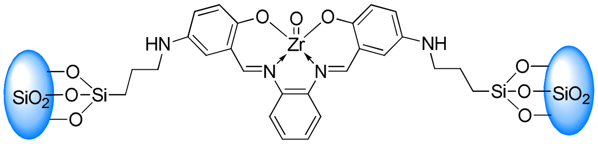
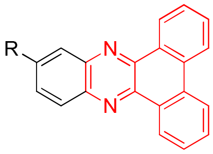
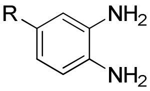
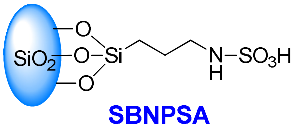
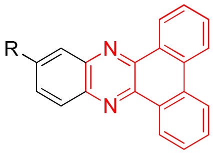
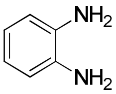
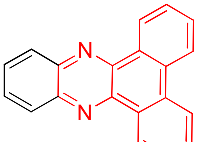
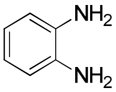
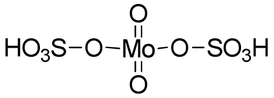
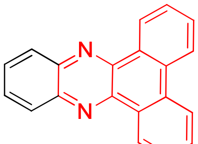
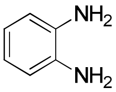
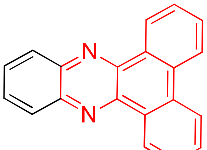
Entry	1,2-Diamine (87)	Conditions	Product (86)–Isolated yield	Ref.
18	 **87i**	EtOH - conc. HCl, (20:1), reflux, 4 h.	 **86j**, 83%	121
19	 **87a**	[bmim]Br (1.5 equiv.), MW (500 W), 130 °C, 30 min.  **[bmim]Br** (Ionic liquid 1-butyl-3-methylimidazolium bromide)	 **81a**, 83%	122
20	 **87a (R= H)** **87i (R= CH_3)**	EtOH, catalyst (10 wt.%), rt, 1.7-2.0 h.  **Catalyst**	 **81a (R= H)**, 89% **81j (R= CH_3)**, 87%	123
21	 **87a (R= H)** **87i (R= CH_3)**	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	 **87a**	Polyethylene glycol (PEG-600) - H_2O (1:1), rt, 5 min.	 **81a**, 97%	125
23	 **87a**	EtOH, MSA (5 mol %), rt, 8 min.  $HO_3S{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{Mo}}{-}O{-}SO_3H$ **MSA** (Molybdate sulfuric acid)	 **81a**, 98%	126
24	 **87a**	Glycerol – H_2O (5 :2), 90 ºC, 4h.	 **81a**, 90%	127

Table 1. Continued

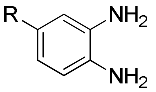
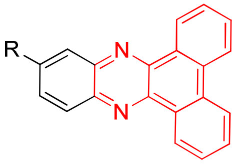
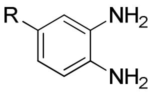
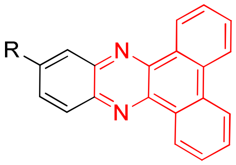
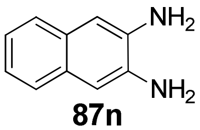
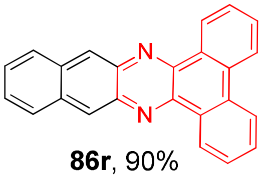
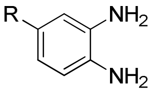
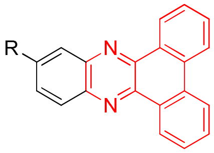
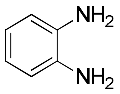
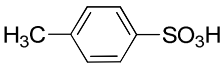
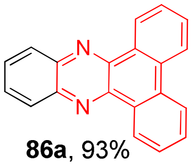
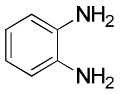
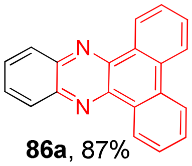
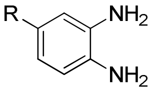
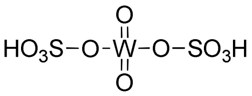
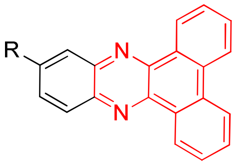
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
25	 **87a (R= H)** **87i (R= CH_3)**	EtOH, $MgSO_4·7H_2O$ (20 mol %), rt, 15 min.	 **81a (R= H)**, 90% **81j (R= CH_3)**, 92%	128
26	 **87a (R= H)** **87i (R= CH_3)**	1,2-Dichloroethane, nano-TiO_2 (2.5 mol %), rt, 20-25 min.	 **81a (R= H)**, 90% **81j (R= CH_3)**, 91%	129
27	 **87n**	EtOH, reflux, 2 h.	 **86r**, 90%	130
28	 **87a (R= H)** **87i (R= CH_3)**	Ball-milling, solvent free, rt, 4 h.	 **86a (R= H)**, >99% **86j (R= CH_3)**, 95%	131
29	 **87a**	H_2O, PTSA (5 mol %), NaPTSA (40 wt.%), rt, 7 min.  **PTSA**	 **86a**, 93%	132
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= CH_3)**	Solvent free, TSA (5 mol %), grinding, rt, 20-22 min.  $HO_3S{-}O{-}\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{W}}{-}O{-}SO_3H$ **TSA** (Tungstate sulfuric acid)	 **86a (R= H)**, 91% **86j (R= CH_3)**, 90%	134

Table 1. Continued

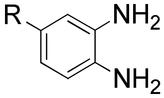
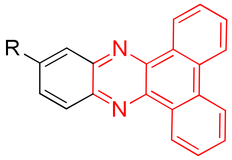
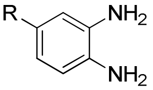
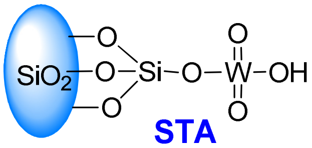
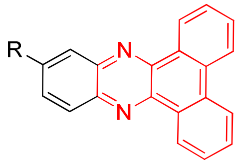
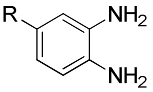
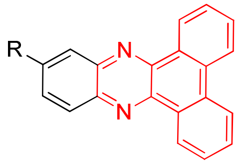
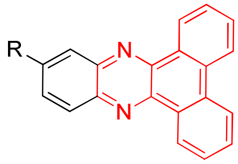
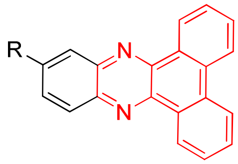
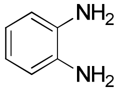
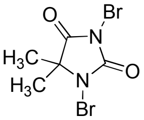
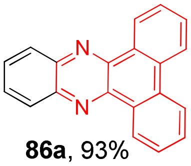
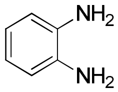
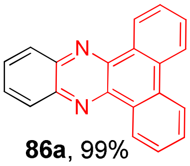
Entry	1,2-Diamine (87)	Conditions	Product (86)–Isolated yield	Ref.
32	 **87a (R= H)** **87i (R= CH_3)** **87k (R= Cl)**	EtOH, LiCl (10 mol %), rt, 8-42 min.	 **86a (R= H)**, 95% **86j (R= CH_3)**, 95% **86l (R= Cl)**, 84%	135
33	 **87a (R= H)** **87i (R= CH_3)**	Solvent free, STA (2 mol %), grinding, rt, 5 min.  **STA** (Silica tungstic acid)	 **86a (R= H)**, 90% **86j (R= CH_3)**, 90%	136
34	 **87a (R= H)** **87i (R= CH_3)**	EtOH, $CrCl_2 \cdot 6H_2O$ (10 mg to 1.1 mmol **87a,i**), r.t., 9 min.	 **86a (R= H)**, 96% **86j (R= CH_3)**, 94%	137
		EtOH, $PbBr_2$ (10 mg to 1.1 mmol **87a,i**), r.t.,16 min.	 **86a (R= H)**, 96% **86j (R= CH_3)**, 95%	
		EtOH, $CuSO_4 \cdot 5H_2O$ (10 mg to 1.1 mmol **87a,i**), r.t., 32 min.	 **86a (R= H)**, 92% **86j (R= CH_3)**, 90%	
35	 **87a**	Solvent free, DBH (6 mol %), oil bath, 110 ºC, 30 min.  **DBH** (1,3-Dibromo-5,5-dimethylhyndantoin)	 **86a**, 93%	138
36	 **87a**	EtOH-H_2O (7:3), PhOH (20 mol %), rt, 2 min.	 **86a**, 99%	139

Table 1. Continued

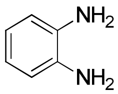
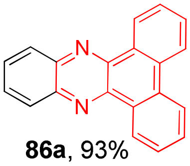
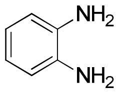
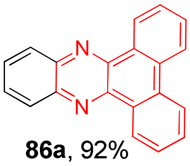
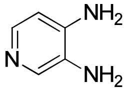
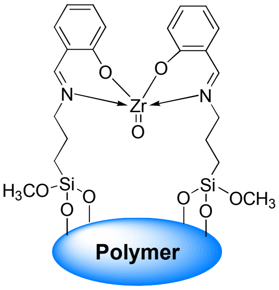
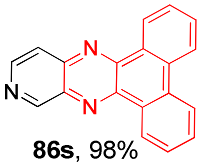
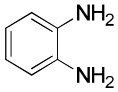
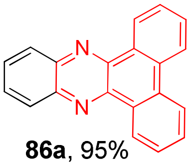
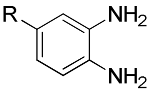
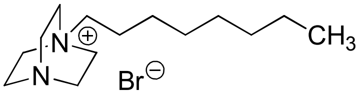
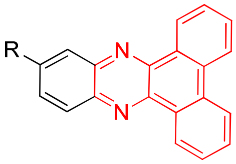
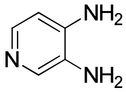
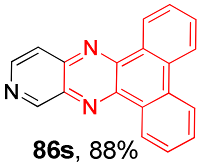
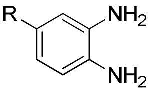
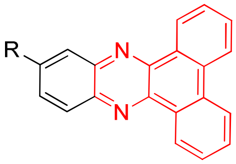
Entry	1,2-Diamine (87)	Conditions	Product (86)– Isolated yield	Ref.
37	 **87a**	EtOH, graphite (2 equiv.), rt, 30 min.	 **86a**, 93%	140
38	 **87a**	CH_3CN – H_2O (1:1), rice husk (0.35 mol %), 50 ºC, 20 min.	 **86a**, 92%	141
39	 **87o**	H_2O, catalyst (10 mg to 1.0 mmol **87o**), reflux, 2 h.  **Catalyst**	 **86s**, 98%	142
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= CH_3)**	H_2O, catalyst (1 equiv.), rt for 10 min. and 70 °C for 35-38 min..  **Catalyst**	 **86a (R= H)**, 90% **86j (R= CH_3)**, 85%	144
42	 **87o**	EtOH, $FeCl_3$ (20 mmol %), reflux, 80 min.	 **86s**, 88%	145
43	 **87a (R= H)** **87i (R= CH_3)**	EtOH, $PbCl_2$ (20 mol %), rt, 10 min.	 **86a (R= H)**, 95% **86j (R= CH_3)**, 95%	146

Table 1. Continued

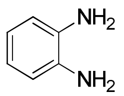
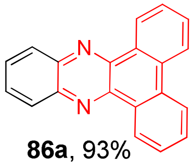
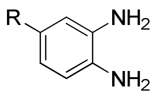
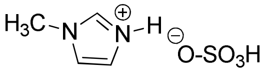
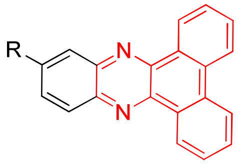
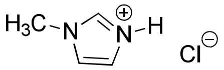
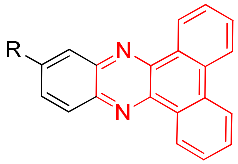
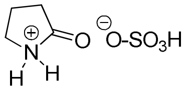
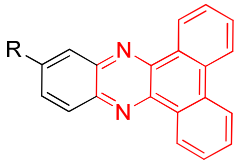
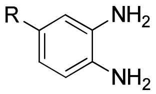
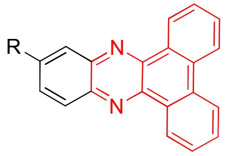
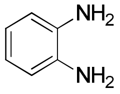
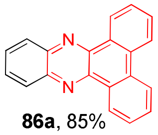
Entry	1,2-Diamine (87)	Conditions	Product (86)–Isolated yield	Ref.
44	 **87a**	Solvent free, nano-ZnO (1.1 mol %), rt, 20 min.	 **86a**, 93%	147
45	 **87a (R= H)** **87i (R= CH_3)**	H_2O, ionic liquid [Hmim]HSO_4 (10 mol %), rt, 3 min.  [Hmim]HSO_4 (1-Hydrogen-3-methylimidazolium hydrogen sulfate)	 **86a (R= H)**, 95% **86j (R= CH_3)**, 97%	148
		H_2O, 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_2O, ionic liquid [Hnhp]HSO_4 (10 mol %), rt, 7 min.  [Hnhp]HSO_4 (2-Pyrrolidonium hydrogen sulfate)	 **86a (R= H)**, 94% **86j (R= CH_3)**, 90%	
46	 **87i (R= CH_3)** **87p (R= NO_2)**	EtOH – H_2O (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

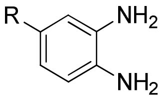
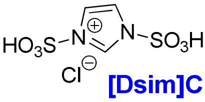
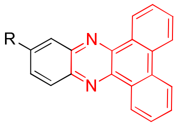
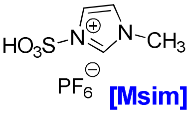
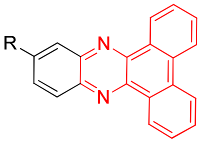
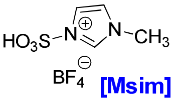
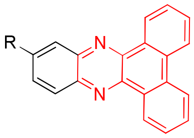
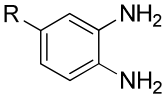
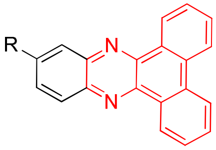
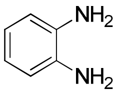
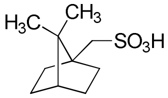
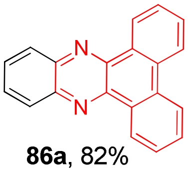
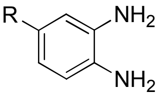
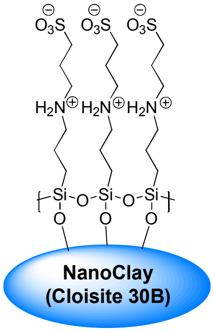
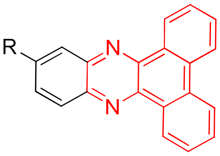
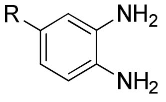
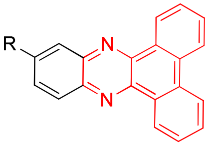
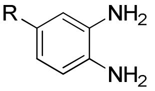
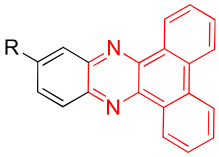
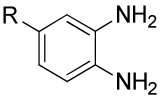
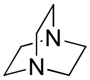
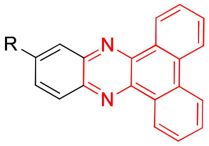
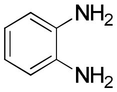
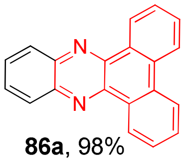
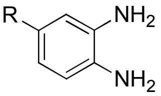
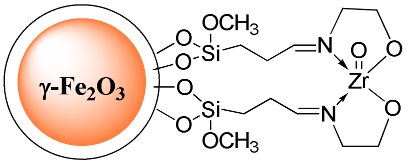
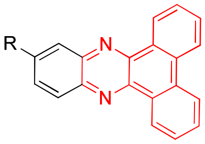
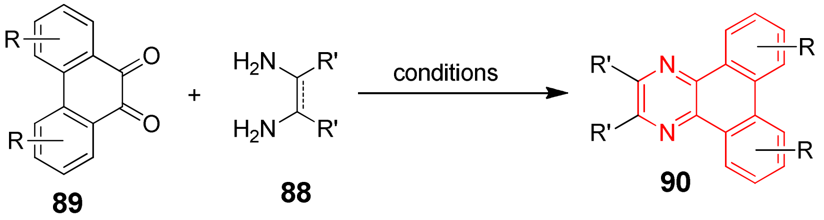
Entry	1,2-Diamine (87)	Conditions	Product (86)–Isolated yield	Ref.
48	 **87a (R= H)** **87i (R= CH_3)** **87p (R= NO_2)**	Solvent free, ionic liquid [Dsim]Cl (10 mol%), 110 °C, 2-20 min.  **[Dsim]Cl** (1,3-Disulfonic acid imidazolium chloride)	 **86a (R= H)**, 99% **86j (R= CH_3)**, 96% **86t (R= NO_2)**, 94%	151
		Solvent free, ionic liquid [Msim]PF_6 (10 mol%), 110 °C, 3-20 min.  **[Msim]PF_6** (3-Methyl-1-sulfonic acid imidazolium hexafluorophosphate)	 **86a (R= H)**, 96% **86j (R= CH_3)**, 93% **86t (R= NO_2)**, 90%	
		Solvent free, ionic liquid [Msim]BF_4 (10 mol%), 110 °C, 3-35 min.  **[Msim]BF_4** (3-Methyl-1-sulfonic acid imidazolium tetrafluoroborate)	 **86a (R= H)**, 97% **86j (R= CH_3)**, 95% **86t (R= NO_2)**, 89%	
49	 **87a (R= H)** **87k (R= Cl)** **87p (R= NO_2)**	5 M aqueous NaCl solution, 95 °C, 0.5-3 h.	 **86a (R= H)**, 92% **86l (R= Cl)**, 92% **86t (R= NO_2)**, 83%	152
50	 **87a**	EtOH – H_2O (1:3), DL-camphorsulfonic acid (5 mol%), rt, 20 min.  **DL-camphorsulfonic acid**	 **86a**, 82%	153
51	 **87a (R= H)** **87p (R= NO_2)**	EtOH, sulfonated nanoClay (5 mol%), rt, 15-25 min.  **Sulfonated nanoClay**	 **86a (R= H)**, 99% **86t (R= NO_2)**, 90%	154

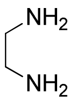
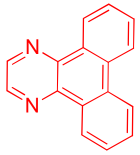
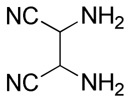
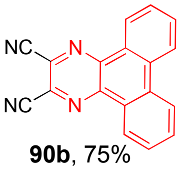
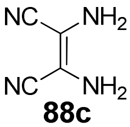
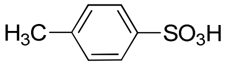
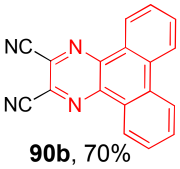
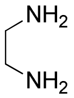
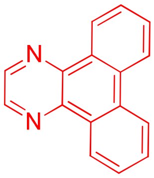
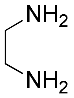
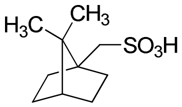
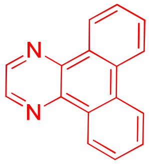
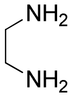
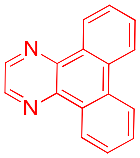
Table 1. Continued

Entry	1,2-Diamine (87)	Conditions	Product (86)–Isolated yield	Ref.
52	 **87a (R= H)** **87i (R= CH_3)** **87p (R= NO_2)**	EtOH – H_2O (7:3), phthalic acid (5 mol%), rt, 2-20 min.	 **86a (R= H)**, 99% **86j (R= CH_3)**, 95% **86t (R= NO_2)**, 93%	155
53	 **87a (R= H)** **87i (R= CH_3)**	H_2O, propylsulfonic acid functionalized nanozeolite clinoptilolite (10 mg to 1.0 mmol **87a,i**), rt, 10-15 min.	 **86a (R= H)**, 92% **86j (R= CH_3)**, 92%	156
54	 **87a (R= H)** **87i (R= CH_3)** **87p (R= NO_2)**	H_2O – CH_3COOH – DABCO (3:1:1), 80 °C, 20-40 min.  **DABCO** (1,4-Diazabicyclo[2.2.2]octane)	 **86a (R= H)**, 90% **86j (R= CH_3)**, 82% **86t (R= NO_2)**, 82%	157
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= NO_2)**	EtOH, nanoparticles (4 mg to 1.5 mmol **87a,p**), 60 °C, 3-60 min.  **Nanoparticles** (A zirconium Schiff base complex immobilized on starch-coated maghemite nanoparticles)	 **86a (R= H)**, 97% **86t (R= NO_2)**, 88%	159

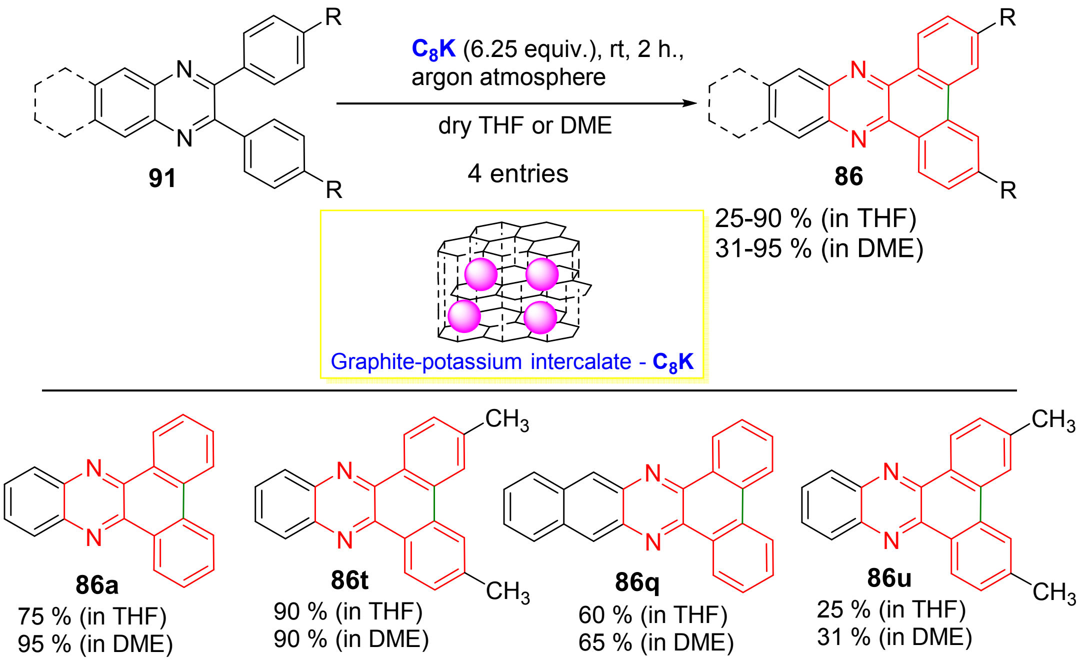


Scheme 31. Synthesis of dibenzo[*f,h*]quinoxaline (**90**) by condensation of ethylenediamines (**88**) with substituted phenanthren-9,10-diones (**89**).

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

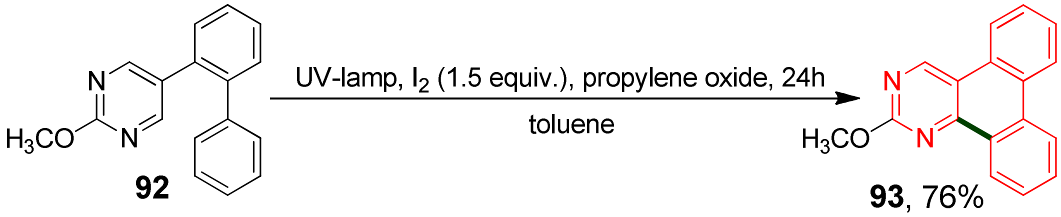
Entry	1,2-Diamine (**88**)	Conditions	Product (**90**) – Isolated yield	Ref.
1	 **88a**	EtOH – CH_3COOH (3:10), reflux, 20 min.	 **90a**, 78%	160
2	 **88b**	EtOH, reflux with catalytic amount CH_3COOH, 2 h.	 **90b**, 75%	161
3	 **88c**	EtOH, PTSA (0.26 mol %), reflux, 5 h.  **PTSA**	 **90b**, 70%	162
4	 **88a**	5 M aqueous NaCl solution, 95 °C, 1 h.	 **90a**, 82%	152
5	 **88a**	EtOH – H_2O (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 (**C_8K**) 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]



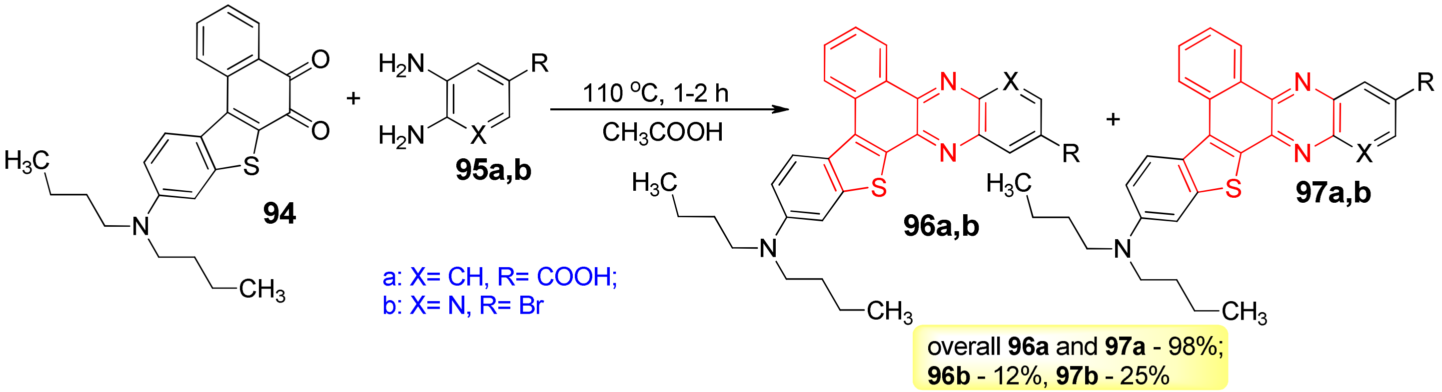
Scheme 32. Synthesis of dibenzo[*a,c*]phenazines (**86**) by the reductive coupling reaction of 2,3-diphenyl substituted quinoxalines (**91a,q,t,u**), proceeding with graphite-potassium intercalate (**C_8K**) in dry tetrahydrofuran (THF) or dimethoxyethane (DME).[165]

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-methoxypyrazine (**92**) with UV-light in the presence of iodine, as oxidant, and propylene oxide, as an acid scavenger (Scheme 33).[52]



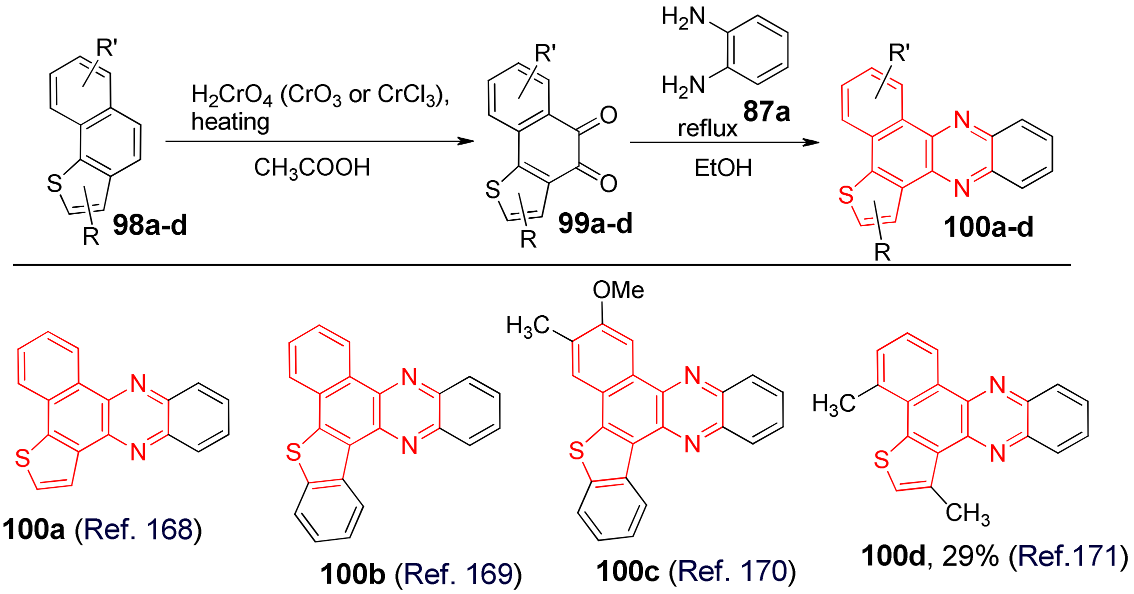
Scheme 33. Synthesis of 2-methoxydibenzo[*f,h*]quinoxaline (**93**) by the oxidative photocyclization of 2-(biphenyl-2-yl)-5-methoxypyrazine (**92**).

There is only one publication[166] 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]



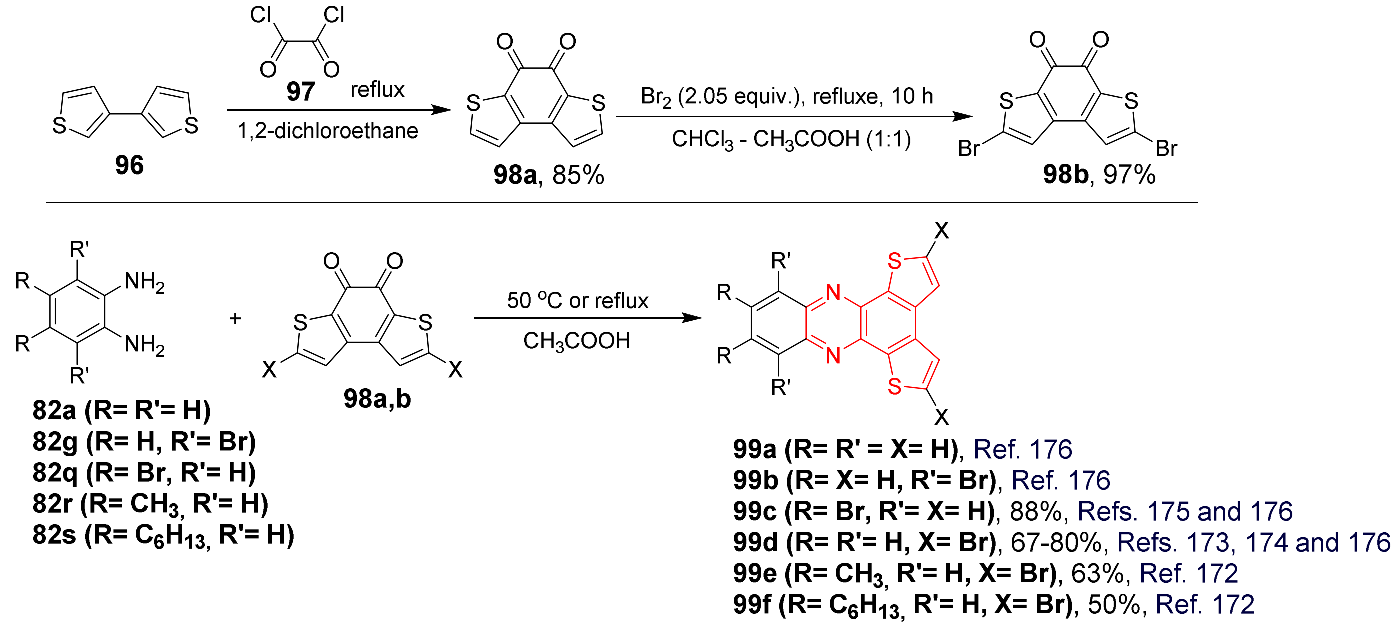
Scheme 34. Synthesis of benzo[*f*]thieno[3,2-*h*]quinoxalines (**96a,b** and **97a,b**) by condensation of 9-dibutylaminobenzo[*b*]naphtho[1,2-*d*]thiophene-5,6-dione (**94**) with 3,4-diaminobenzoic acid (**95a**) or 2,3-diamino-5-bromopyridine (**95b**).

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).



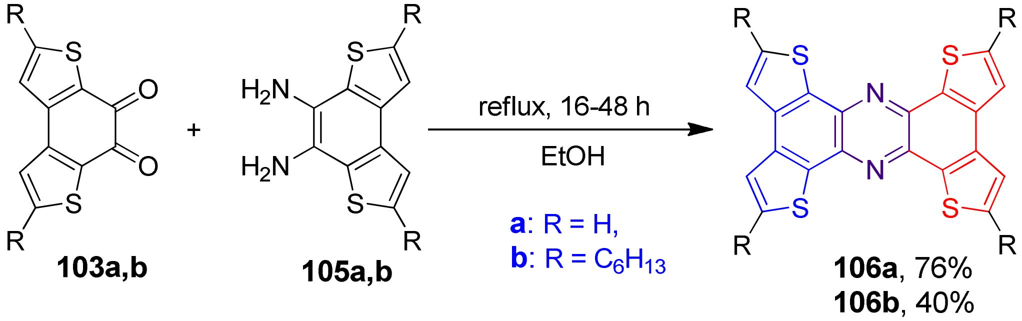
Scheme 35. Synthesis of benzo[*f*]thieno[2,3-*h*]quinoxaline derivatives (**100a-d**).

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]



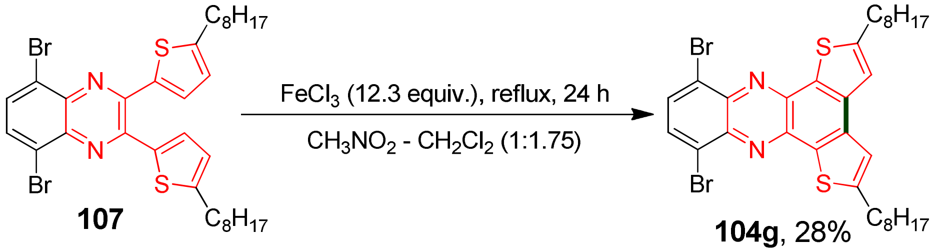
Scheme 36. Synthesis of dithieno[2,3-*a*:3′,2′-*c*]phenazine derivatives (**104a-f**).

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]

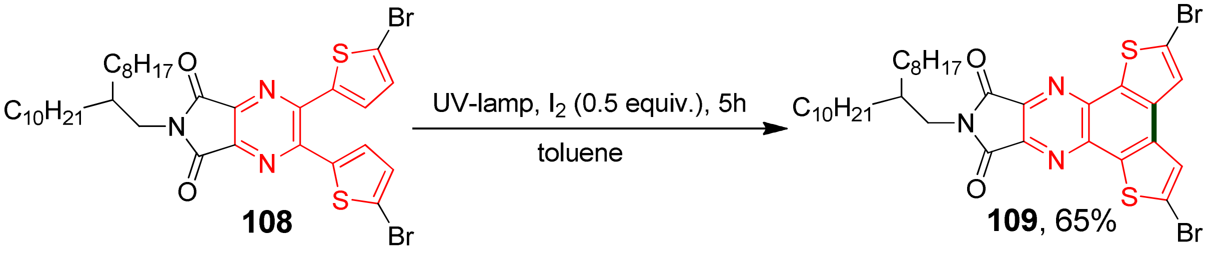


Scheme 37. Synthesis of 2,5,9,12-tetrasubstituted tetrathieno[2,3-*a*:3′,2′-*c*:2″,3″-*h*:3‴,2‴-*j*]phenazines (**106a,b**).

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]

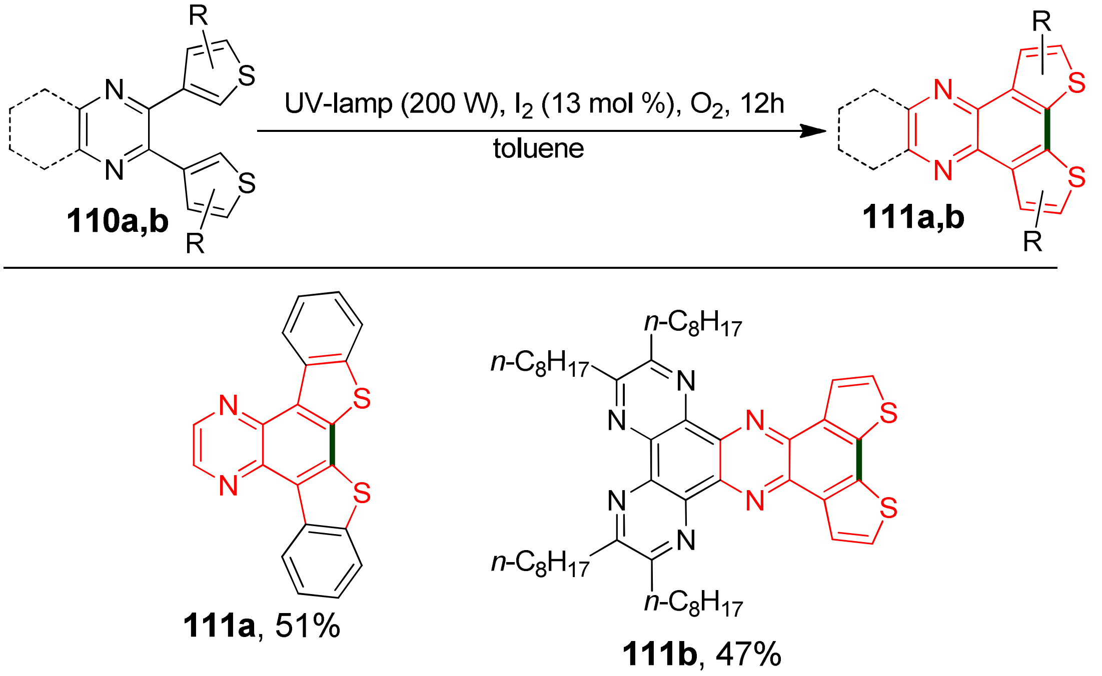


Scheme 38. Synthesis of dithieno[2,3-*f*:3′,2′-*h*]quinoxaline (**XXX**) skeleton by using the Scholl reaction.



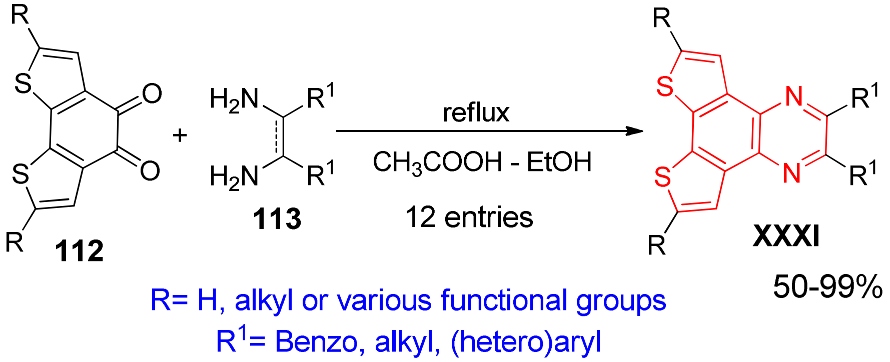
Scheme 39. Synthesis of dithieno[2,3-*f*:3′,2′-*h*]quinoxaline (**XXX**) skeleton using oxidative photocyclization.

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]

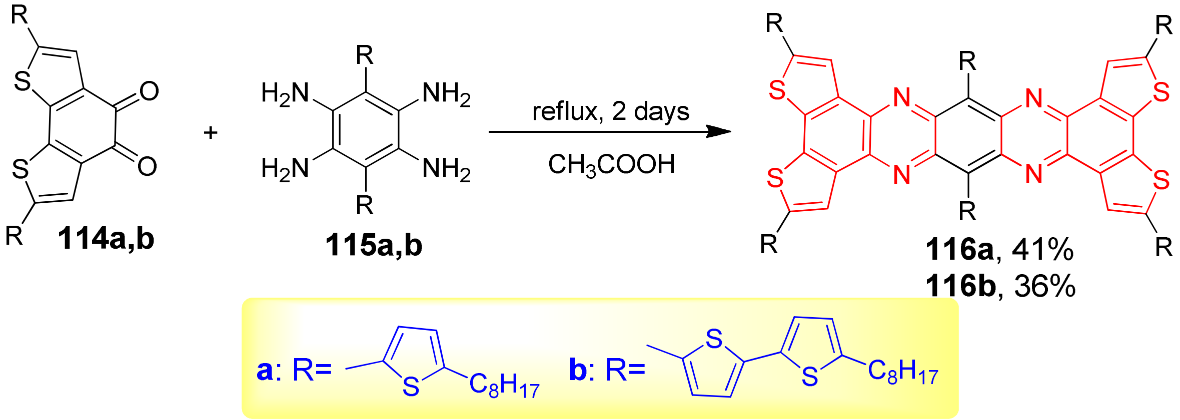


Scheme 40. Synthesis of dithieno[3,2-*f*:2′,3′-*h*]quinoxalines (**111a,b**) through the oxidative photocyclization of the corresponding 2,3-di(thiophen-3-yl)pyrazine derivatives (**110a,b**).

A common approach to the synthesis of dithieno[3,2-*f*:2′,3′-*h*]quinoxalines (**XXXI**) is condensation of 2,7-disubstututed 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-tetra-aminobenzenes (**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]

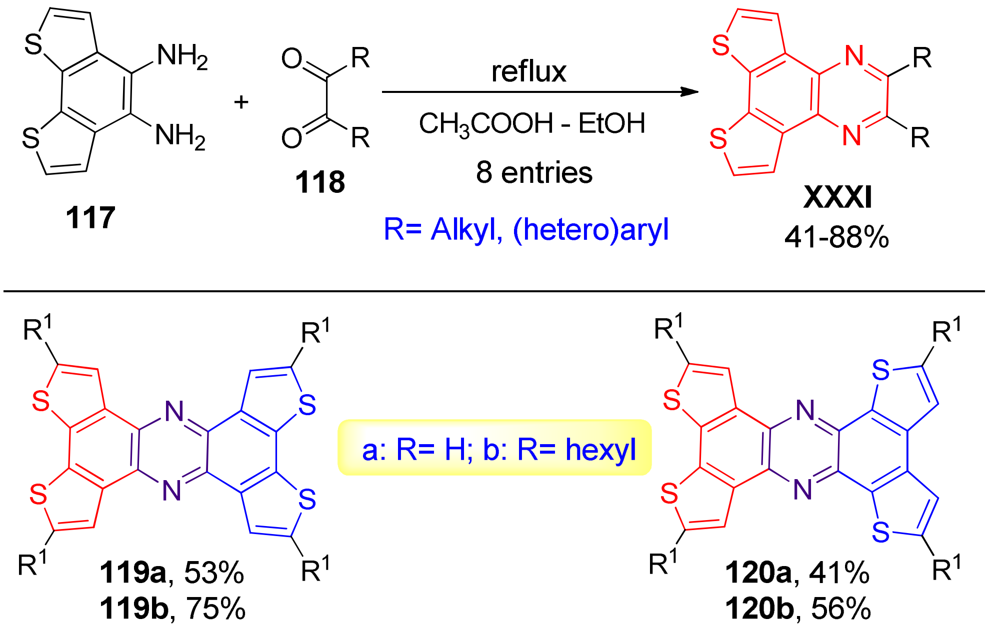


Scheme 41. Synthesis of dithieno[3,2-f:2′,3′-h]quinoxalines (**XXXI**) by condensation of benzo[1,2-*b*:6,5-b′]-dithiophen-4,5-dione (**112**) with 1,2-diamine derivative (**113**).



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 naphtho-thiophenes. 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.

6. Acknowledgements

The research was financially supported by the Russian Science Foundation (Project No. 16-13-10435) and the Russian Foundation for Basic Research (research project №. 17-03-00011-A).

References

1. Harvey, R.G. In *Polycyclic Aromatic Hydrocarbons*. New York: Wiley-VCH. 1997; p 682.
2. Boorum, M. M.; Scott, L. T. *Modern Arene Chemistry*. Astruc, D., Ed.; Wiley-VCH: Weinheim, 2002; pp 20−31.
   https://doi.org/10.1002/3527601767.ch1
3. Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev*. **1999**, *99*, 1747-1786.
   https://doi.org/10.1021/cr970073+
4. Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev*. **2001**, *101*, 1267-1300.
   https://doi.org/10.1021/cr990322p
5. Bendikov M, Wudl F, Perepichka DF. *Chem. Rev*. **2004**, *104*, 4891-4945.
   https://doi.org/10.1021/cr030666m
6. Harvey, R. G. *Curr. Org. Chem*. **2004**, *8*, 303-323.
   https://doi.org/10.2174/1385272043485918
7. Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994-5007.
   https://doi.org/10.1002/anie.200400661
8. Anthony, J. E. *Chem. Rev*. **2006**, *106*, 5028-5048.
   https://doi.org/10.1021/cr050966z
9. Sergeyev, S.; Pisula, W.; Geerts, Y H. *Chem. Soc. Rev*. **2007**, *36*, 1902-1929.
   https://doi.org/10.1039/b417320c
10. Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718-747.
    https://doi.org/10.1021/cr068010r
11. Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev*. **2007**, *107*, 1066-1096.
    https://doi.org/10.1021/cr0501386
12. Grimsdale, A. C.; Müllen, K. *Macromol. Rapid Commun*. **2007**, *28*, 1676-1702.
    https://doi.org/10.1002/marc.200700247
13. Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed*. **2007**, *46*, 4832-4887.
    https://doi.org/10.1002/anie.200604203
14. Wu, J. *Curr. Org. Chem*. **2007**,*11*, 1220-1240.
15. Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452-483.
    https://doi.org/10.1002/anie.200604045
16. Feng, X.; Pisula, W.; Müllen, K. *Pure Appl. Chem*. **2009**, *81*, 2203-2224.
    https://doi.org/10.1351/PAC-CON-09-07-07
17. Avlasevich, Y.; Li, C.; Müllen, K. *J. Mater. Chem*. **2010**, *20*, 3814-3826.
    https://doi.org/10.1039/c000137f
18. Weil, T.; Vosch, T.; Hofkens, J.; Peneva, K.; Müllen, K. *Angew. Chem., Int. Ed*. **2010**, *49*, 9068-9093.
    http://dx.doi.org/10.1002/anie.200902532
19. Zhang, H.; Wu, D.; Hua Liu, S.; Yin, J. *Curr. Org. Chem*. **2012**, *16*, 2124-2158.
    http://dx.doi.org/10.2174/138527212803532477
20. Pérez, D.; Guitián, E. *Chem. Soc. Rev*. **2004**, *33*, 274-283.
    http://dx.doi.org/10.1039/B305549N
21. Kumar, S. *Chem. Soc. Rev*. **2006**, *35*, 83-109.
    http://dx.doi.org/10.1039/B506619K

22. Park, J. E; Kim, J. M.; Jung, J. H.; Min, S. H.; Jung, S. Y.; Baek, Y. G.; Kim, J. Y. *Patent Repub. Korean Kongkae Taeho Kongbo*, KR 2007102243 A , **2007**.
23. Mahoney, S. J.; Ahmida, M. M.; Kayal, H.; Fox, N.; Shimizu, Y.; Eichhorn, S. H. *J. Mater. Chem.* **2009**, *19*, 9221-9232.
http://dx.doi.org/10.1039/B914290H
24. Levell, J. W.; Ruseckas, A.; Henry, J. B.; Wang, Y.; Stretton, A. D.; Mount, A. R.; Galow, T. H.; Samuel, I. D. W. *J. Phys. Chem. A* **2010**, *114*, 13291-13295.
http://dx.doi.org/10.1021/jp106622n
25. Wen, R.; Yan, C.-J.; Yan, H.-J.; Pan, G.-B.; Wan, L.-J. *Chem. Commun*. **2011**, *47*, 6915-6917.
http://dx.doi.org/10.1039/C1CC11358E
26. Shimizu, M.; Nagao, I.; Tomioka, Y.; Kadowaki, T.; Hiyama, T. *Tetrahedron* **2011**, *67*, 8014-8026.
http://dx.doi.org/10.1016/j.tet.2011.08.019
27. Wang, H.; Xu, X.-H.; Kojtari, A.; Ji, H.-F. *J. Phys. Chem. C* **2011**, *115*, 20091-20096.
http://dx.doi.org/10.1021/jp204786f
28. Amsharov, K. Yu.; Merz, P. *J. Org. Chem*. **2012**, *77*, 5445-5448.
http://dx.doi.org/10.1021/jo300783y
29. Togashi, K.; Nomura, S.; Yokoyama, N.; Yasuda, T.; Adachi, C. *J. Mater. Chem*. **2012**, *22*, 20689-20695.
http://dx.doi.org/10.1039/C2JM33669C
30. Iwasaki, M.; Iino, S.; Nishihara, Y. *Org. Lett*. **2013**, *15*, 5326-5329.
http://dx.doi.org/10.1021/ol4025869
31. Collins, K. D.; Honeker, R.; Vasquez-Cespedes, S.; Tang, D.-T. D.; Glorius, F. *Chem. Science* **2015**, *6*, 1816-1824.
http://dx.doi.org/10.1039/C4SC03051F
32. Iwasaki, M.; Araki, Y.; Iino, S; Nishihara, Y. *J. Org. Chem.*, **2015**, *80*, 9247-9263.
http://dx.doi.org/10.1021/acs.joc.5b01693
33. Shanmugaraju, S.; Mukherjee, P. S. *Chem. Commun*. **2015**, *51*, 16014-16032.
http://dx.doi.org/10.1039/C5CC07513K
34. Zint, S.; Ebeling, D.; Ahles, S.; Wegner, H. A.; Schirmeisen, A. *J. Phys. Chem. C* **2016**, *120*, 1615-1622.
http://dx.doi.org/10.1021/acs.jpcc.5b10602
35. Zhang, R.-F.; Hu, W.-J.; Liu, Y. A.; Zhao, X.-L.; Li, J.-S.; Jiang, B.; Wen, K. *J. Org. Chem*. **2016**, *81*, 5649-5654.
http://dx.doi.org/10.1021/acs.joc.6b01115
36. Kwong, R. *Patent* U.S. 20160285016 A1, **2016**.
37. Pan, S.; Jiang, H.; Zhang, Y.; Chen, D.; Zhang, Y. *Org. Lett*. **2016**, *18*, 5192-5195.
http://dx.doi.org/10.1021/acs.orglett.6b02071
38. Iwao, M.; Lee, M. L.; Castle, R. N. *J. Heterocycl. Chem*. **1980**, *17*, 1259-1264.
http://dx.doi.org/10.1002/jhet.5570170623
39. Sidorenko, T. N.; Terent'eva, G. A.; Aksenov, V. S. *Khim. Geterotsikl. Soed.* **1983**, *2*, 197-199.
40. Rademacher, P.; Heinemann, C.; Jansch, S.; Kowski, K.; Weiss, M. E. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* **2000**, *56A*, 1179-1190.
http://dx.doi.org/10.1016/S1386-1425(99)00220-6
41. Seixas de Melo, J.; Pina, J.; Rodrigues, L. M.; Becker, R. S. *J. Photochem. Photobiology, A: Chemistry* **2008**, 194, 67-75.
http://dx.doi.org/10.1016/j.jphotochem.2007.07.014
42. Kim, T. H.; Kim, H. S.; Son, H. S. *Patent* WO 2013009032 A2, **2013**.

43. Cho, D. M.; Parkin, S. R.; Watson, M. D. *Org. Lett*. **2005**, *7*, 1067-1068.
http://dx.doi.org/10.1021/ol050019c
44. Park, S. J.; Bae, H. C.; Lee, I. H.; Kim, E. J.; Baek, Y. M.; Kim, Y. B.; Park, H. C.; Kim, T. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2015030794 A, **2015**.
45. Xiao, S.; Zhou, H.; Stuart, A. C.; You, W. *PMSE Preprints* **2009**, *100*, 741-743.
46. Zhou, H.; Yang, L.; Price, S. C.; Knight, K. J.; You, W. *Angew. Chem., Int. Ed.* **2010**, *49*, 7992-7995.
http://dx.doi.org/10.1002/anie.201003357
47. Rungtaweevoranit, B.; Butsuri, A.; Wongma, K.; Sadorn, K.; Neranon, K.; Nerungsi, C.; Thongpanchang, T. *Tetrahedron Lett*. **2012**, *53*, 1816-1818.
http://dx.doi.org/10.1016/j.tetlet.2012.01.122
48. Kageyama, T.; Uneme, S.; Takase, M.; Nomura, K.; Nishinaga, T. *Australian J. Chem.* **2014**, *67*, 722-728.
http://dx.doi.org/10.1071/CH13522
49. Löbert, M.; Mishra, A.; Uhrich, C.; Pfeiffer, M.; Bäuerle, P. *J. Mater. Chem. C*, **2014**, *2*, 4879-4892.
http://dx.doi.org/10.1039/c4tc00335g
50. Desai, H. S.; Tilak, B. D. *J. Sci. Ind. Res.* **1961**, *20B*, 22-30.
51. Stępień, M.; Gońka, E.; Żyła, M.; Sprutta, N. *Chem. Rev*. **2017**, *117*, 3479-3716.
http://dx.doi.org/10.1021/acs.chemrev.6b00076
52. Kwong, R.; Lam, S. T.; Lee, C. H. *Patent* US 20140332758 A1, **2014**.
53. Thompson, M. E.; Saris, P.; Djurovich, P. I.; Chen, S. H.-F. *Patent* WO 2015066244 A1, **2015**.
54. Altiparmakian, R. H.; Braithwaite, R. S. W. *J. Chem. Soc. C* **1967**, 1973-1979.
http://dx.doi.org/10.1039/J39670001973
55. Cort, L.A.; Mahesar, M. A. *J. Chem. Soc., Perkin Trans 1* **1979**, 2034-2043.
http://dx.doi.org/10.1039/P19790002034
56. Young, B. S.; Köhler, F.; Herges, R.; Haley, M. M. *J. Org. Chem.* **2011**, *76*, 8483-8487.
http://dx.doi.org/10.1021/jo201378t
57. Chercheja, S.; Klívar, J.; Jančařík, A.; Rybáček, J.; Salzl, S.; Tarábek, J.; Pospíšil, L.; Chocholoušová, J. V.; Vacek, J.; Pohl, R.; Císařová, I.; Starý, I.; Stará, I. G. *Chem. Eur. J.* **2014**, *20*, 8477-8482.
http://dx.doi.org/10.1002/chem.201402312
58. Tapolcsányi, P.; Maes, B. U. W.; Monsieurs, K.; Lemière, G. L. F.; Riedl, Z.; Hajós, G.; art Van den Driessche, B.; Dommissea, R. A.; Mátyus, P. *Tetrahedron* **2003**, *59*, 5919-5926.
http://dx.doi.org/10.1016/S0040-4020(03)00953-0
59. Tokita, S.; Hiruta, K.; Ishikawa, S.; Kitahara, K.; Nishi, H. *Synthesis* **1982**, 10, 854-855.
http://dx.doi.org/10.1055/s-1982-29973
60. Bahashwan, S. A.; Al-Harbi, N. O.; Fayed, A.; Amr, A. E.-G.; Shadid, K. A.; Alalawi, A. M.; Bassati, I. M. S. *Int. J. Biol. Macromol*. **2012**, *51*, 7-17.
http://dx.doi.org/10.1016/j.ijbiomac.2012.05.002
61. Braña, M. F.; Cacho, M.; García, M. L.; Mayoral, E. P.; López, B.; de Pascual-Teresa, B.; Ramos, A.; Acero, N.; Llinares, F.; Muñoz-Mingarro, D.; Lozach, O.; Meijer, L. *J. Med. Chem*. **2005**, *48*, 6843-6854.
http://dx.doi.org/10.1021/jm058013g
62. Kashimura, N.; Sumino, F.; Nakagawa, M.; Nagahara, S. *Patent Jpn. Kokai Tokkyo Koho* JP 02064553 A, **1990**.
63. Kim, S. I.; Sim, S. Y.; Yoo, S. J.; Lee, S. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2013142967 A, **2013**.
64. Park, J. H.; Kim, S. I.; Yang, B. S. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014004005 A, **2014**.

65. Shin, B. G.; Park, J. H.; Park, B. B.; Yoon, J. H.; Park, G. H.; Lee, B. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014120089 A, **2014**.
66. Shin, B. G.; Park, J. H.; Park, B. B.; Yoon, J. H.; Park, G. H.; Lee, B. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014120090 A, **2014**.
67. Yang, B. S.; Sim, S. Y.; Yoo, S. J.; Lee, S. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014001764 A, **2014**.
68. Shin, B. G.; Park, J. H.; Park, B. B.; Yoon, J. H.; Park, G. H.; Lee, B. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014114490 A, **2014**.
69. Shin, B. G.; Park, J. H.; Park, B. B.; Yoon, J. H.; Park, G. H.; Lee, B. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014114489 A, **2014**.
70. Park, J. K.; Choi, Y. H.; Park, H. K.; Cho, H. M.; Lee, D. W.; Lee, H. Y. *Patent* WO 2014178532 A1, **2014**.
71. Sim, S. Y.; Yoo, S. J.; Lee, S. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014141071 A, **2014**.
72. Sim, S. Y.; Y., Se J.; Lee, S. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2014141970 A, **2014**.
73. Park, J. H.; Park, J. G.; Jung, H. Y.; Kang, M. S.; Ha, Jong J.; Kim, W. S.; Kim, S. G.; Lee, M. J. *Patent Repub. Korea* KR 1555680 B1, **2015**
74. Park, J. G.; Choi, Y. H.; Park, H. G.; Moon, S. Y.; Lee, D. W.; Lee, H. Y.; Cho, H. M. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2015122343 A, **2015**.
75. Park, H. K.; Choi, Y. H.; Park, J. K.; Cho, H. M.; Lee, D. W.; Kim, S. H. *Patent* WO 2015083948 A1, **2015**.
76. Sim, S. Y.; Yoo, S. J.; Lee, S. H. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2015009297 A, **2015**.
77. Cho, H. M.; Lee, S. H.; Park, H. G.; Park, J. G.; Lee, D. W.; Moon, S. Y.; Hwang, S. P. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2015134923 A, **2015**.
78. Hara, T.; Inoue, H.; Takahashi, T.; Hamada, T.; Seo, S. *Patent* US 20160190479 A1, **2016**.
79. Yamada, Y.; Inoue, H.; Seo, H.; Takahashi, T. *Patent* US 20160181550 A1, **2016**.
80. Jang, J. W.; Jung, H. Y.; Kim, S.-G.; Kim, W. S.; Byun, J. H.; Park, J. H.; Hwang, S. P. *Patent* WO 2016032150 A2, **2016**.
81. Jang, J. W.; Kim, S. G.; Kim, W. S.; Kim, Y. R.; Kwon, J. T. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2016005944 A, **2016**.
82. Hyun, S. Y.; Jung, S. U.; Kim, D. W. *Patent Repub. Korean Kongkae Taeho Kongbo* KR 2016041223 A, **2016**.
83. Mahmoodi, N. O.; Khodaee, Z. *Mendeleev Commun*. **2004**, *14*, 304-306. http://dx.doi.org/10.1070/MC2004v014n06ABEH002014
84. Olivera, R.; Pascual, S.; Herrero, M.; SanMartin, R.; Domínguez, E. *Tetrahedron Lett*. **1998**, *39*, 7155-7158. http://dx.doi.org/10.1016/S0040-4039(98)01531-7
85. Olivera, R.; SanMartin, R.; Tellitu, I.; Domínguez, E. *Tetrahedron* **2002**, *58*, 3021-3037. http://dx.doi.org/10.1016/S0040-4020(02)00194-1
86. Kadiyala, R. R.; Tilly, D.; Nagaradja, E.; Roisnel, T.; Matulis, V. E.; Ivashkevich, O. A.; Halauko, Y. S.; Chevallier, F.; Gros, P. C.; Mongin, F. *Chem. Eur. J*. **2013**, *19*, 7944-7960. http://dx.doi.org/10.1016/S0040-4020(02)00194-1
87. Chupakhin, O. N.; Charushin, V. N. *Tetrahedron Lett*. **2016**, *57*, 2665-2672. https://doi.org/10.1016/j.tetlet.2016.04.084
88. Rempala, P.; Kroulik, J.; King, B. T. *J. Am. Chem. Soc*. **2004**, *126*,15002-15003. http://dx.doi.org/10.1021/ja046513d
89. Rempala, P.; Kroulík, J.; King, B. T. *J. Org. Chem*. **2006**, *71*, 5067-5081. http://dx.doi.org/10.1021/jo0526744
90. Olivera, R.; SanMartin, R.; Pascual, S.; Herrero, M.; Domínguez, E. *Tetrahedron Lett*. **1999**, *40*, 3479-3480.

http://dx.doi.org/10.1016/S0040-4039(99)00428-1

91. Nagarajan, S.; Barthes, C.; Gourdon, A. *Tetrahedron* **2009**, *65*, 3767-3772. http://dx.doi.org/10.1016/j.tet.2009.02.029
92. Draper, S. M.; Gregg, D. J.; Madathil, R. *J. Am. Chem. Soc*. **2002**, *124*, 3486-3487. http://dx.doi.org/10.1021/ja017394u
93. Draper, S. M.; Gregg, D. J.; Schofield, E. R.; Browne, W. R.; Duati, M.; Vos, J. G.; Passaniti, P. *J. Am. Chem. Soc*. **2004**, *126*, 8694-8701. http://dx.doi.org/10.1021/ja0491634
94. Gregg, D. J.; Bothe, E.; Höfer, P.; Passaniti, P.; Draper, S. M. *Inorg. Chem*. **2005**, *44*, 5654-5660. http://dx.doi.org/10.1021/ic050335n
95. Wijesinghe, L. P.; Lankage, B. S.; Máille, G. M. Ó.; Perera, S. D.; Nolan, D.; Wang, L.; Draper, S. M. *Chem. Commun*. **2014**, *50*, 10637-10640. http://dx.doi.org/10.1039/c4cc03577a
96. Delaney, C.; Máille, G. M. Ó.; Twamley, B.; Draper, S. M. *Org. Lett.* **2016**, *18*, 88-91. http://dx.doi.org/10.1021/acs.orglett.5b03312
97. Mohamed, R. K.; Mondal, S.; Guerrera, J. V.; Eaton, T. M.; Albrecht-Schmitt, T. E.; Shatruk, M.; Alabugin., I. V. *Angew. Chem. Int. Ed*. **2016**, *55*, 12054-12058. http://dx.doi.org/10.1002/anie.201606330
98. Wei, W.; Li, C.; Wang, Liu, D.; Zhang, Z. *Tetrahedron* **2016**, *72*, 5037-5046. http://dx.doi.org/10.1016/j.tet.2016.04.080
99. Xue, P.; Du, Z.; Wang, T.; Zhang, Z. *Synthesis* **2015**, *47*, 3385-3391. http://dx.doi.org/10.1055/s-0034-1380455
100. Verbitskiy, E. V.; Rusinov, G. L.; Chupakhin, O. N.; Charushin, V. N. *ARKIVOC* **2016**, iv, 204-216. http://dx.doi.org/ 10.3998/ark.5550190.p009.623
101. Verbitskiy, E. V.; Cheprakova, E. M.; Makarova, N. I.; Dorogan, I V.; Metelitsa, A. V.; Minkin, V. I.; Slepukhin, P. A.; Svalova, T. S.; Ivanova, A. V.; Kozitsina, A. N.; Rusinov, G. L.; Chupakhin, O. N.; Charushin, V. N. *Eur. J. Org. Chem*. **2016**, 1420-1428. http://dx.doi.org/10.1002/ejoc.201501450
102. Verbitskiy, E. V.; Slepukhin, P. A.; Valova, M. A.; Cheprakova, E. M.; Schepochkin, A. V.; Rusinov, G. L.; Charushin, V. N. *Eur. J. Org. Chem*. **2014**, 8133-8141. http://dx.doi.org/10.1002/ejoc.201403212
103. Martynoff, M. *Bull. Soc. Chim. France* **1951**, 214-20.
104. Boyer, J. H.; Buriks, R.S.; Toggweiler, U. *J. Am. Chem. Soc*. **1960**, *82*, 2213-2215. http://dx.doi.org/10.1021/ja01494a030
105. Banerji, K. D.; Mazumdar, A. K. D.; Saha, N. K.; Guha, S. K. *J. Indian Chem. Soc*. **1980**, 57, 86-88.
106. Minsky, A.; Cohen, Y.; Rabinovitz, M. *J. Am. Chem. Soc*. **1985**, *107*, 1501-1505. http://dx.doi.org/10.1021/ja00292a009
107. Grivas, S.; Tian, W. *Acta Chem. Scand*. **1992**, *46*, 1109-1113. http://dx.doi.org/10.3891/acta.chem.scand.46-1109
108. Demirayak, S.; Benkli, K.; Mohsen, U. A.; Guven, K. *Acta Pharm. Turcica* **1998**, *40*, 193-196.
109. Abramov, I. G.; Smirnov, A. V.; Abramova, M. B.; Begunov, R. S.; Kalandadze, L. S.; Smirnova, O. V.; Plakhtinskii, V. V. *Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya* **2001**, *44*, 134-139.

110. Edelmann, E.M.; Raimundo, J.-P.; Utesch, N. F.; Diederich, F. *Helvetica Chimica Acta* **2002**, *85*, 2195-2213.
http://dx.doi.org/10.1002/1522-2675(200207)85:7<2195::AID-HLCA2195>3.0.CO;2-G
111. Balakirev, A. E.; Maizlish, V. E.; Shaposhnikov, G. P. *Russ. J. General Chem*. **2002**, *72*, 311-314.
http://dx.doi.org/10.1023/A:1015406625722
112. Nishida, J.; Murai, S.; Fujiwara, E.; Tada, H.; Tomura, M.; Yamashita, Y. *Org. Lett*. **2004**, 6, 2007-2010.
http://dx.doi.org/10.1021/ol0494010
113. Lecloux, D. D.; Guidry, M. A.; Herron, N.; Radu, N. S.; Smith, E. M.; Wang, Y. *Patent* WO 2004006355 A2, **2004**.
114. Akar, D.; İncesu, Z.; Gündoğdu-Karaburun, N.; Benkli, K.; Işikdağ, İ. *Turkish J. Pharm. Sci*. 2004, 1, 193-202.
115. Ding, Y.; Girardet, J.-L.; Smith, K. L.; Larson, G.; Prigaro, B.; Lai, V. C. H.; Zhong, W.; Wu, J. Z. *Bioorg. Med. Chem. Lett*. **2005**, *15*, 675-678.
http://dx.doi.org/10.1016/j.bmcl.2004.11.028
116. Kumamoto, K.; Iida, H.; Hamana, H.; Kotsuki, H.; Matsumoto, K. *Heterocycles* **2005**, *66*, 675-681.
http://dx.doi.org/10.3987/COM-05-S(K)69
117. Gautrot, J. E.; Hodge, P. *Polymer* **2007**, *48*, 7065-7077.
http://dx.doi.org/10.1016/j.polymer.2007.09.045
118. Sherif, M. H.; Assy, M. G.; Zahran, F.; Khalil, A. *Afinidad* **2008**, *65*, 156-162.
119. Niknam, K.; Zolfigol, M. A.; Tavakolic, Z.; Heydari, Z. *J. Chin. Chem. Soc*. **2008**, *55*, 1373-1378.
http://dx.doi.org/10.1002/jccs.200800206
120. Niknam, K.; Saberi, D.; Mohagheghnejad, M. *Molecules* **2009**, *14*, 1915-1926.
http://dx.doi.org/10.3390/molecules14051915
121. Dubey, R. K.; Kumpulainen, T.; Efimov, A.; Tkachenko, N. V.; Lemmetyinen, H. *Eur. J. Org. Chem*. **2010**, 3428-3436.
http://dx.doi.org/10.1002/ejoc.201000136
122. Abdolkarim, Z.; Alireza, H.; Abolfath, P.; Reza, M.-Z. A.; Fatemeh, K.; Zahra, P.; Maasoomeh, A.-S.; Maasoomeh, K.; Mehrnoosh, R.; Hanafieh, D. *J. Serb. Chem. Soc*. **2010**, *75*, 1315-1324.
http://dx.doi.org/10.2298/JSC091014109Z
123. Sharma, R. K.; Sharma, C. *Catalysis Commun*. **2011**, *12*, 327-331.
http://dx.doi.org/10.1016/j.catcom.2010.10.011
124. Rashedian, F.; Saberib, D.; Niknam, K. *J. Chin. Chem. Soc*. **2010**, *57*, 998-1006.
http://dx.doi.org/10.1002/jccs.201000139
125. Chavan, H. V.; Adsul, L. K.; Bandgar, B. P. *J. Chem. Sci*. **2011**, *123*, 477-483.
126. Karami, B.; Khodabakhshi, S.; Nikrooz, M. *Polycyclic Aromatic Compounds* **2011**, *31*, 97-109.
http://dx.doi.org/10.1080/10406638.2011.572577
127. Bachhav, H. M.; Bhagat, S. B.; Telvekar, V. N. *Tetrahedron Lett*. **2011**, 52, 5697- 5701.
http://dx.doi.org/10.1016/j.tetlet.2011.08.105
128. Karami, B.; Khodabakhshi, S. *J. Serb. Chem. Soc*. **2011**, *76*, 1191-1198.
http://dx.doi.org/10.2298/JSC100801104K
129. Heshmatollah, A.; Mahmood, T.; Fatemeh, S.; Pourya, B. *Bull. Korean Chem. Soc*. **2011**, 32, 3720-3725.
http://dx.doi.org/10.5012/bkcs.2011.32.10.3720
130. Guo, W.; Engelman, B. J.; Haywood, T. L.; Blok, N. B.; Beaudoin, D. S.; Obare, S. O. *Talanta* **2011**, *87*, 276-283.

http://dx.doi.org/10.1016/j.talanta.2011.10.015

131. Carlier L.; Baron, M.; Chamayou, A.; Couarraze, G. *Tetrahedron Lett*. **2011**, *52*, 4686-4689. http://dx.doi.org/10.1016/j.tetlet.2011.07.003
132. Kumbhar, A.; Kamble, S.; Barge, M.; Rashinkar, G.; Salunkhe, R. *Tetrahedron Lett*. **2012**, *53*, 2756-2760. http://dx.doi.org/10.1016/j.tetlet.2012.03.097
133. Hasaninejad, A.; Shekouhy, M.; Zare, A. *Catal. Sci. Technol*. **2012**, *2*, 201-214. http://dx.doi.org/10.1039/C1CY00332A
134. Karami, B.; Khodabakhshi, S.; Nikrooz, M. *J. Chin. Chem. Soc*. **2012**, *59*, 187-192. http://dx.doi.org/10.1002/jccs.201100421
135. Karami, B.; Rooydel, R.; Khodabakhshi, S. *Acta Chim. Slov.* **2012**, *59*, 183-188.
136. Khodabakhshi, S.; Karami, B. *Catal. Sci. Technol*. **2012**, *2*, 1940-1944. http://dx.doi.org/10.1039/C2CY20227A
137. Soleymani, R.; Niakan, N.; Tayeb, S.; Hakimi, S. *Oriental J. Chem*. **2012**, *28*, 687-701. https://doi.org/10.13005/ojc/280208
138. Habibzadeh, S. *Org. Chem. Ind. J*. **2012**, *8*, 473-476.
139. Sajjadifar, S.; Zolfigol, M. A.; Mirshokraie, S. A.; Miri, S.; Louie, O.; Nezhad, E. R.; Karimian, S.; Darvishi, G.; Donyadari, E.; Farahmand, S. *Amer. J. Org. Chem*. **2012**, 2, 97-104. http://dx.doi.org/10.5923/j.ajoc.20120204.04
140. Kadam, H. K.; Khan, S.; Kunkalkar, R. A.; Tilve, S. G. *Tetrahedron Lett*. **2013**, *54*, 1003-1007. http://dx.doi.org/10.1016/j.tetlet.2012.12.041
141. Shirini, F., Akbari-Dadamahaleh, S.; Mohammad-Khah, A.; Aliakbar, A.-R. *Comptes Rend. Chimie* **2013**, *16*, 207-216. http://dx.doi.org/10.1016/j.crci.2012.12.004
142. Malakooti, R.; Bardajee, G. R.; Mahmoudi, H.; Kakavand, N. *Catal. Lett.* **2013,** *143*, 853-861. http://dx.doi.org/10.1007/s10562-013-0999-1
143. Jafarpour, M.; Rezaeifard, A.; Ghahramaninezhad, M.; Tabibi, T. *New J. Chem*. **2013**, *37*, 2087-2095. http://dx.doi.org/10.1039/C3NJ00058C
144. Mulik, A.; Chandam, D.; Patil, P.; Patil, D.; Jagdale, S.; Deshmukh, M. *J. Molecular Liquids* 2013, 179, 104-109. http://dx.doi.org/10.1016/j.molliq.2012.12.006
145. Bardajee, G. R.; Mizani, F.; Rostami, I.; Mohamadi, A. *Polycyclic Aromatic Compounds* **2013**, *33*, 419-429. http://dx.doi.org/10.1080/10406638.2013.791995
146. Karami, B.; Khodabakhshi, S. *J. Chil. Chem. Soc.* **2013**, 58, 1655-1658. http://dx.doi.org/10.4067/S0717-97072013000200002
147. Sadeghi, B.; Karimi, F. *Iranian J. Catalysis* **2013**, *3*, 1-7.
148. Nezhad, E. R.; Sajjadifar, S.; Miri, S.; Karimian, S.; Abbasi, Z. *Iranian J. Catalysis* **2013**, *3*, 191-196.
149. Kolvari, E.; Zolfigol, M. A.; Koukabi, N.; Gilandust, M.; Kordi, A.-V. *J. Iran. Chem. Soc*. **2013**, *10*, 1183-1191. http://dx.doi.org/10.1007/s13738-013-0252-2
150. Jafarpour, M.; Rezapour, E.; Ghahramaninezhad, M.; Rezaeifard, A. *New J. Chem*. **2014**, *38*, 676-682. http://dx.doi.org/10.1039/C3NJ00655G
151. Sajjadifar, S.; Nezhad, E. R., Khosravani, E. *Chem. Science Trans*. **2014**, *3*, 292-302. http://dx.doi.org/10.7598/cst2014.506
152. Samanta, S.; Gupta, A. D.; Mallik, A. K. *Monatsh. Chem*. **2014**, *145*, 1669-1673. http://dx.doi.org/10.1007/s00706-014-1242-5

153. Bandyopadhyay, D.; Zavala, D.; Banik, B. K. *Current Organocatalysis* **2014**, *1*, 59-65.
http://dx.doi.org/10.2174/22133372114016660001
154. Tajbakhsh, M.; Bazzar, M.; Ramzanian, S. F.; Tajbakhsh, M. *Applied Clay Science* **2014**, *88-89*, 178-185.
http://dx.doi.org/10.1016/j.clay.2013.12.023
155. Sajjadifar, S.; Miri, S. *Int. J. ChemTech Res*. **2014**, *6*, 5433-5440.
156. Baghbanian, S. M. *Chinese Chem. Lett.* **2015**, *26*, 1113-1116.
http://dx.doi.org/10.1016/j.cclet.2015.04.037
157. Mulik, A. G.; Chandam, D. R.; Patil, D. R.; Patil, P. P.; Mulik, G. N.; Salunkhe, S. T.; Deshmukh, M. B. *Res. Chem. Intermed*. **2015**, *41*, 10085-10096.
http://dx.doi.org/10.1007/s11164-015-2014-5
158. Shamsi-Sani, M.; Shirini, F.; Abedini, M.; Seddighi, M. *Res. Chem. Intermed*. **2016**, *42*, 1091-1099.
http://dx.doi.org/10.1007/s11164-015-2075-5
159. Jafarpour, M.; Rezaeifard, A. *Transition Met. Chem*. **2016**, *41*, 205-211.
http://dx.doi.org/10.1007/s11243-015-0012-5
160. Zhang, C.; Zhang, Y.; Liu, Q.; Gao, R. *Yingyong Huagong* **2008**, *37*, 430-433.
161. Amer, A. M.; El-Farargy, A. F.; Yousif, N. M.; Fayed, A. A. *Chem. Heterocycl. Compds*. **2011**, *47*, 101-107.
http://dx.doi.org/10.1007/s10593-011-0726-z
162. Khodaee, Z.; Yahyazadeh, A.; Mahmoodi, N. O.; Zanjanchi, M. A.; Azimi, V. *J. Mol. Struct.* **2012**, *1029*, 92-97.
http://dx.doi.org/10.1016/j.molstruc.2012.06.021
163. Kijak, M.; Peukert, S.; Mengesha, E.; Sepioł, J.; Gil, M. *J. Phys. Chem. A* **2016**, *120*, 7817-7827.
http://dx.doi.org/10.1021/acs.jpca.6b06475
164. Tamarkin, D.; Cohen, Y.; Rabinovitz, M. *Synthesis* **1987**, *2*, 196-197.
http://dx.doi.org/10.1055/s-1987-27889
165. Rabinovitz, M.; Tamarkin, D. *Synthetic Metals* **1988**, *23*, 487-491.
http://dx.doi.org/10.1016/0379-6779(88)90526-7
166. Tamarkin, D.; Rabinovitz, M. *J.Org. Chem*. **1987**, *52*, 3472-3474.
http://dx.doi.org/10.1021/jo00391a065
167. Yoshida, K.; Hayashi, A.; Mamura, T. *Patent* JP 2008195749 A, **2008**.
168. Kruber, O.; Raeithel, A. *Chemische Berichte* **1953**, *86*, 366-371.
http://dx.doi.org/10.1002/cber.19530860309
169. Badger, G. M.; Christie, B. J. *J. Chem. Soc*. **1956**, 3435-3437 .
http://dx.doi.org/10.1039/JR9560003435
170. Marie, C.; Buu-Hoï, N. P.; Jacquignon, P. *J. Chem. Soc. C* **1971**, 431-434.
http://dx.doi.org/10.1039/J39710000431
171. Kurokawa, S. *Bull. Chem. Soc. Jpn* **1970**, *43*, 1454-1459.
172. Meyer, A.; Sigmund, E.; Luppertz, F.; Schnakenburg, G.; Gadaczek, I.; Bredow, T.; Jester, S.-S.; Höger, S. *Beilstein J. Org. Chem*. **2010**, *6*, 1180-1187.
http://dx.doi.org/10.3762/bjoc.6.135
173. Guo, Z.-H.; Lei, T.; Jin, Z.-X.; Wang, J.-Y.; Pei, J. *Org. Lett*. **2013**, 15, 3530-3533.
http://dx.doi.org/10.1021/ol4012025
174. Chaudhuri, D.; Sigmund, E.; Meyer, A.; Röck, L; Klemm, P.; Lautenschlager, S.; Schmid, A.; Yost, S. R.; Van Voorhis, T.; Bange, S.; Höger, S.; Lupton, J. M. *Angew. Chem. Int. Ed*. **2013**, *52*, 13449-13452.
http://dx.doi.org/10.1002/anie.201307601

175. Putta, A.; Mottishaw, J. D.; Wang, Z.; Sun, H. *Cryst. Growth Des*. **2014**, *14*, 350-356.
http://dx.doi.org/10.1021/cg401637a
176. Chen, Y.; Lu, X.; Xiang, C.; Ling, Y.; Zhou, G. *Chem. Asian J*. **2016**, *11*, 874-881.
http://dx.doi.org/10.1002/asia.201501389
177. Xie, Y.; Fujimoto, T.; Dalgleish, S.; Shuku, Y.; Matsushita, M. M.; Awaga, K. *J. Mater. Chem. C* **2013**, *1*, 3467-3481.
http://dx.doi.org/10.1039/c3tc30346b
178. Zhang, J.; Cai, W.; Huang, H.; Wang, E.; Zhong, C.; Liu, S.; Wang, M.; Duan, C.; Yang, T.; Cao, Y. *Macromolecules* **2011**, *44*, 894-901.
http://dx.doi.org/10.1021/ma1027164
179. Keshtov, M. L.; Kuklin, S. A.; Chen, F. C.; Khokhlov, A. R.; Kurchania, R.; Sharma, G. D. *J. Polym. Sci., Part A: Polym. Chem*. **2015**, *53*, 2390-2398.
http://dx.doi.org/10.1002/pola.27699
180. Black, H. T.; Liu, S.; Ashby, V. S. *Org. Lett*. **2011**, *13*, 6492-6495.
http://dx.doi.org/10.1021/ol202662s
181. Qian, C.; Zhao, W.-H.; Tian, Y.; Jiang, G.-F.; Zhan, T.-G.; Zhao, X. *Chem. Asian J*. **2016**, *11*, 839-843.
http://dx.doi.org/10.1002/asia.201600018
182. Xiao, S.; Zhou, H.; You, W. *Macromolecules* **2008**, *41*, 5688-5696.
http://dx.doi.org/10.1021/ma800776q
183. Guégano, X.; Kanibolotsky, A. L.; Blum, C.; Mertens, S. F. L.; Liu, S.-X.; Neels, A.; Hagemann, H.; Skabara, P. J.; Leutwyler, S.; Wandlowski, T.; Hauser, A.; Decurtins, S. *Chem. Eur. J*. **2009**, *15*, 63-66.
http://dx.doi.org/10.1002/chem.200802011
184. Kirner, H. J.; Chebotareva, N.; Aebischer, O. F. *Patent* WO 2010136401 A2, **2010**.
185. Zhang, Y.; Zou, J.; Yip, H.-L.; Chen, K.-S.; Davies, J. A.; Sun, Y.; Jen, A., K.-Y. *Macromolecules* **2011**, *44*, 4752-4758.
http://dx.doi.org/10.1021/ma2008699
186. Chen, W.; Tan, S. Y.; Zhao, Y.; Zhang, Q. *Org. Chem. Front***.** **2014**, *1*, 391-394.
http://dx.doi.org/10.1039/C4QO00032C
187. Aboubakr, H.; Brisset, H.; Siriand, O.; Raimundo, J.-M. *Anal. Chem*. **2013**, 85, 9968-9974.
http://dx.doi.org/10.1021/ac4027934
188. Bhuwalka, A.; Mike, J. F.; Intemann, J. J.; Ellern, A.; Jeffries-EL, M. *Org. Biomol. Chem*. **2015**, *13*, 9462-9470.
http://dx.doi.org/10.1039/C5OB01135C
189. Zhang, Y.; Shi, J.; He, X.; Tu, G. *J. Mater. Chem. A* **2016**, *4*, 13519-13524.
http://dx.doi.org/10.1039/C6TA03784D
190. Getmanenko, Y. A.; Marder, S. R.; Hwang, D. K.; Kippelen, B. *Patent* WO 2013023107 A1, **2013**.
191. Getmanenko, Y. A.; Marder, S. R.; Hwang, D. K.; Kippelen, B. *Patent* WO 2013023108 A1, **2013**.
192. Getmanenko, Y. A.; Fonari, M.; Risko, C.; Sandhu, B.; Galán, E.; Zhu, L.; Tongwa, P.; Hwang, D. K.; Singh, S.; Wang, H.; Tiwari, S. P.; Loo, Y.-L.; Brédas, J.-L.; Kippelen, B.; Tatiana T.; Marder, S. R. *J. Mater. Chem. C* **2013**, *1*, 1467-1481.
http://dx.doi.org/10.1039/C2TC00805J
193. Ni, J.-S.; Kao, W.-S.; Chou, H.-J.; Lin, J. T. *ChemSusChem* **2015**, *8*, 2932-2939.
http://dx.doi.org/10.1002/cssc.201500193

194. Huang, Z.-S.; Zang, X.-F.; Hua, T.; Wang, L.; Meier, H.; Cao, D. *ACS Appl. Mater. Interfaces* **2015**, 7, 20418-20429.
http://dx.doi.org/10.1021/acsami.5b06404
195. Arroyave, F. A.; Richard, C. A.; Reynolds, J. R. *Org. Lett*. **2012**, *14*, 6138-6141.
http://dx.doi.org/10.1021/ol302704v

Authors' Biographies

Egor V. Verbitskiy was born in Sverdlovsk (at the present time Ekaterinburg), USSR, in 1981. He received his B.Sc. in Chemistry in 2003 and M.Sc. in 2005 with Organic Chemistry specialization from Ural State University (USU). In 2008, he obtained his Ph.D. at the Institute of Organic Synthesis of Ural Branch of RAS under the supervision of Professor Valery N. Charushin. He is currently a senior researcher at the Institute of Organic Synthesis of Ural Branch of RAS. His current research interests include novel methods in organic synthesis, heterocyclic chemistry, photochemistry, new analytical methods, chemosensors and medicinal chemistry

Gennady L. Rusinov was born in Beelitz, Germany, in 1954. He graduated the Ural Polytechnical Institute (UPI) in 1976. He obtained his Ph.D. in 1980 from the same institute under the supervision of Professor Isaak Postovsky. After that he joined the Institute of Organic Synthesis of Ural Branch of RAS. He is currently a leading researcher in Laboratory of Heterocyclic compounds at the Institute of Organic Synthesis of Ural Branch of RAS. His current research interests include novel methods in organic synthesis, heterocyclic chemistry, fluorine chemistry, green chemistry, coordination chemistry, photochemistry, new analytical methods, chemosensors, molecular recognition, and supramolecular chemistry; medicinal chemistry.

Valery N. Charushin is an Academician of RAS, Professor and Head of the Department of Organic and Biomolecular Chemistry at Ural Federal University, Director of the Institute of Organic Synthesis of Ural Branch of RAS. Prof. Charushin graduated with Honors from the Ural Polytechnical Institute (UPI) in 1973. In 1976, he earned his PhD in Organic Chemistry. In 1981–1982, he joined the research group of Prof. Henk van der Plas (Wageningen University, Wageningen, the Netherlands) where he worked on ring transformations of azaaromatics. In 1987, he earned the Doctor of Science Degree in Organic Chemistry. His current research interests include novel methods in organic synthesis, heterocyclic chemistry, fluorine chemistry, green chemistry, coordination chemistry, photochemistry, new analytical methods, chemosensors, molecular recognition, and supramolecular chemistry; medicinal chemistry.