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Chemistry of 2-aminoanthraquinones

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This review represents a systematic and comprehensive survey of the methods of preparation and the chemical reactivity of 2-aminoanthraquinone. This compound is an important intermediate for the synthesis of a variety of otherwise difficult to obtain synthetically useful and novel heterocyclic systems.

Key Words: 2-Aminoanthraquinone, addition, condensation, acetylation, diazotization, macromolecules, heterocycles

Introduction

2-Aminoanthraquinone (**1**), first produced commercially in the United States in 1921,[1] is used as an intermediate in the synthesis of anthraquinone dyes, which are used in automotive paints, high-quality paints and enamels, plastics, rubber, printing inks, and in textile dyeing.[2,3] Human exposure to 2-aminoanthraquinone may occur occupationally during its production or use. Recent production volumes are proprietary information and not available. The evaluation of 2-aminoanthraquinone had the purpose of elucidating the contributing role of aromatic amines to the increased incidences of bladder cancer observed among workers in the dye manufacturing industry.[4,5] The 2-aminoanthraquinone used for the majority of the studies has a melting point range of 255 to 292 °C, with decomposition noted at 292 °C. The deviation from the determined melting point ranges from those reported in the literature (303 to 306 °C) suggested that the chemicals were either of very low purity or that decomposition occurred before the melting point was reached. Ultraviolet spectrum analysis revealed the presence of an unidentified impurity; however, percent purity estimates were not provided.[6]

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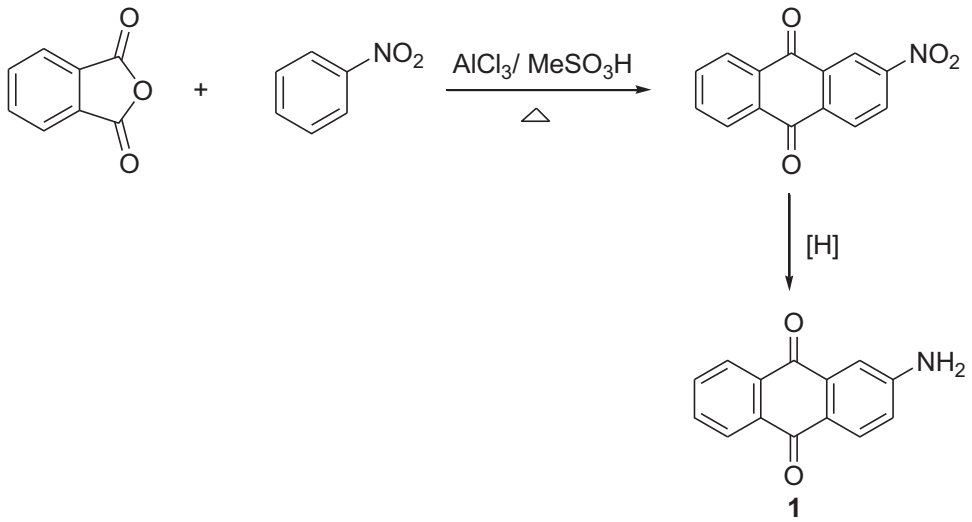
Synthesis

From nitrobenzene

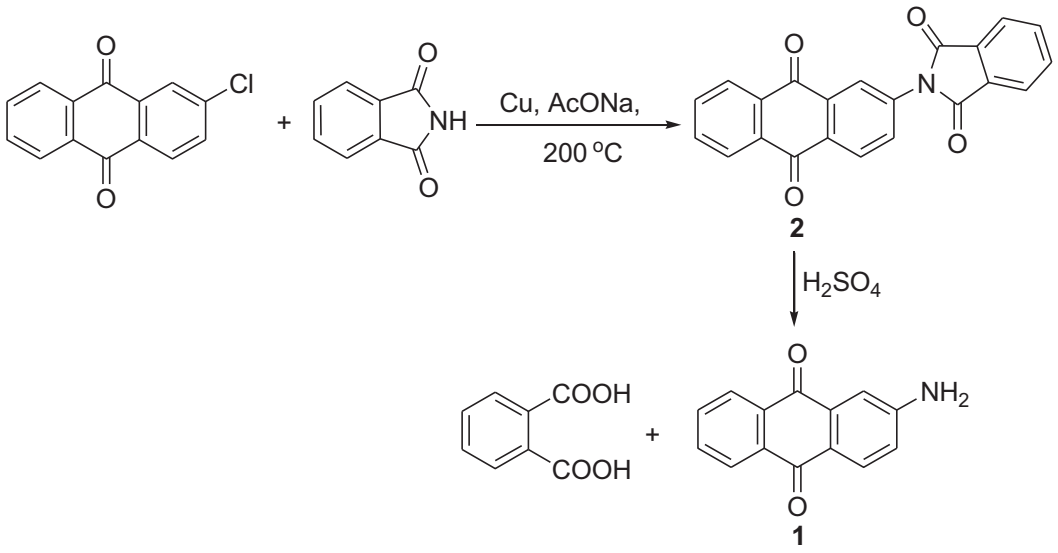
The reaction between phthalic anhydride and nitrobenzene in the presence of aluminum chloride and concentrated methanesulfonic acid gave 2-nitroanthraquinone directly, which upon reduction with SO_2/NO_2 group/mole nitro compound in 30%-60% H_2SO_4 at pH $<$ 3 and 80-180 °C in the presence of HI, $FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $SnCl_2$, or $TiCl_3$ as catalyst afforded 2-aminoanthraquinone (**1**) (Scheme 1).[7,8] Moreover, 2-aminoanthraquinone was prepared in high yields and purities by hydrogenating a finely divided suspension of 2-nitroanthraquinone in H_2O in the presence of base and using Raney Ni or Pd as the catalyst.[9] Furthermore, 2-nitroanthraquinone was reduced to the corresponding amino compound with optionally Pt, Euzonite 70S (Ni-Mo-Fe-Cr alloy), and/or V4A steel alloy (Fe-Cr-Ni-Ti-Mo-Mn-Si-C).[10,11]



Scheme 1

From phthalimide

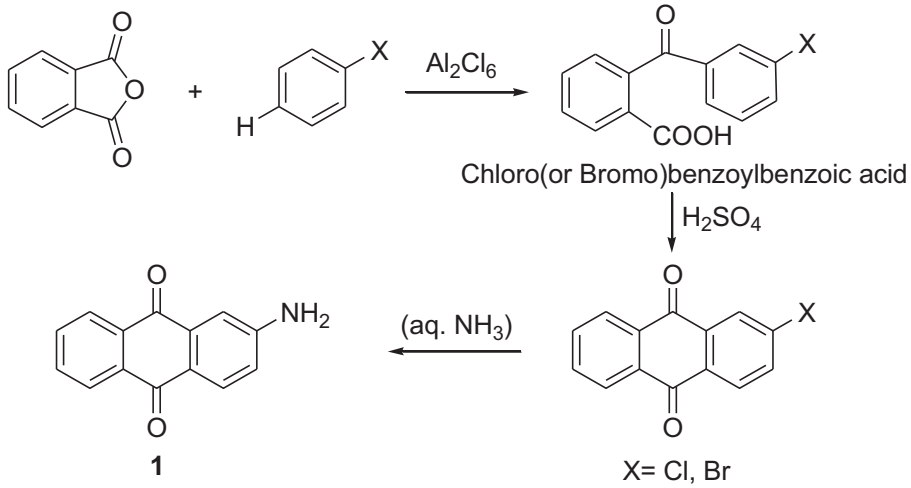
Fusion of 2-chloroanthraquinone with phthalimide at 200 °C in the presence of copper and sodium acetate afforded *N*-2-anthraquinyl phthalimide **2**; by treating this product with H_2SO_4, the phthalic acid regenerated and 2-aminoanthraquinone was formed.[12]



Scheme 2

From phthalic anhydride and chloro(or bromo)benzene

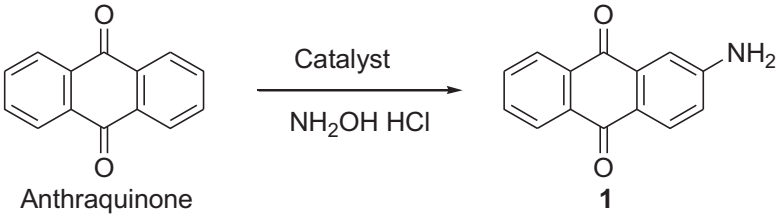
2-Aminoanthraquinone has been prepared according to the Friedel-Crafts reaction from phthalic anhydride and chloro(or bromo)benzene. The synthesis may be divided into 3 steps as follow: (1) preparation of 4'-chloro(or bromo)-2-benzoylbenzoic acid; (2) formation of 2-chloro(or bromo)anthraquinone by ring closure with concentrated sulfuric acid; and (3). Ammonolysis of β-haloanthraquinone in an autoclave with aqueous NH_3 in the presence of $[CuSO_4]$,[13] [Cu, $KClO_3/NH_4NO_3$],[14] $[NH_4NO_3/KClO_3]$,[15] $[Cu(NO_3)_2]$,[16] or fatty acid sulfonates,[17] afforded **1**.[18]



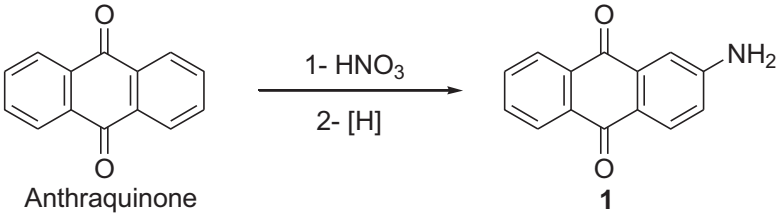
Scheme 3

From anthraquinone

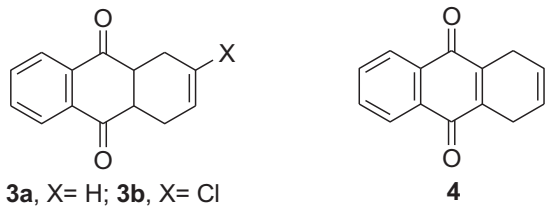
Amination of 9,10-anthraquinone with hydroxylamine in the presence of NO-$SnCl_2$,[19] H_2SO_4 containing $VOSO_4$ and $FeSO_4$,[20] H_2SO_4 containing $FeSO_4.7H_2O$,[21] H_2SO_4 containing $FeSO_4$ or V_2O_5,[22] H_2SO_4 containing $VOSO_4$,[23] or H_2SO_4 containing alkaline metal salt of $HON(SO_3H)_2$, and $(VO)_2(SO_4)_3$,[24] afforded **1**.



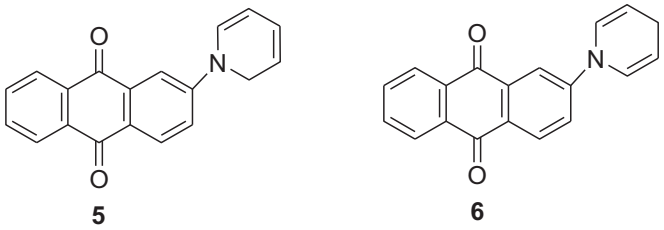
2-Aminoanthraquinone is prepared by treating a solution of anthraquinone in HNO_3 with a solution of Na hydrosulfite in aqueous *iso*-propyl alcohol.[25] 1-Aminoanthraquinone was prepared by nitration of anthraquinone and reduction of nitroanthraquinones by NaHS followed by separation of 1-aminanthraquinone from 2-aminoanthraquinone.[26]



Highly pure 2-aminoanthraquinone (**1**) was prepared by nitration of 1,4,4a,9a-tetrahydroanthraquinone (**3a**) or 1,4-dihydroanthraquinone (**4**) followed by dehydrogenation-reduction in the presence of (halo or alkyl) aromatic or aliphatic hydrocarbons. Thus, nitration of 1,4-dihydroanthraquinone with 98% HNO_3 and treatment of the product in benzene with Na_2S at 95 °C afforded **1**.[27,28] Furthermore, nitration of 1,4,4a,9a-tetrahydroanthraquinone (**3a**) with conc. HNO_3, treatment of the nitration product at 0-50 °C with aqueous alkali at pH 7.5-12, followed by refluxing with aqueous $NaHSO_3$ solution, afforded **1**.[29] Moreover, 2-aminoanthraquinone (**1**) was prepared by heating 2-chloro-1,4,4a,9a-tetrahydroanthraquinone (**3b**) in aqueous NH_3 under pressure using nitrobenzenesulfonic acid as oxidizing agent.[30]



The photoreaction of 9,10-anthraquinone with pyridine under argon atmosphere gave **5** or **6**, which, on treatment with base, gave **1**.[31]

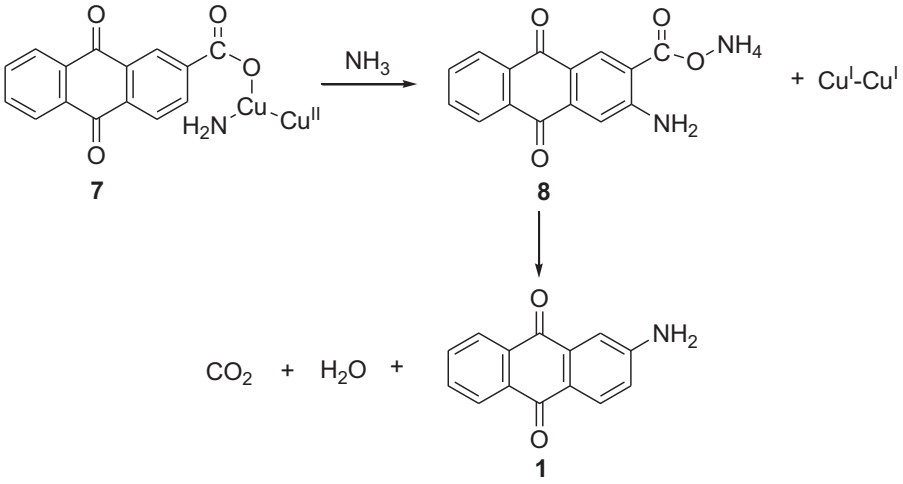


5 **6**

The photoamination of anthraquinone under several conditions (e.g., $NH_2OH.HCl$ in aqueous dioxane, $MeNH_2$ in aqueous isopropanol, NH_3 in aqueous organic solvents in air or argon) was examined. The best yield (33% 2-aminoanthraquinone) was obtained with NH_3 in aqueous isopropanol in air. A radical acceptor, ionol, had no effect. A mechanism involving electron transfer from NH_3 to electronically excited anthraquinone was suggested.[32]

From anthraquinone-2-carboxylic acid

2-Aminoanthraquinone was obtained in 5% yield as a product of the amination of anthraquinone-2-carboxylic acid. The one-isomer was produced in only trace amounts. Direct decarboxylation to anthraquinone was the principal reaction.[33]



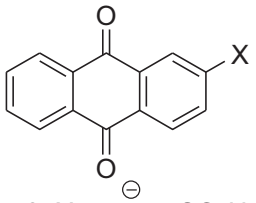
Scheme 4. Mechanism of the amination reaction.

Moreover, **1** was prepared by reaction of the corresponding carboxylic acids with NH_3 and H_2O at 8-10 atmosphere gage and 215-220 °C in the presence of CuO.[34]

From anthraquinone-2-sulfonate

Irradiation of a mixture of sodium anthraquinone-2-sulfonate (**9**) and aqueous ammonia or heating in an autoclave under pressure gave 2-aminoanthraquinone (**1**).[35,36] Moreover, compound **1** was prepared by heating of anthraquinone-2-sulphonic acid or its sulfonate derivatives with concentrated NH_3 solution in the presence of an oxidizing agent such as $NaClO_3$,[37,38] NH_4NO_3, or of a mixture of an alkali nitrate,[39] $BaCl_2/NH_4Cl$,[40] $CaCl_2$

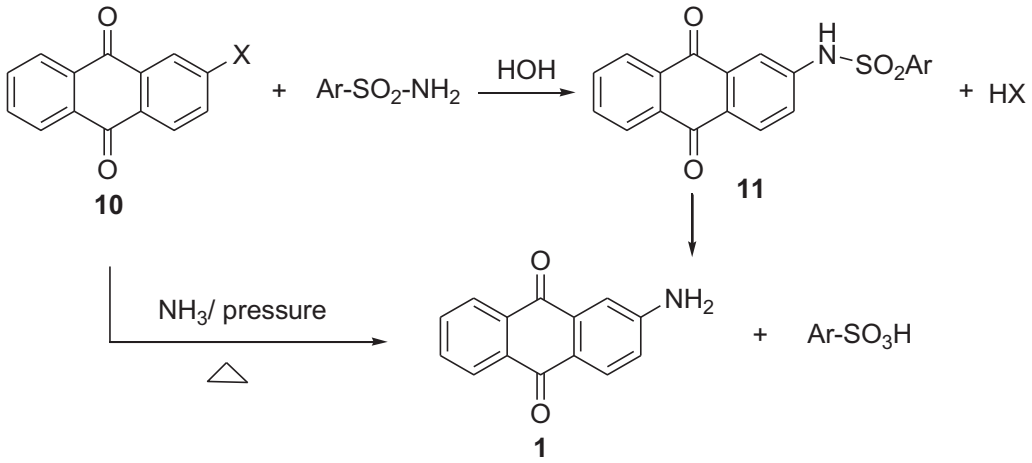
(or $MgCl_2$), and NaCl,[41] $CaCl_2/MgO_2$,[42] $CaCl_2$ together with NH_4Cl, NaCl, or MgCl or a mixture of these chlorides,[43] Na_2HAsO_4,[44,45] $Na_2Cr_2O_7$,[46] a nitro compound, e.g., nitrobenzene, Na nitrobenzenesulfonate, nitrotoluene, dinitrobenzene, nitronaphthalene, dinitronaphthalenes, or their sulfonic acid derivatives.[47–49]



Direct ring amination of Na anthraquinone-β-sulfonate by NH_2OH-$FeSO_4$ in H_2O or conc. H_2SO_4 gave **1**.[50]

From halogenated anthraquinones

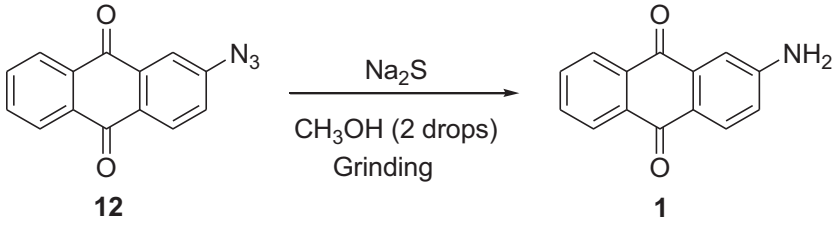
Ullmann,[51] in 1910, discovered that sulfonamides will condense with halogen anthraquinones **10** at ordinary pressure. On hydrolysis the condensation product **11** gives the aminoanthraquinone. Moreover, 2-haloanthraquinone **10** when heated with aqueous ammonia under pressure was converted into the corresponding AAQ.[52,53]



Scheme 5

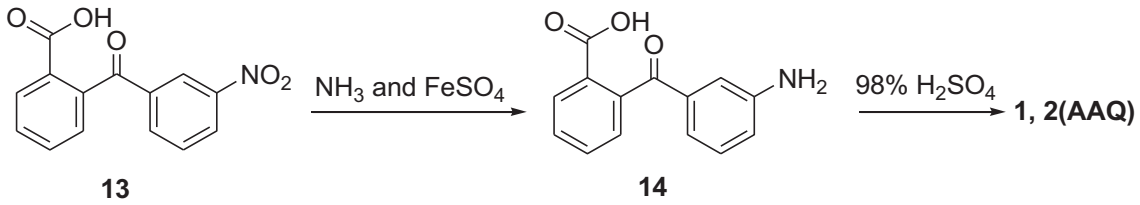
From 2-azido-anthraquinone

Sodium sulfide hydrate has been employed for an efficient reduction of a variety of azides **12** to the primary amines in good to excellent yields under a solvent-free system and without perturbing the very active functionality such as ether, carbonyl, sulfonyl, and nitro.[54]



From 2-(3-aminobenzoyl)benzoic acid

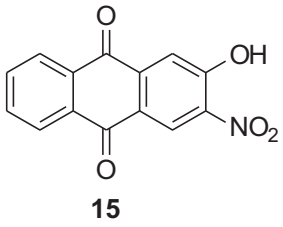
2-(3-Aminobenzoyl)benzoic acid (**14**) was prepared by reduction of 2-(3-nitrobenzoyl)benzoic acid (**13**) with concentrated aqueous NH_3 and $FeSO_4$. Cyclization of **14** by heating in 98% H_2SO_4 gave a mixture of 1-AAQ and 2-AAQ. Heating 2-(3-aminobenzoyl)benzoic acid (**14**) in vacuo in the presence of active terra alba afforded **1**.[55,56]



Scheme 6

From 1,2,3,4-tetrahydro-2-hydroxy-3-nitroanthraquinone

Compound **1** was obtained by treating 1,2,3,4-tetrahydro-2-hydroxy-3-nitroanthraquinone (**15**) with Na_2SO_3 solution.[57]



Purification of 2-aminoanthraquinone

Ten parts crude 2-aminoanthraquinone is mixed with 60 parts paraffin oil and the mixture distilled at 23 mm. The distillation temperature ranges from 265 to 330 °C after which the distillation is halted. The distillate is washed with petroleum ether and dried to give 9 parts pure 2AAQ, 302-304 °C.[58]

Paper chromatographic separation and identification

The chromatographic distillation and identification of 2-aminoanthraquinone was satisfactory in the following solvent systems: Pr-OH-25% NH_3 (2:1); BuOH standardized with 2.5 N HCl or PrOH-HCl-H_2O (5:1:3), by

using Whatman No. 1 paper. Following the 16 h runs the chromatograms were developed by one of the following techniques: Ehrlich reagent, 0.01% diazotized 2,4-dinitroaniline spray followed by spraying with 10% aq. KOH or direct diazotization on paper with N_2O_3 followed by coupling with, for instance, 1% resorcinol in 5% NaOH.[59]

Hydrogen-bridge bonding and chromatographic separation

Adsorption of a variety of aminoanthraquinones was determined by passing C_6H_6 solutions through columns packed with silica gel or Al_2O_3. Compounds with H-bridge forms passed through the column; the others were adsorbed. This provides a method for separating isomers, 1,2-, 1,3-, 1,6-, or 1,7-dihydroxyanthraquinones, which are adsorbed while the other isomers pass through a calcite-packed column. On calcite, 2-hydroxyanthraquinone was adsorbed but 2-aminoanthraquinone passed through.[60]

Reactions

Chemical structure of 2-aminoanthraquinone

On treatment of 2-aminoanthracene-9,10-dione with various reagents the attack can take place at 6 sites; the nucleophile is able to attack the carbon of the carbonyl function (positions 3, 4), while the amino group (position 3) is able to attack electrophiles. The amino group in position 1, β-carbon position 2, and 2 oxygen atoms of carbonyl positions 5, 6 are able to attack electrophiles.

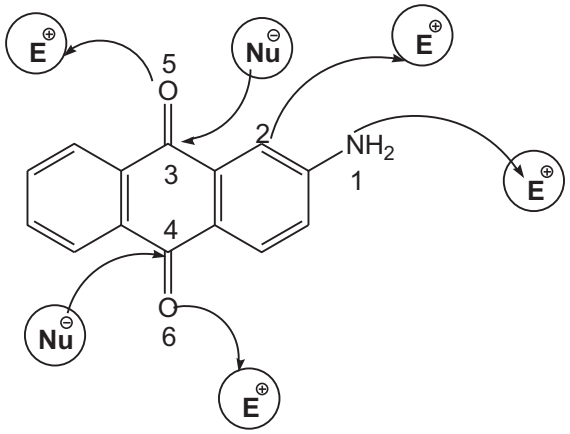


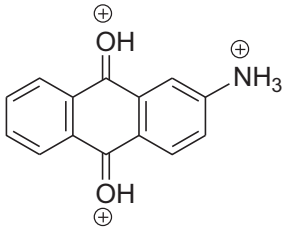
Figure 1

Synonyms

2-Amino-9,10-anthraquinone, β-aminoanthraquinone, 2-aminoanthraquinone, and β-anthraquinonylamine.

Protonation

Protonation in H_2SO_4 and H_2SO_4-AcOH solutions occurs at the amino and carbonyl groups to give compound **16**.[61]



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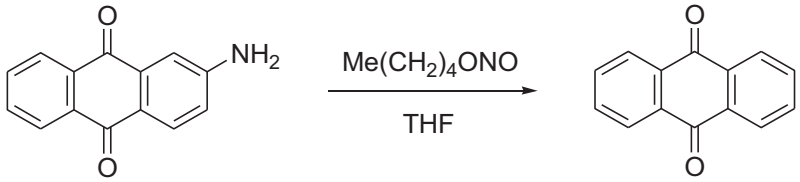
Deamination

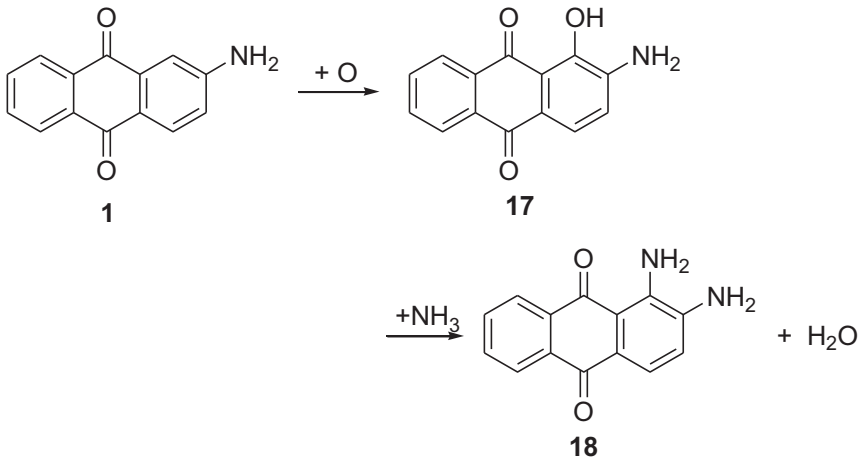
2-Aminoanthraquinone (**1**) was de-aminated by the reaction with nitrosoxypentane in THF to afford anthraquinone.[62]



1

Formation of 1,2-diaminoanthraquinone

The formation of 1,2-diaminoanthraquinone (**17**)[63] can be explained on the basis of a preliminary formation of 1-hydroxy-2-aminoanthraquinone (**18**) as a result of oxidation:[64]



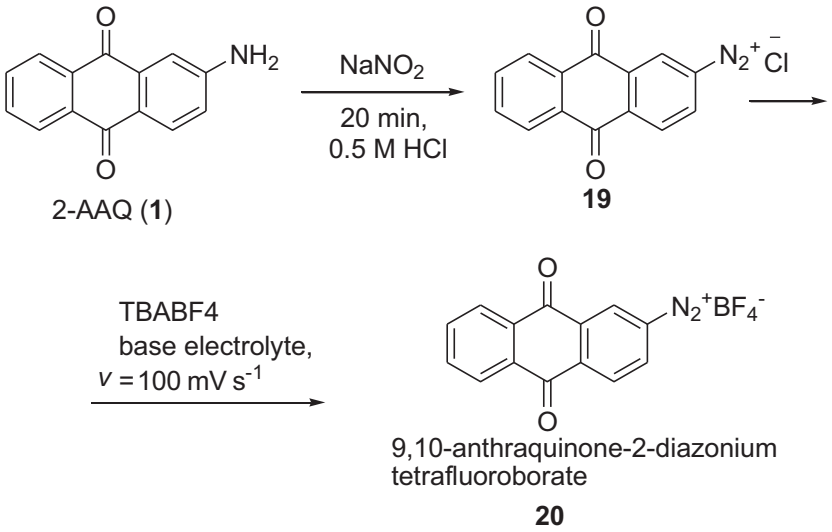
1 **17** **18**

Scheme 7

Diazotization

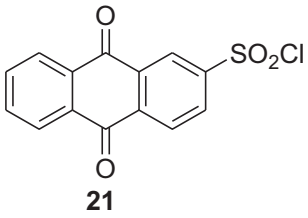
The electrochemical reduction of oxygen on glassy carbon (GC) electrodes modified with in situ generated diazonium cations of anthraquinone (AQ) has been studied using the rotating disk electrode (RDE) technique.

The electrografting of the GC electrodes was carried out in 2 different media: in acetonitrile and in an aqueous acidic solution (0.5 M HCl). 2-Aminoanthraquinone was used as starting compound for the formation of the corresponding diazonium derivatives (**19**). The anthraquinone diazonium cation was generated by reaction of the aminoanthraquinone with sodium nitrite in 0.5 M HCl. For comparison purposes, the previously synthesized and crystallized diazonium tetrafluoroborate of anthraquinone **20** was used for the GC surface modification.[65]



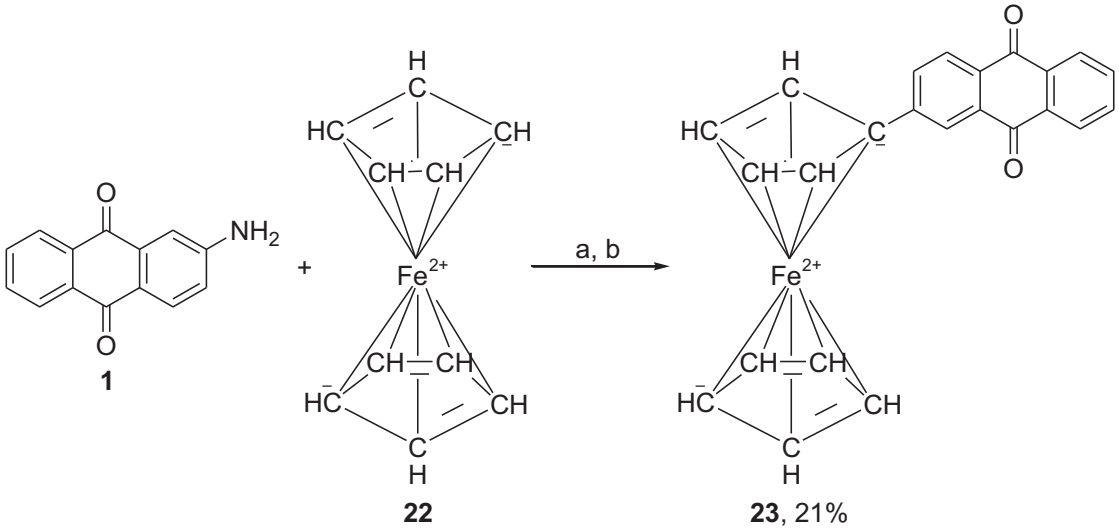
Scheme 8. Diazotization of 2-aminoanthraquinone with $NaNO_2$ in 0.5 M HCl.

The diazonium salt **19** afforded the sulphonyl chloride **21** upon treatment with SO_2 in the presence of $CuCl_2$.[66]

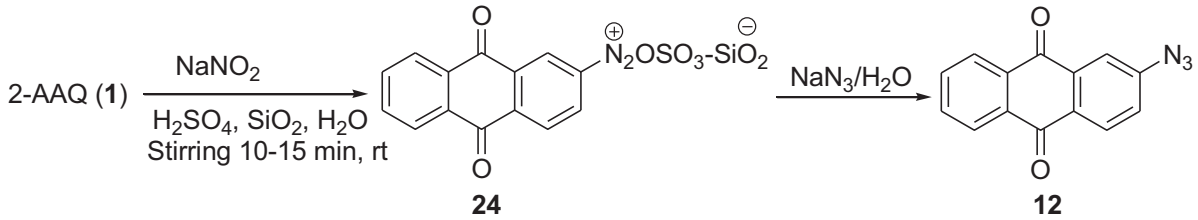


Diazotization of 2-aminoanthraquinone with subsequent treatment with **22** ferrocene afforded 2-ferrocenylanthracene **23**.[67]

A mixture of **1** with silica sulfuric acid and sodium nitrite was ground in a mortar with apisite for a few minutes to afford the corresponding diazonium silica sulfate **24**. The latter diazonium salt was sufficiently stable and could be kept at room temperature under anhydrous conditions. Stirring of diazonium salt **24** with sodium azide at room temperature under mild conditions afforded 2-azide anthraquinone **12** (Scheme 9).[68]

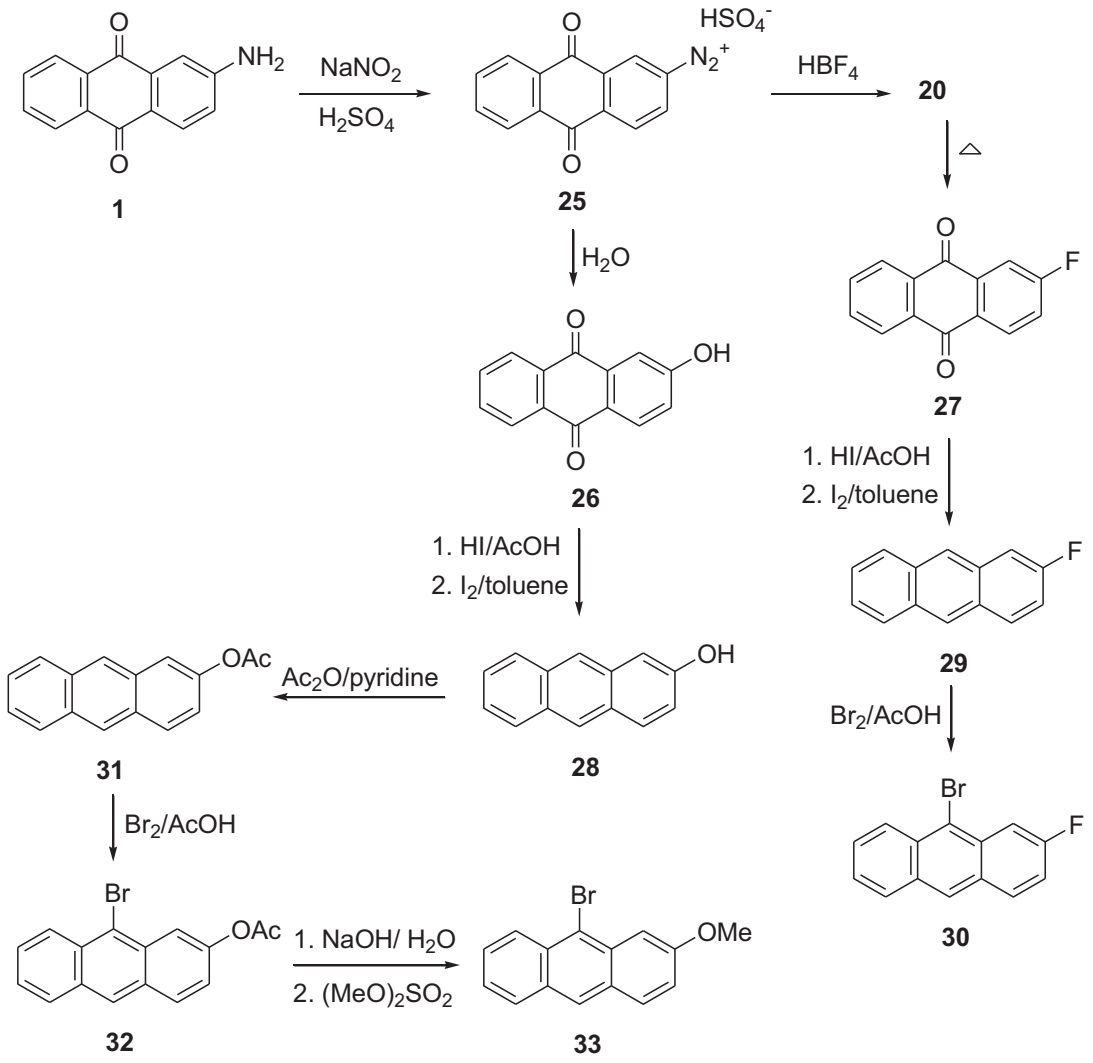


a, $NaNO_2$, HCl, H_2O, 0 °C; b, AcOH, 0 °C, 10 h, rt, overnight.



Scheme 9

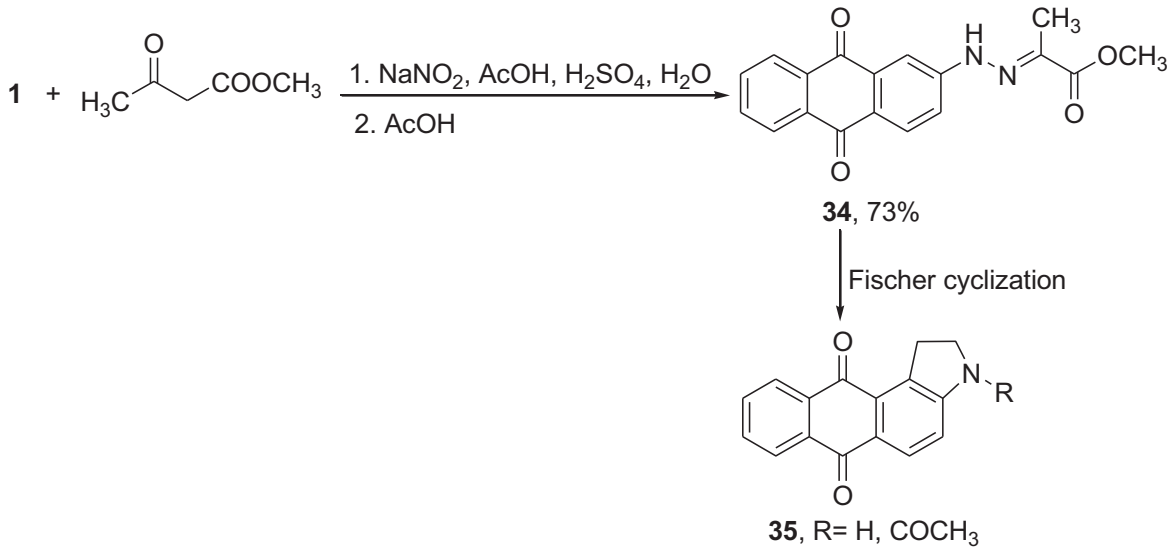
2-AAQ (**1**) was diazotized in concentrated H_2SO_4 and the diazonium salt **25** was hydrolyzed to 2-hydroxyanthraquinone **26**.[69,70] Alternatively, the diazonium tetrafluoroborate **20** was isolated and thermally decomposed to 2-fluoroanthraquinone **27**; also treatment of **1** with nitrosonium tetrafluoroborate in dichloromethane afforded **20**, and the resulting tetrafluroborate **20** was heated without isolation on drying to give **27**.[71] When the anthraquinones **26** and **27** were reduced to the anthracenes **28** and **29** by hydroboration with $NaBH_4/BF_3$ in diglyme,[72] the yields of the desired anthracenes were 35% due to formation of the byproducts 2-substituted anthrones and 9,10-dihydroxy-9,10-dihydroanthracenes. Reduction with HI in AcOH at ca. 120 °C was more effective and gave a mixture of the desired anthracene and up to 40% of the 9,10-dihydro derivative, which on treatment with iodine afforded the anthracene in 80%-90% yield. Careful bromination of 2-fluoroanthracene (**29**) afforded a good yield (70%) of 9-bromo-2-fluoroanthracene (**30**), accompanied by a small amount of the 9,10-dibromo derivative. 2-Hydroxyanthracene **28** could not be selectively brominated at C-9 or C-10.[73] It was therefore first acetylated to 2-acetoxyanthracene (**31**), which was brominated to 9-bromo-2-acetoxyanthracene (**32**), analogously to **29**. In a one-pot procedure, **32** was hydrolyzed and the product was O-methylated to the 9-bromo-2-methoxyanthracene (**33**).[74]



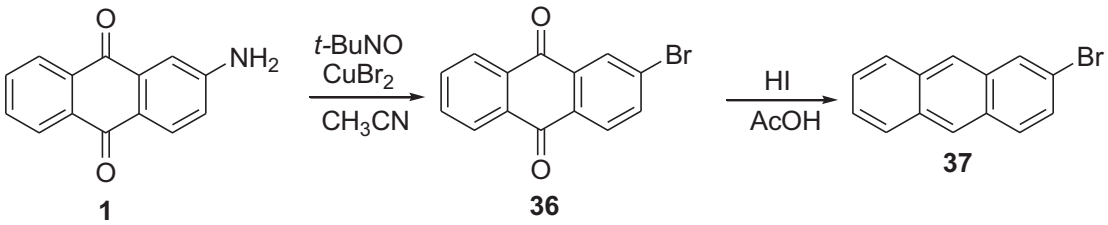
Scheme 10

Naphth[2,3-*c*]indol-4,9-diones (**35**; R= Ac, H) were synthesized by the Fischer cyclization of pyruvic acid 2-anthraquinonylhydrazone; the latter was obtained via coupling of **25** with methyl-3-oxo-butanate in acetic acid.[75]

t−Butyl nitrite and cupric bromide was reacted with 2-aminoanthraquinone (**1**) to give 2-bromoanthraquinone (**36**),[76] as a yellow solid. 2-Bromoanthracene (**37**) was produced by the general procedure for the reduction of anthraquinones.[77] The reaction of 2-bromo-anthraquinone (**36**) in a mixture of acetic acid, hydriodic acid, and hypophosphorous acid afforded 2-bromoanthracene (**37**).

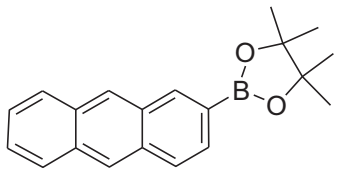


Scheme 11



Scheme 12

2-Bromoanthracene (**37**) reacts with *bis*(pinacolato)diboron and potassium acetate in anhydrous DMSO to afford 2-anthracen-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (**38**) by the general procedure for the arylboronate synthesis.[78]



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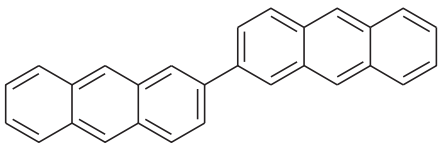
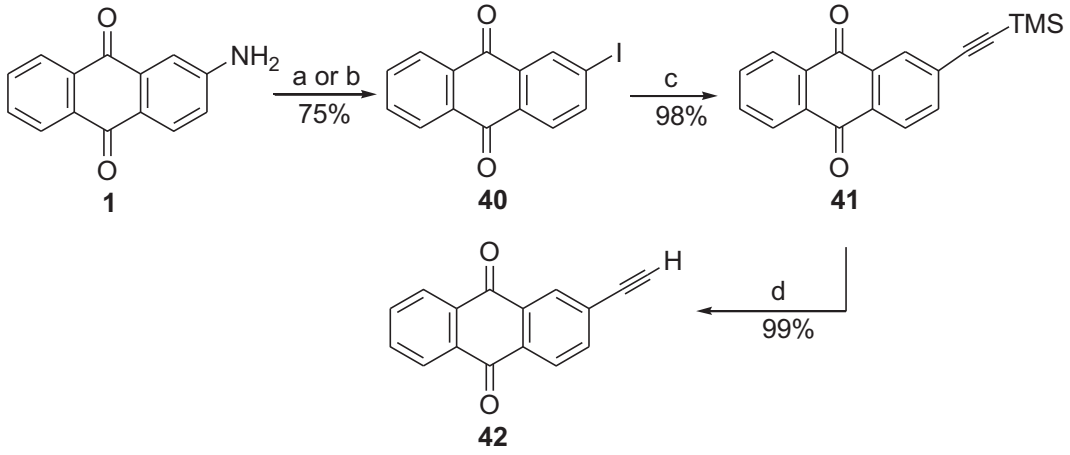
Furthermore, 2-bromoanthracene (**37**) reacts with 2-anthracen-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (**38**) in toluene and Na_2CO_3 to afford [2,2']bianthracenyl (**39**).[78,79]



39

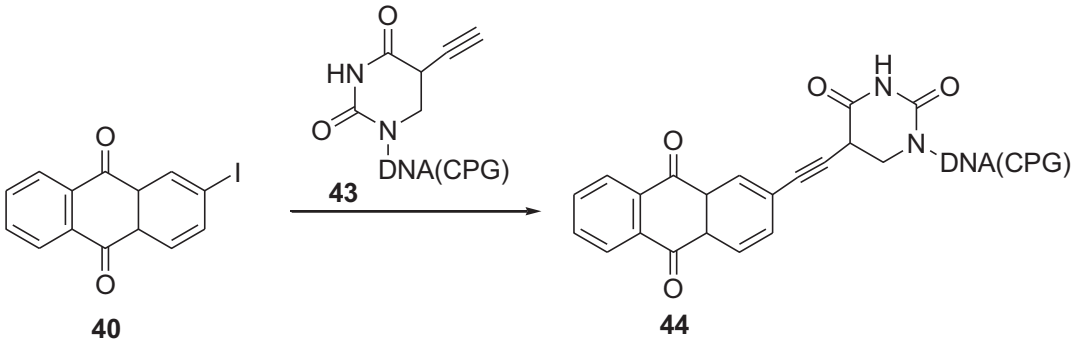
To form 2-iodoanthraquinone (**40**), 2-AAQ (**1**) was diazotized with nitrous acid that was prepared in situ from HCl and $NaNO_2$ and then substituted with iodide in a manner similar to the Sandmeyer reaction. Baik et al.[80] prepared **40**,[81] via a one pot-reaction of **1** with HI and $NaNO_2$ in DMSO. Furthermore, **40** was prepared via stirring of **25** with KI at room temperature.[82]

Compound **42** was prepared in 2 steps beginning with **40**. In the first step, $Pd(Ph_3P)_2Cl_2$ catalyzed cross-coupling of trimethylsilylacetylene (TMSA) with **40** gives 2-(trimethylsilylethynyl)anthraquinone (**41**); then the terminal alkyne of **41** is de-protected with KF to give 2-ethynylanthraquinone **42**. Although 2-chloroanthraquinone is commercially available, its Pd(0)-catalyzed cross-coupling reaction is likely to occur less readily than those for either 2-bromo or 2-iodoanthraquinone. Moreover, direct bromination of commercially available anthraquinone yields a mixture of polybromoanthraquinones that is difficult to separate.[83] Other reported syntheses of 2-bromoanthraquinone either have low yields,[84] or require harsh conditions.[85] For these reasons, as well as the fact that iodide is a better leaving group than bromide, **40**[86] appears to be a good precursor for forming **42**.[87]

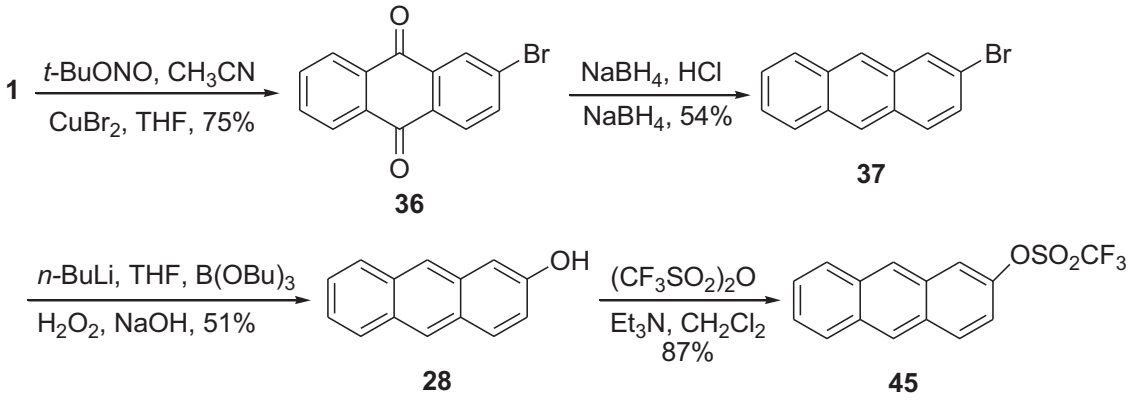


Scheme 13. Reagents and conditions: (a) i. HCl, $NaNO_2$, THF/H_2O, 0 °C; ii. KI, 0 °C, 75 min; (b) HI, $NaNO_2$, DMSO, 35 °C 20 min; (c) $Pd(Ph_3P)_2Cl_2$, CuI, Et_3N, THF, TMSA, rt, 10 min; (d) KF, THF/MeOH, rt, 1 h.

The coupling of the 2-iodoanthraquinone (**40**) to the ethynyluracil-modified DNA (**43**) was performed while the DNA was still attached to controlled pore glass (CPG) solid support.[88]



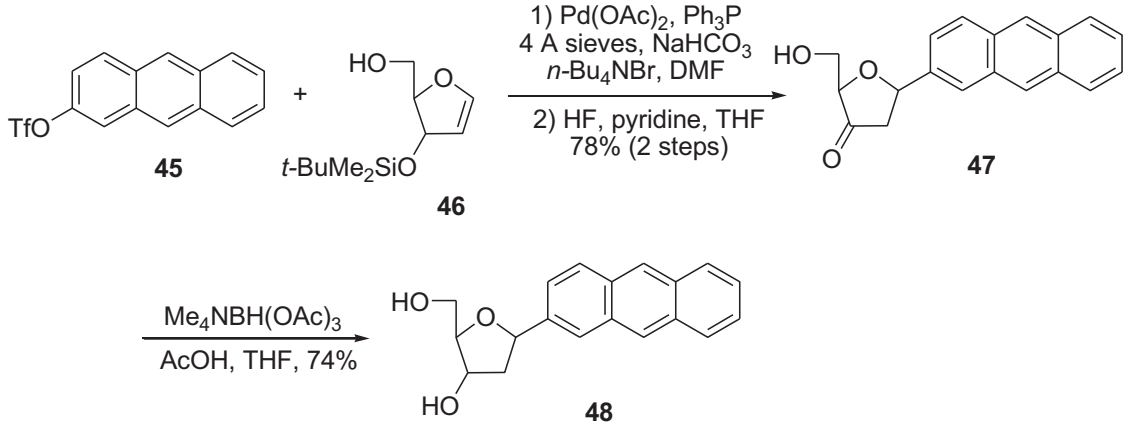
The quinone of **36** was reduced also, to the aromatic system by the 3-step sequence of reduction, elimination, and reduction[89] to afford 2-bromoanthracene (**37**). Conversion of the bromide of **37** to the corresponding phenol proceeded in modest yield via the intermediate anthracenyllithium species, which was trapped as the di, tri-butyl borinate that was oxidized in situ to afford 2-hydroxyanthracene (**28**). Installation of the trifluoromethanesulfonate ester proceeded in high yield to afford coupling partner **45**.[90]



Scheme 14

Stereocontrolled C-glycoside construction

Heck coupling of triflate **45** with glycal **46**, prepared conveniently from thymidine in 3 steps,[91,92] followed by in situ fluoride-promoted desilylation, afforded the aryl β-*C*-glycoside **47** in 78% yield.[90]

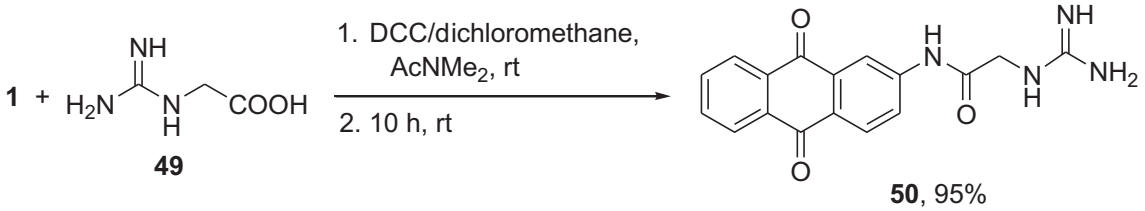


Scheme 15

Hydroxyldirected reduction of the ketone of **47** using tetramethylammonium triacetoxyborohydride[93] in the presence of acetic acid provided the diol **48** in acceptable yields.[90]

Reaction with 2-(amidinoamino)acetic acid

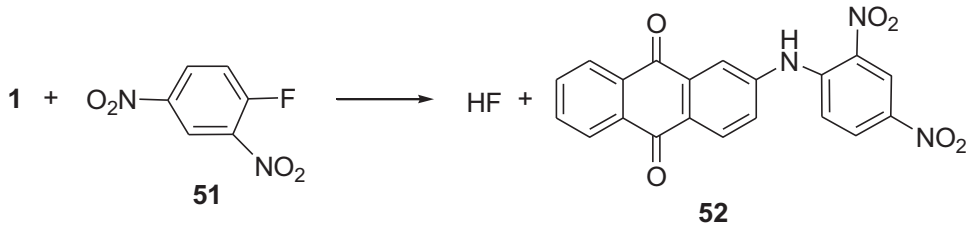
Stirring of 2-(amidinoamino)acetic acid (**49**) with **1** at room temperature with dimethylacetamide in the presence of DCC afforded the amidinoamino **50**.[94]



Reaction with halo compounds

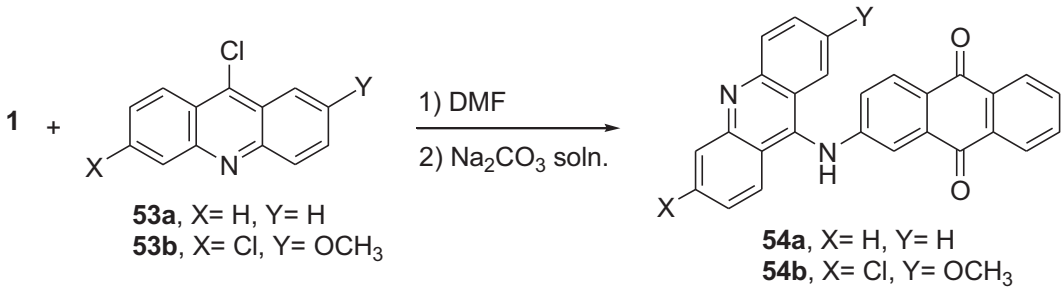
With 1-fluoro-2,4-dinitrobenzene

Aromatic amines are very important compounds in the heavy organic chemicals industry, e.g., in the production of dyes. 1-Fluoro-2,4-dinitrobenzene (**51**) reacts with primary aromatic amines to produce 2,4-dinitrophenyl derivative (**52**) of anthraquinone moiety, since 1-fluoro-2,4-dinitrobenzene contains electronegative substituents in positions 2 and 4. The fluorine in position 1 is very reactive and it is expected that this reagent will react with most aromatic amines.[95]



With 9-chloroacridine and 3,9-dichloro-7-methoxy-1,4-dihydro-acridine

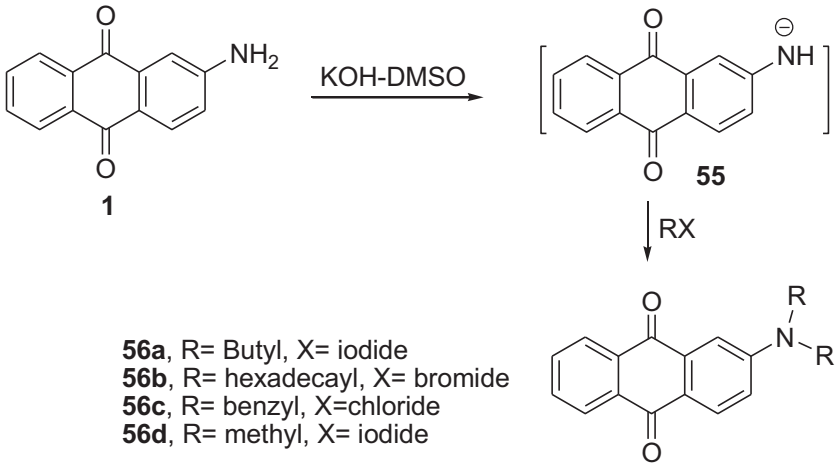
9-Chloro-acridine (**53a**) or 3,9-dichloro-7-methoxy-1,4-dihydro-acridine (**53b**) on condensation with 2-aminoanthraquinone (**1**) in DMF gave the condensed product 2-(acridin-9-ylamino)-anthraquinone (**54a**) and 2-(3-chloro-7-methoxy-1,4-dihydro-acridin-9-ylamino)-anthraquinone (**54b**), respectively.[96,97]



Reaction with alkyl halide

Amide ions (**55**) were formed by the loss of a proton from the amino group of anthraquinones in the presence of powdered potassium hydroxide (KOH) in DMSO.[98,99] The amide ion of 2-AAQ reacted with ex-

cess alkyl halides such as 1-iodobutane, 1-bromohexadecane, benzyl chloride, and methyl iodide to yield 2-dialkylaminoanthraquinones (**56a-d**) in good yield.[99,100]

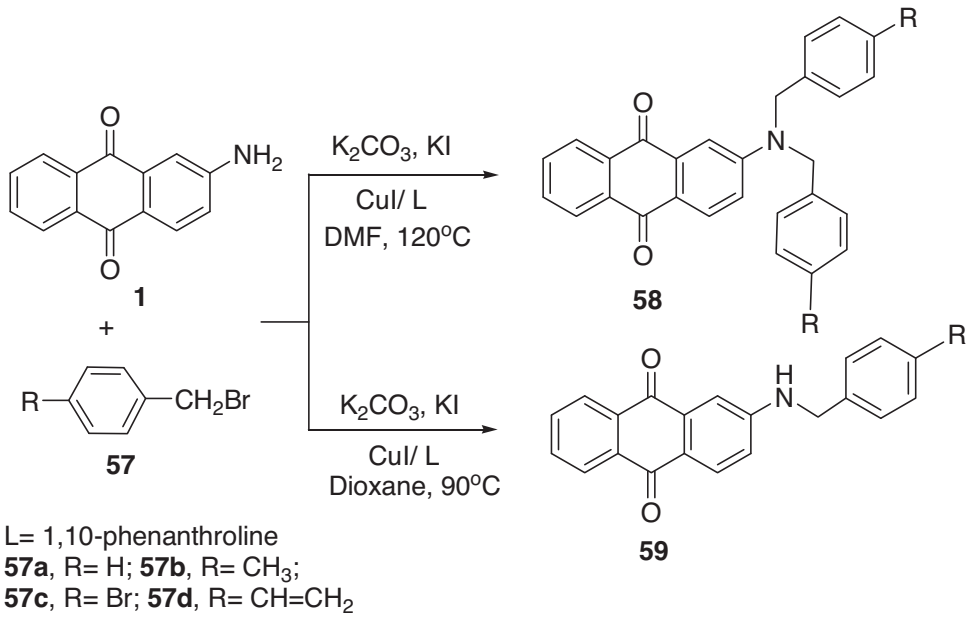


Scheme 16

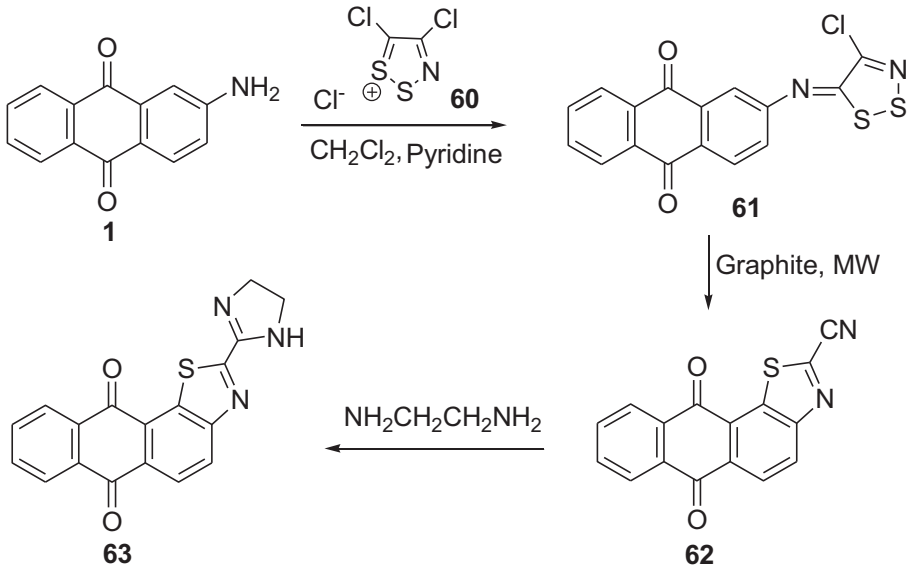
The nucleophilicity of aminoanthraquinones is too weak owing to the 2 electron-attracting groups (carbonyl) attached to the amino substituted aromatic rings. Therefore, the quaternary ammonium salt can be avoided and multiple benzylation can be controlled.[101] Moreover, at higher applied temperature more bisbenzyl substituted 2-aminoanthraquinones **58** are produced. Thus, during the synthesis of monobenzyl substituted 2-AAQ's **59**, the temperature must be maintained below 100 °C. Meanwhile, the benzyl bromide **57** should be added dropwise and 2-AAQ must be in excess.[101]

Reaction with 4,5-dichloro-l,2,3-dithiazolium chloride

2-AAQ was condensed with 4,5-dichloro-l,2,3-dithiazolium chloride (**60**) in dichloromethane at room temperature, followed by addition of pyridine, to give the desired 2-(4-chloro-[1,2,3]dithiazol-5-ylideneimino)-anthraquinone (**61**) in good yields.[102] Microwave irradiation (150 W) of imino-l,2,3-dithiazole derivative **61** at 150 °C in the presence of a small amount of graphite (10% by weight) surprisingly afforded the angular 2-cyanobenzothiazole **62**. No trace of the linear counterpart was detected. The cyano group in position-2 of the benzothiazole ring is very reactive and its transformation into acid, amide, amidine, and imidate may be easily realized. The condensation of 2-cyanobenzothiazole with the commercially available ethylenediamine in various solvents (e.g. ethanol, THF) was studied to give the desired imidazoline **63**.[102]



Scheme 17

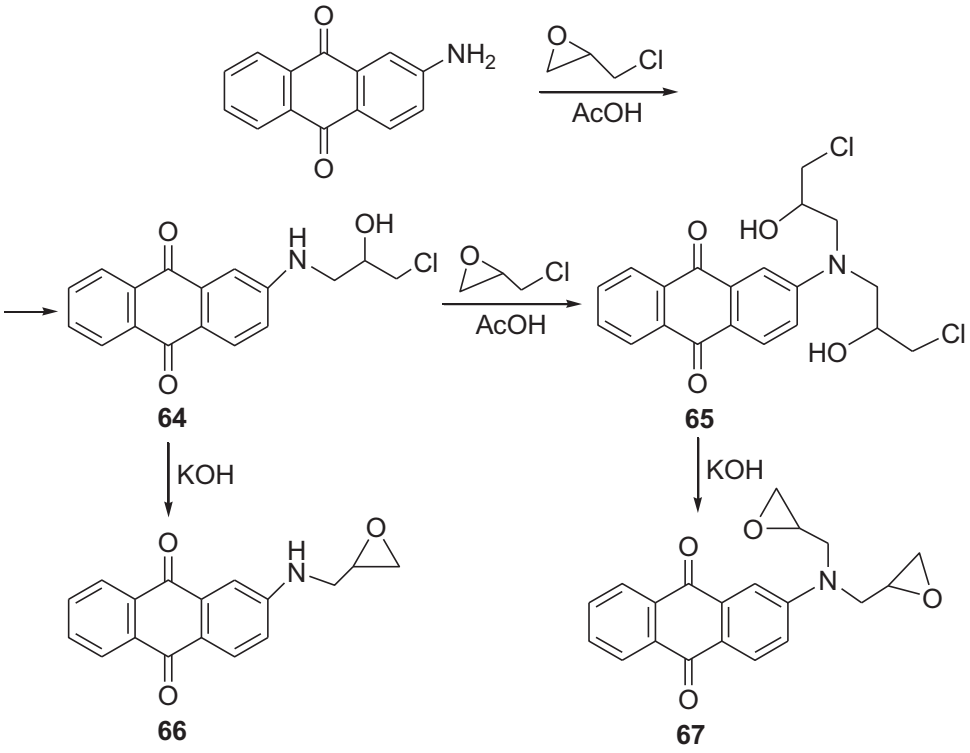


Scheme 18

Reaction with 1-chloro-2,3-epoxypropane (CEP)

2-Aminoanthraquinones were used as starting materials for the synthesis of electron-transporting materials (ETMs). The corresponding mono and *bis* derivatives, i.e., 2-(3-chloro-2-hydroxypropylamino)anthraquinone (**64**) and 2-[*bis*(3-chloro-2-hydroxypropyl)amino] anthraquinone (**65**), were obtained from 2-aminoanthraquinone under analogous conditions. Treatment of the solutions of **64** and **65** in dioxane with 85% powdered potassium hydroxide gave the corresponding epoxy compounds 2-(2,3-epoxypropylamino)anthraquinones (**66**) and

2-(2,3-epoxypropylamino)anthraquinone (**67**).[103]

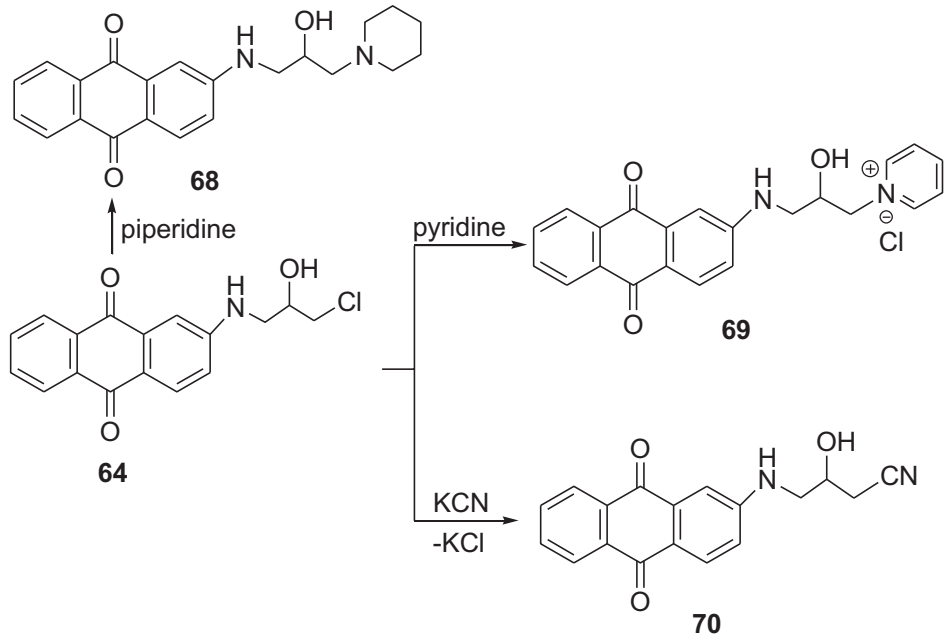


Scheme 19

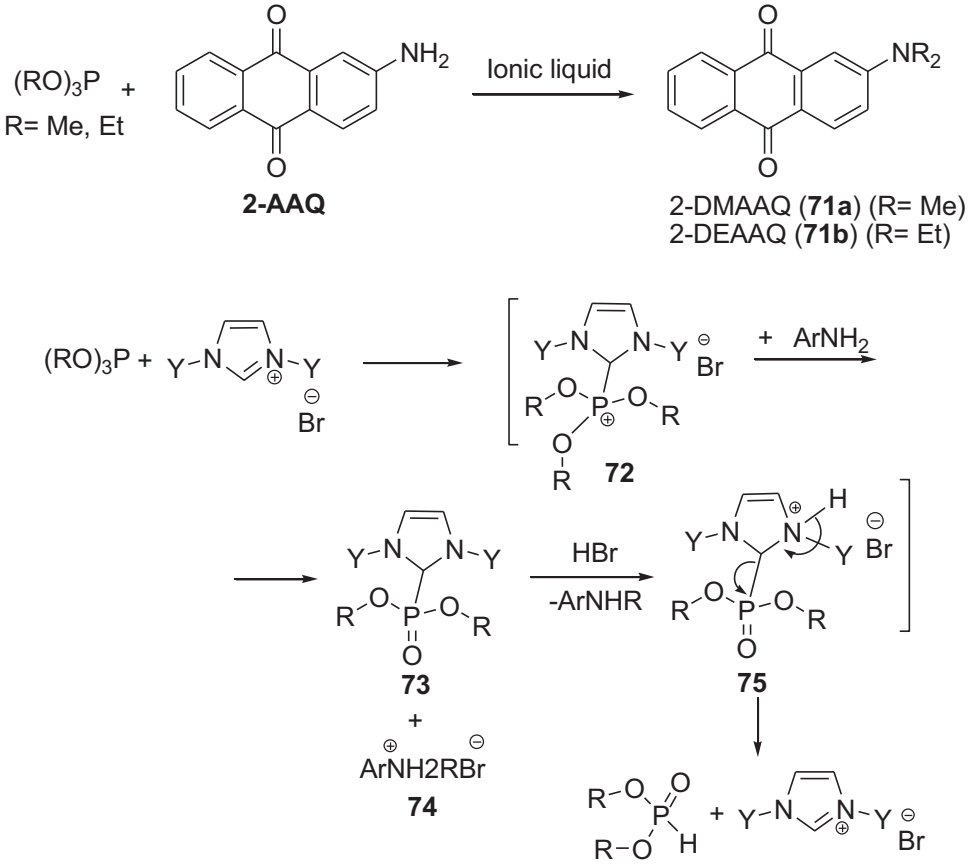
In addition to the above mentioned reaction, other reactions characteristic of 3-chloro-2-hydroxypropyl compounds with piperidine, pyridine, diethylamine, isopropylamine, and potassium cyanide were also carried out in order to confirm the structure of compounds **64**. Here the following compounds were obtained: 1-(2-hydroxy-3-piperidinopropylamino) anthraquinone (**68**), 1-[3-(anthraquinone-1(2)-amino)-2-hydroxypropyl]pyridinium chlorides (**69**), and 4-[anthraquinone-1(2)-amino]-3-hydroxybutanenitriles (**70**).[103]

Reaction with trialkyl phosphites

The reaction of 2-AAQ with trialkyl phosphites was studied in different imidazolium-based ionic liquids at various temperatures. Although 2-MAAQ is expected to be less nucleophilic compared to 2-DMAAQ (**71a**) in conventional solvents,[104] the reactivity of the former towards *N*-alkylation in the ILs used is at least 2 orders of magnitude. Dialkylation of 2-AAQ takes place in the presence of 1 equiv of TMP. In order to obtain information about the mechanism of this transformation, the reaction mixture of 2-AAQ and TMP was monitored by ^{1}H- and ^{31}P-NMR spectroscopy.[105] ILs are proved to be useful and novel reaction media for the *N*-alkylation of 2-AAQ by trialkyl phosphites, avoiding the use of base and highly polar organic solvents. The effects of reaction temperature and the type of IL used on the activity and selectivity were investigated. The IL [bpim][Br] was found to be the most effective. The use of room temperature imidazolium ILs significantly enhanced the rate of *N*-alkylation of 2-AAQ.[105]



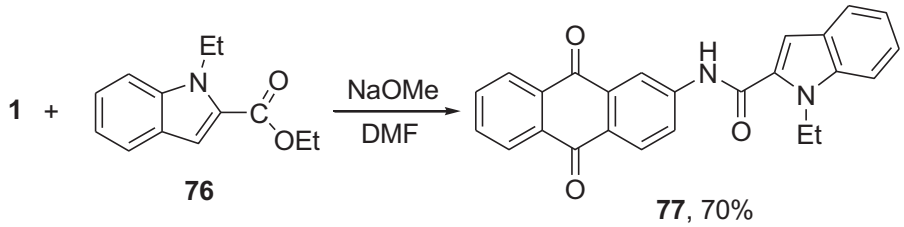
Scheme 20



Scheme 21. Plausible mechanism for the alkylation of AAQ by trialkyl phosphites.

Reaction with ethyl 1-ethyl-1H-indole-2-carboxylates

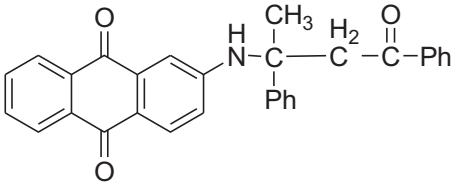
Treatment of ethyl 1-ethyl-1*H*-indole-2-carboxylate (**76**) with 2-aminoanthraquinone in sodium ethoxide gave 1*H*-indole-2-carboxamide analogue **77**.[106]



76 **77**, 70%

Reaction with acetophenone

The interaction of **1** with acetophenone in diethyl ether and in the presence of BF_3 afforded the corresponding anthraquinone (**78**).[107]



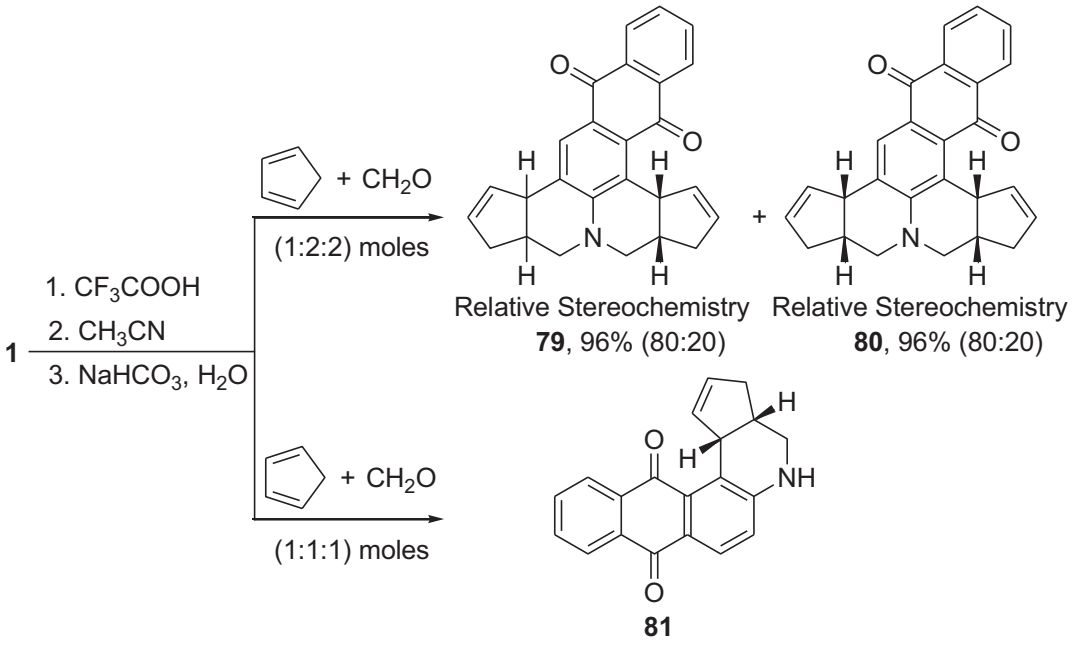
78

Reaction with formaldehyde & cyclopentadiene

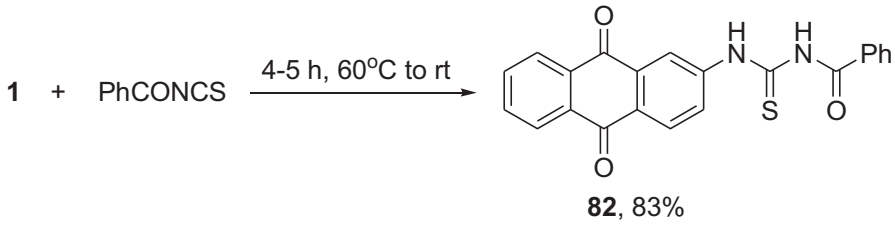
Cyclocondensation of 2-AAQ with 2 equiv of formaldehyde and cyclopentadiene in acetonitrile in the presence of trifluoroacetic acid affords the tetrahydroquinolines **79** and **80**, whereas when the reaction carried out using equal molar amounts the tetraquinoline **81** was formed.[108]

Reaction with isocyanates

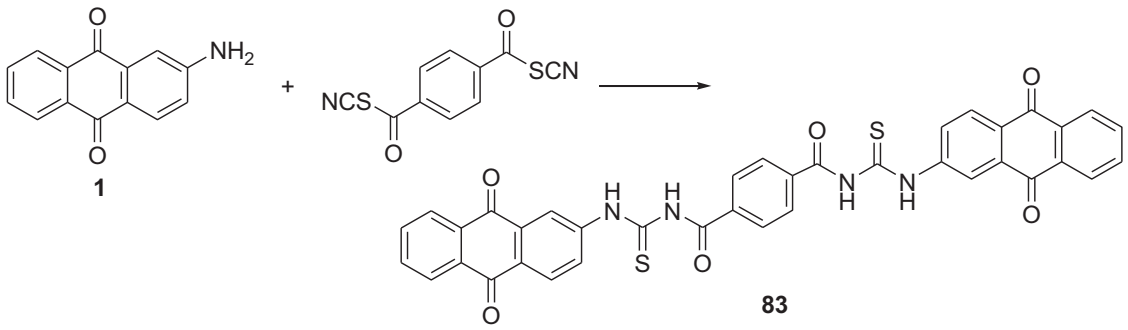
The reaction of benzoyl isothiocyanate with 2-aminoanthraquinone in ionic liquids leads to an efficient synthesis of *N*-substituted-*N′*-benzoyl thiourea **82**, containing 9,10-anthraquinone moiety.[109]



Scheme 22

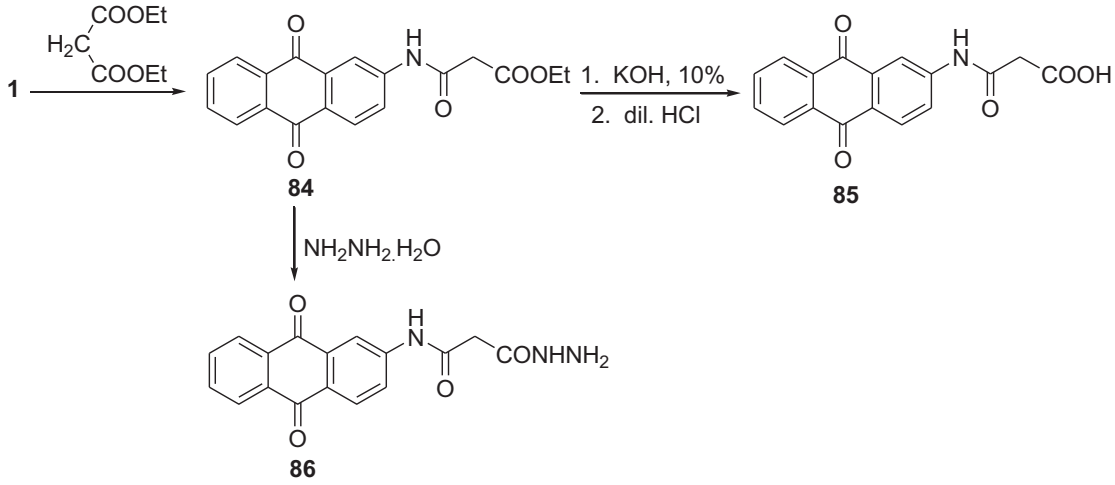


Under similar conditions terphthaloyl isothiocyanate react with **1** to give *bis*-thiourea **83**.[110]



Reaction with diethylmalonate

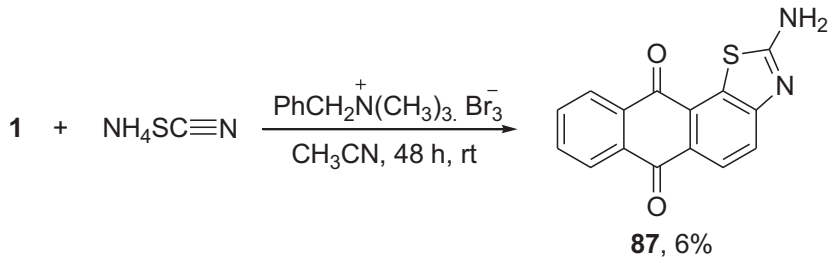
Condensation reaction of 2-amino-9,10-anthraquinone with diethyl malonate gave the corresponding ethyl malonamate **84**, which gave the acid **85** with 10% alc. KOH and the hydrazide **86** with hydrazine hydrate.[111]



Scheme 23

Reaction with ammonium thiocyanate

Aminothiazole **87** was achieved by stirring a mixture of **1**, ammonium thiocyanate, and benzyltriammonium tribromide in acetonitrile at room temperature.[112]

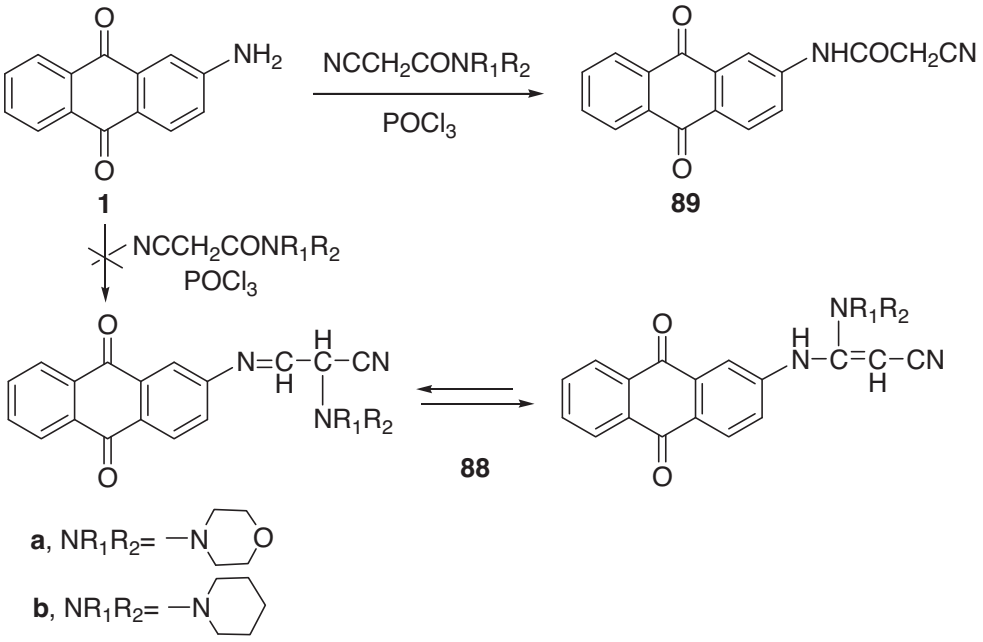


Reaction with cyanoacetamide derivatives

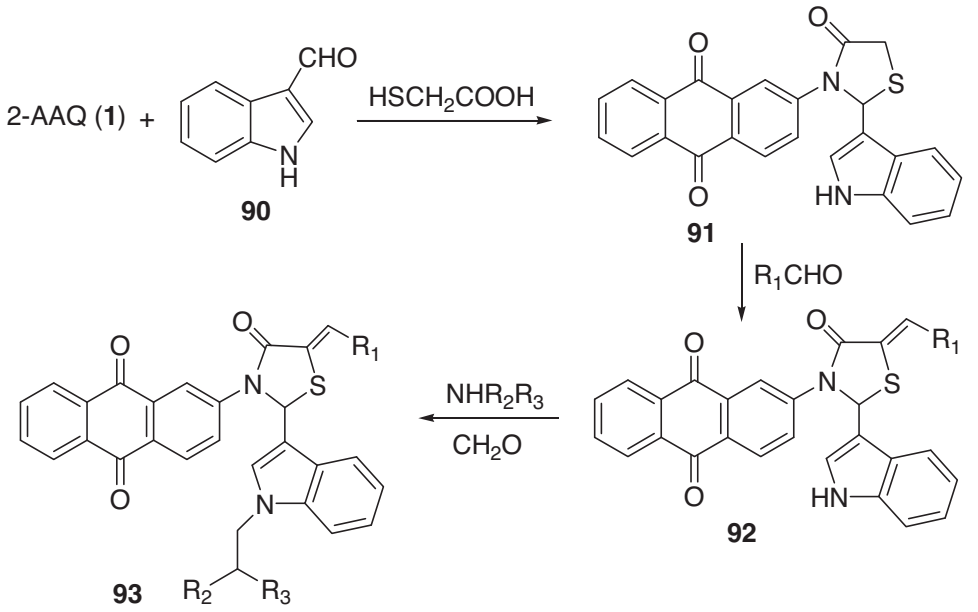
The Vilsmeier reaction of 2-AAQ using tertiary amides of cyanoacetic acid in the presence of phosphorus oxychloride was expected to yield the amidine derivative **88a** or the tautomeric enamine structure **88b**. However, the product obtained from this reaction was found to be the cyanoacetyl derivative **89** of 2-aminoanthraquinone.[113]

Reaction with thioglycolic acid and indole-3-carboxaldehyde

Cyclocondensation of indole-3-carboxaldehyde (**90**) with 2-AAQ in the presence of thioglycolic acid will give compound **91**, which condensed with R_1CHO to give compound **92**. Mannich reaction of compound **92** with NHR_2R_3 will give compound **93**.[114]



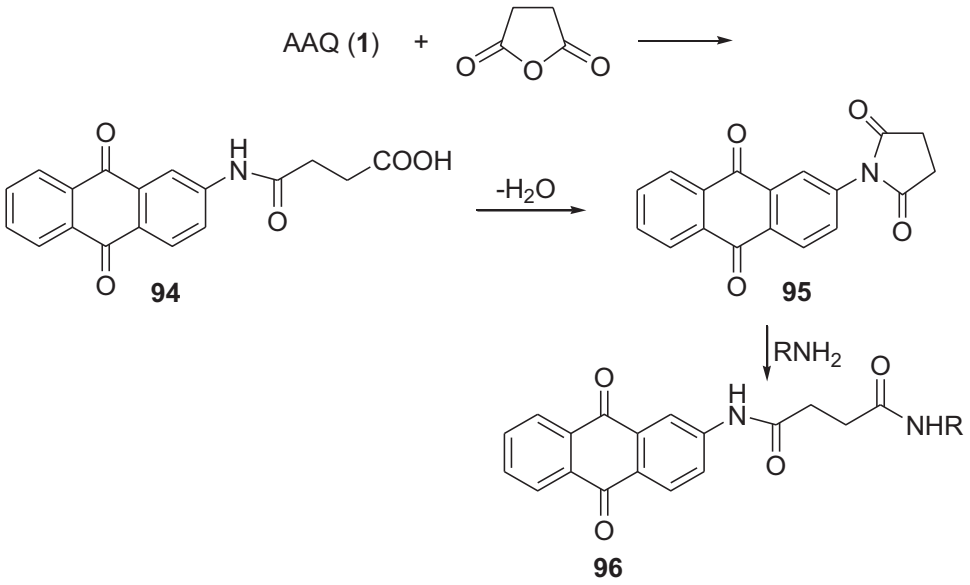
Scheme 24



Scheme 25

Reaction with succinic anhydride

The reaction of **1** with succinic anhydride in a glacial acetic acid medium gave 2-anthraquinonesuccinamic acid (**94**), which was cyclized with Ac_2O to form 2-anthraquinonesuccinimide (**95**). In the reaction of **95** with fatty amines, substituted amides of anthraquinone succinamic acid **96** were formed.[115]

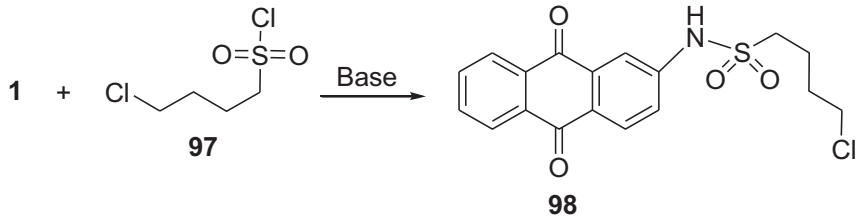


Scheme 26

Reaction with acid chloride

Reaction with 4-chlorobutane-1-sulfonyl chloride

4-Chlorobutane-1-sulfonyl chloride (**97**) reacted with **1** to give 4-chloro-*N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)butane-1-sulfonamide (**98**).[116]

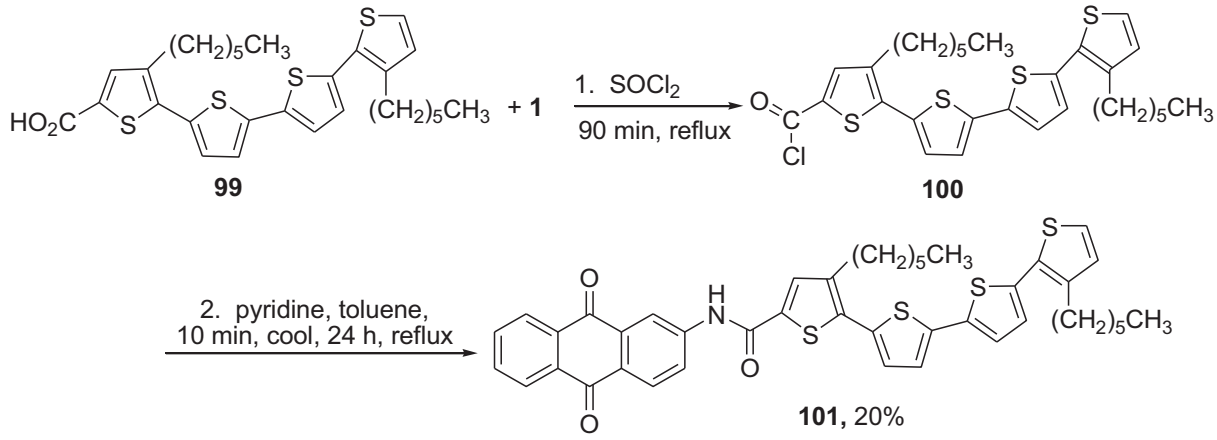


Reaction with quaterthiophene2-acid chlorides

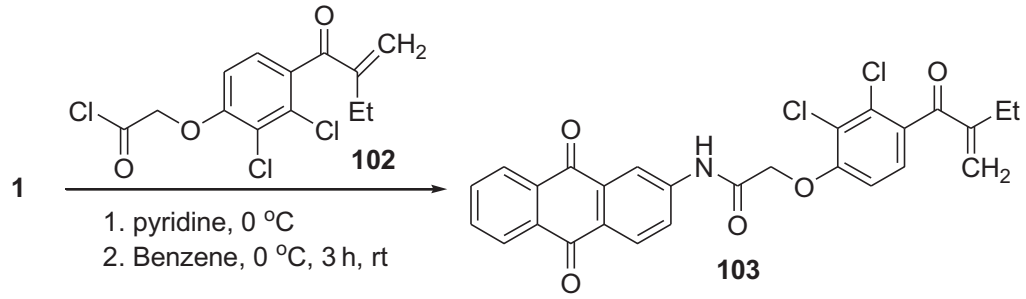
Quaterthiopheneanthraquinone dye **101** was prepared via refluxing the acid **99** with thionyl chloride followed by treating the formed acid chloride **100** with 2-AAQ.[117]

Reaction with 2-(2,3-dichloro-4-(2-methylenebutanoyl)phenoxy)acetyl chloride

Treatment of **1** with 2-(2,3-dichloro-4-(2-methylenebutanoyl)phenoxy)acetyl chloride (**102**) in pyridine afforded 2-(2,3-dichloro-4-(2-methylenebutanoyl)phenoxy)-*N*-(9,10-dioxo-9,10-dihydroanthracen-2-yl)acetamide (**103**).[118]

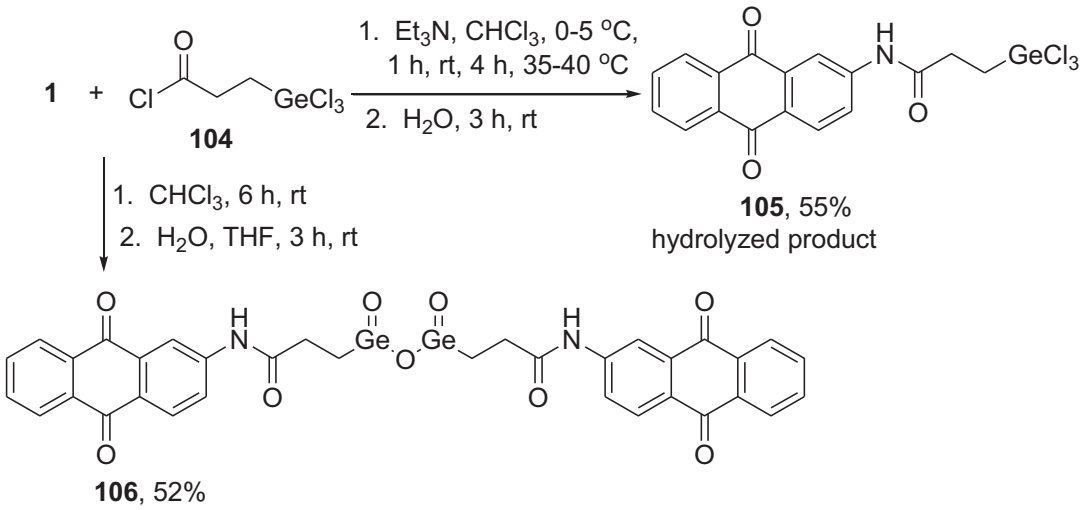


Scheme 27



Reaction with propionyl chloride

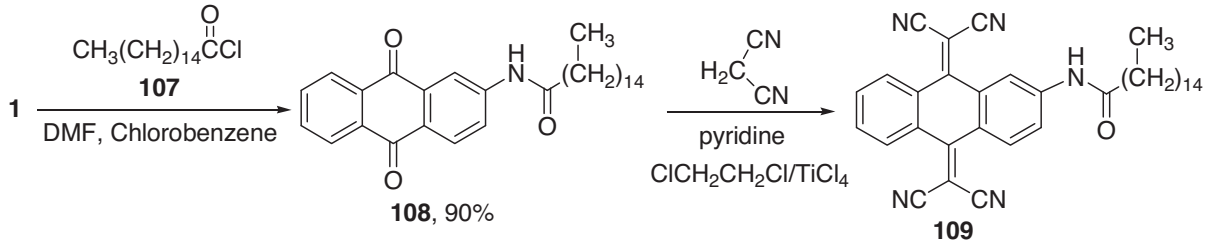
Novel organogermanium sesquioxide with anthraquinone moiety **105** was synthesized via treatment of the corresponding acid chloride **104** with 2-aminoanthraquinonein $CHCl_3$/TEA. Chen-Ping et al. studied the interaction of **104** with 2-aminoanthraquinone in chloroform, and they separated the *bis* derivative **106**.[119,120]



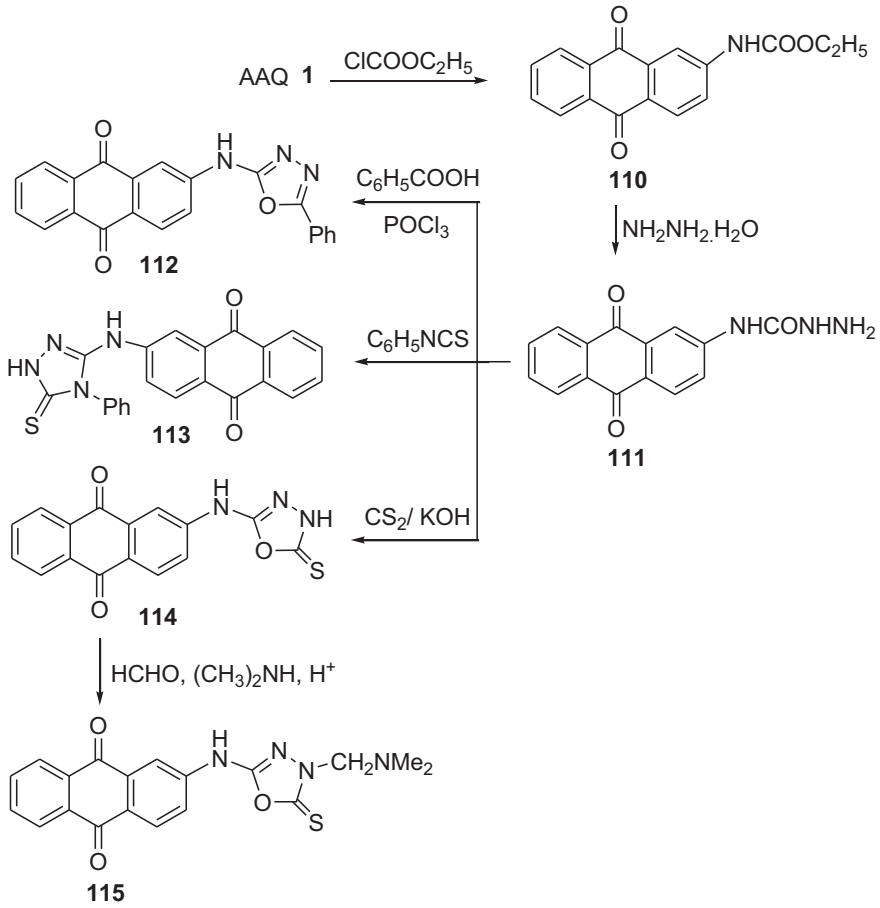
Scheme 28

Reaction with hexadecanoyl chloride

Treatment of **1** with hexadecanoyl chloride **107** in DMF afforded amide **108**, which upon refluxing with malononitrile in pyridine/$ClCH_2CH_2Cl/TiCl_4$ gave 11,11,12,12-tetracyanoanthraquinodimethanes **109**.[121]



Scheme 29



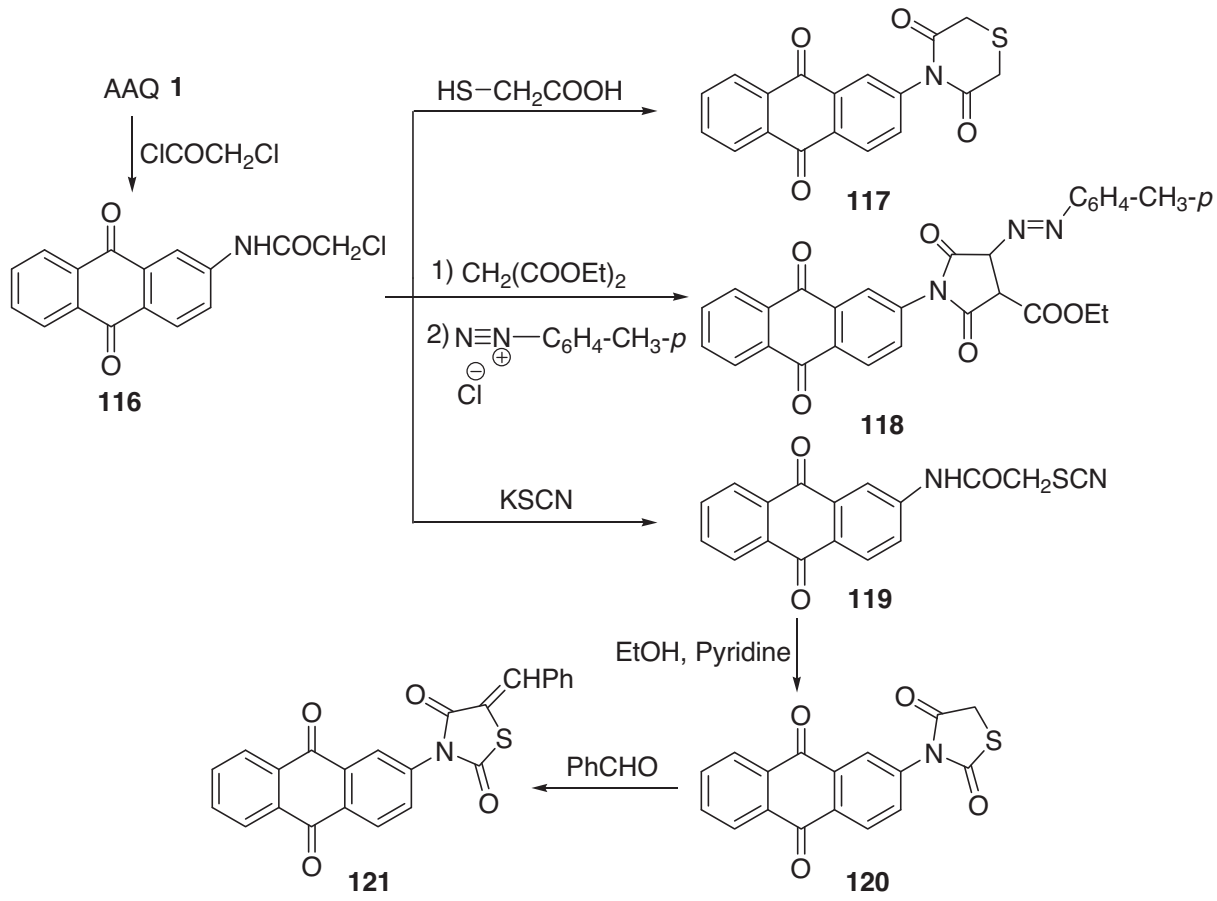
Scheme 30

Reaction with ethyl chloroformate

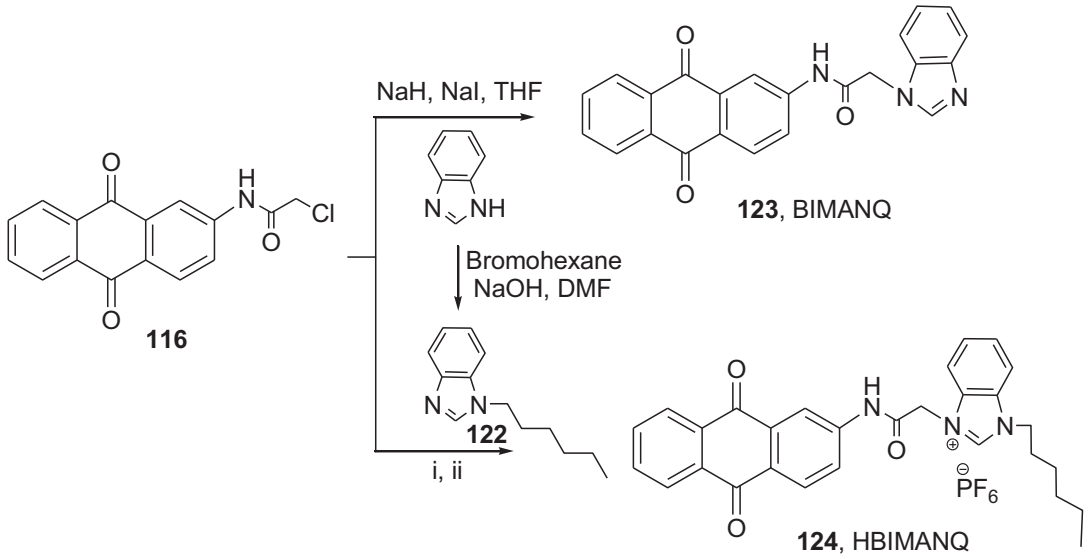
It reacts with ethyl chloroformate to afford carbamate **110**, which reacts with hydrazine hydrate to give semicarbazide **111**. Compound **111** reacts with benzoic acid, phenyl isothiocyanate, and carbon disulfide to afford oxadiazoles **112**, **114**, and triazole derivative **113**, respectively. Oxadiazole derivative **114** undergo a Mannich reaction with dimethylamine to afford derivative **115**.[122]

Reaction with chloroacetyl chloride

The reaction of AAQ (**1**) with chloroacetyl chloride in pyridine/dichloromethane furnished chloroacetyl derivative **116**. Chloroacetyl derivative **116** was reacted with thioglycolic acid in refluxing pyridine to give 4-(anthraquinon-2-yl)-1,4-thiazin-3,5-dione (**117**). On the other hand, the reaction between **116** and diethyl malonate in the presence of piperidine gave pyrolidendione derivative, which upon reaction with *p*-tolyl diazonium chloride produced the azo component **118**. Furthermore, compound **116** was reacted with potassium thiocyanate in DMF to give **119**, which underwent cyclization to give **120** by refluxing in ethanol/pyridine. Compound **120** reacted with benzaldehyde to give thiazoldione derivative **121**.[122]

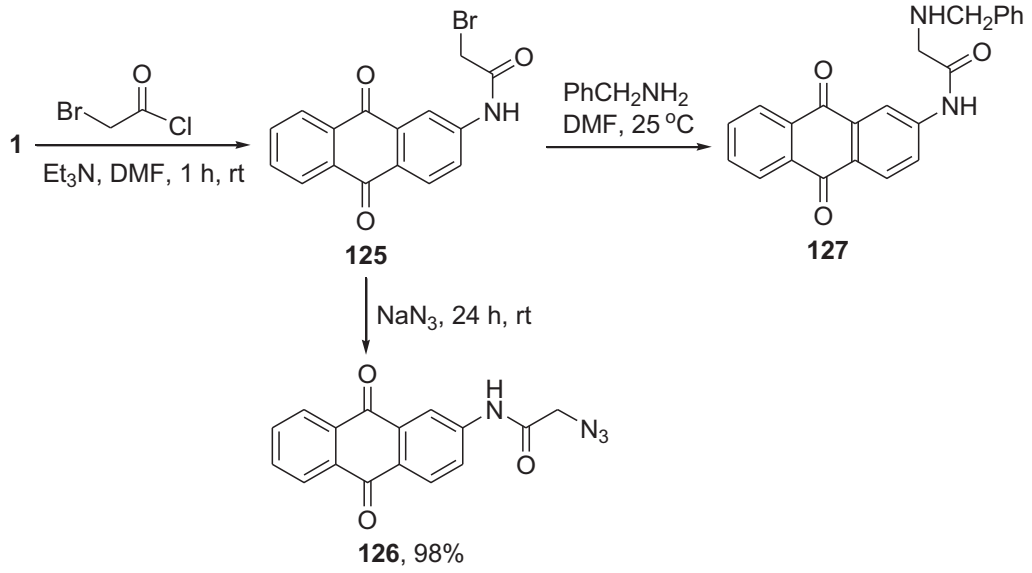


Scheme 31



i, NaI, acetone, CH_3Cl, RT; ii, KPF_6, THF, rt

Scheme 32



Scheme 33

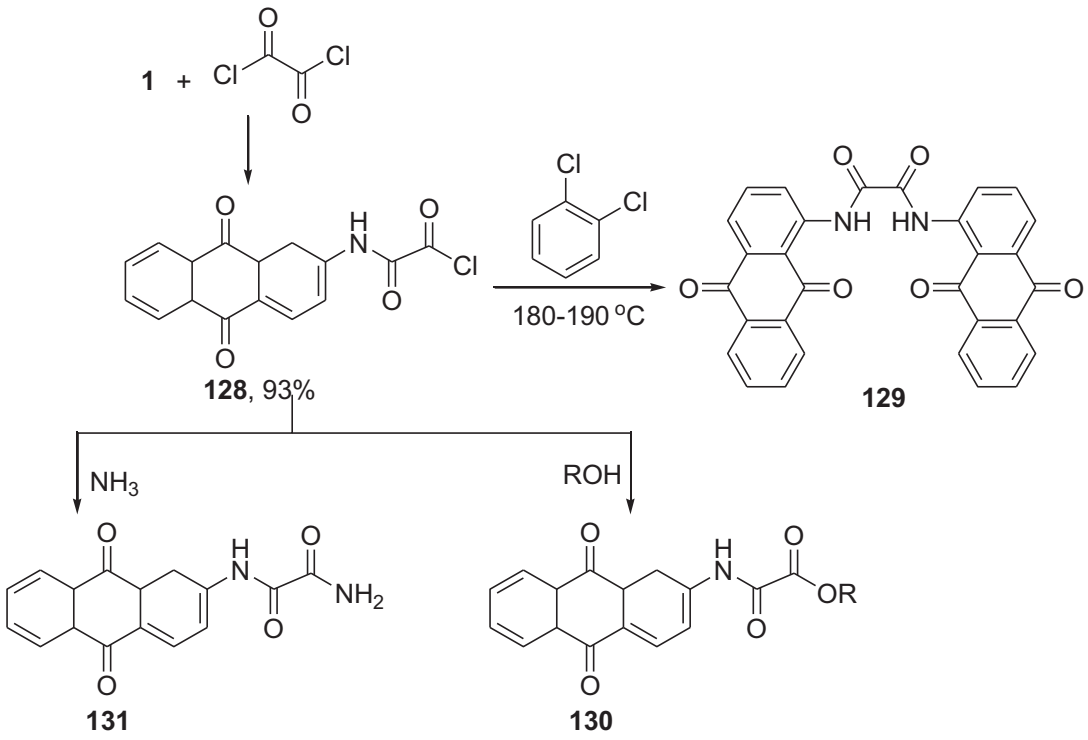
The synthesis of HBIMANQ (**124**) was started by a reaction between benzimidazole and 1-bromohexane using NaOH as base in DMF at reflux to give compound **122** in 80% yield. A coupling reaction of **122** with compound **116** in a mixture of acetone and chloroform in the presence of NaI followed by conversion of counter anions using KPF6 in THF yielded HBIMANQ (**124**) in 85% yield. BIMANQ (**123**) was synthesized in 80% yield by coupling benzimidazole with compound **116** using NaH as base in THF.[123]

Reaction with bromoacetyl chloride

Treatment of **1** with bromoacetyl chloride in DMF/TEA afforded bromoacetamide **125**.[124] Treatment of **125** with sodium azide or benzyl amine afforded the azide derivative **126** and the benzyl aminoacetanide **127**, respectively.[125,126]

Reaction with oxalyl chloride

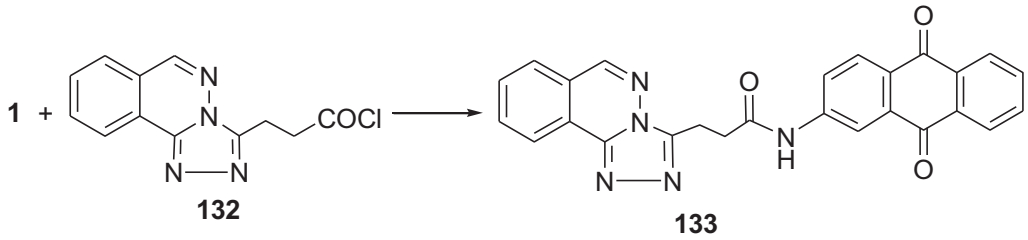
The reaction of 2-amino-9,10-anthraquinone with oxalyl chloride gave the corresponding *N*-anthraquinonyloxamoyl chloride **128**. Heating of 2-(9,10-dioxo-1,8a,9,9a,10,10a-hexahydroanthracen-2-ylamino)-2-oxoacetyl chloride (**128**) at 180-190 °C with 2-aminoanthraquinone (**1**) in 1,2-dichlorobenzene gave the *N*, *N*′-*bis*(anthraquinonyl)oxamide (**129**). Refluxing **128** with alcohols and amines or NH_3 gave the corresponding oxamidate ester **130** and oxamide **131**, respectively.[127]



Scheme 34

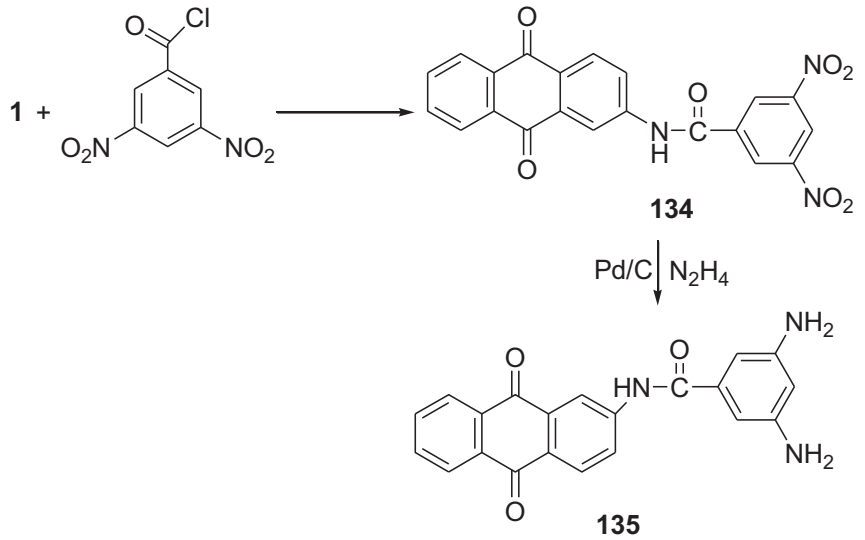
Reaction with 3-[1,2,4]triazolo[3,4-a]phthalazin-3-yl-propionyl chloride

The reaction of 2-aminoanthraquinone with 3-[1,2,4]triazolo[3,4-*a*]phthalazin-3-yl-propionyl chloride (**132**) afforded *N*-(9,10-dioxo-9,10-dihydro-anthracen-2-yl)-3-[1,2,4]triazolo[3,4-*a*]phthalazin-3-yl-propionamide (**133**).[128]



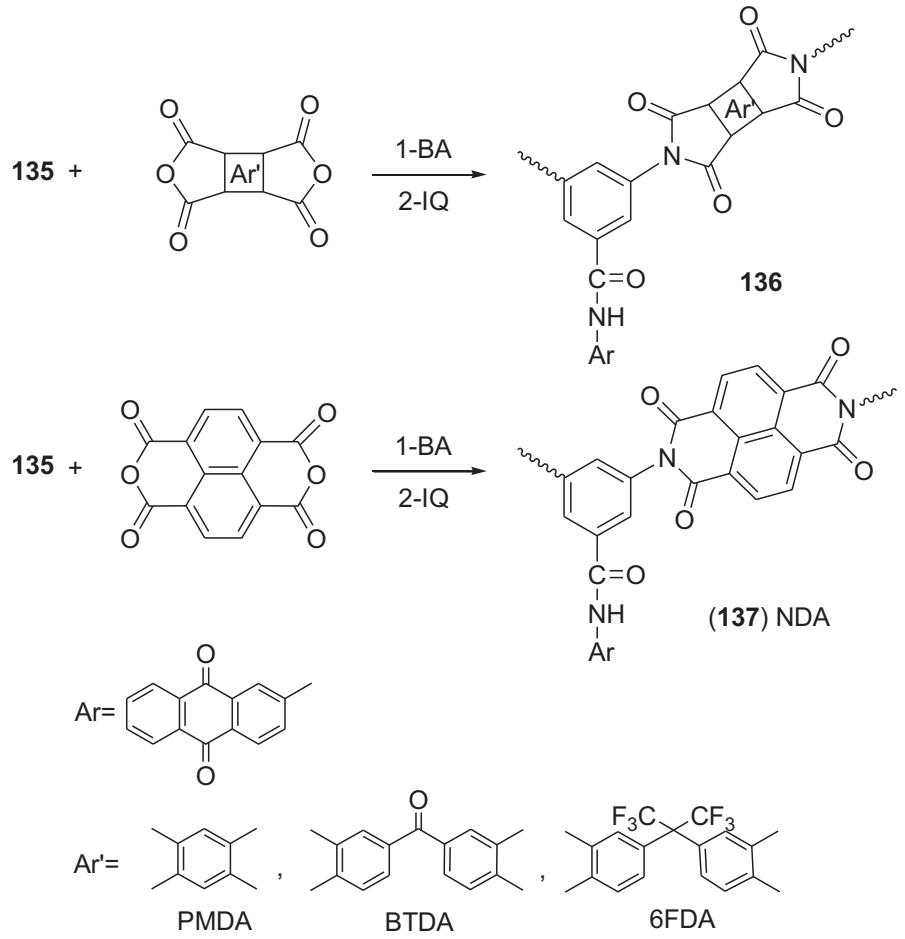
Reaction with 3,5-dinitrobenzoyl chloride

Amide diamine **135** containing bulky pendant units was prepared in 2 steps: nucleophilic substitution reactions of **1** with 3,5-dinitrobenzoyl chloride to form amide containing dinitro derivative **134**, and then reduction of the resulting dinitro compound with hydrazine monohydrate in the presence of palladium/activated carbon.[129]



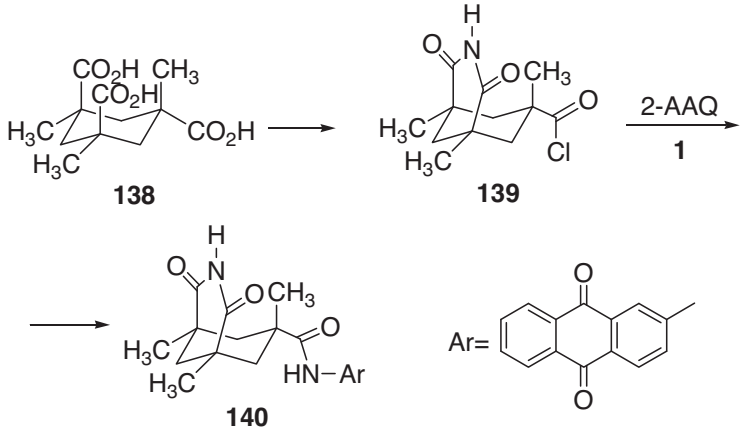
Scheme 35. Preparation of dinitro compound (**134**) and diamine compound (**135**).

A series of new poly(amide–imide)s were prepared from the reactions of diamine with various dianhydrides by a one-step polyimidation process.[129]



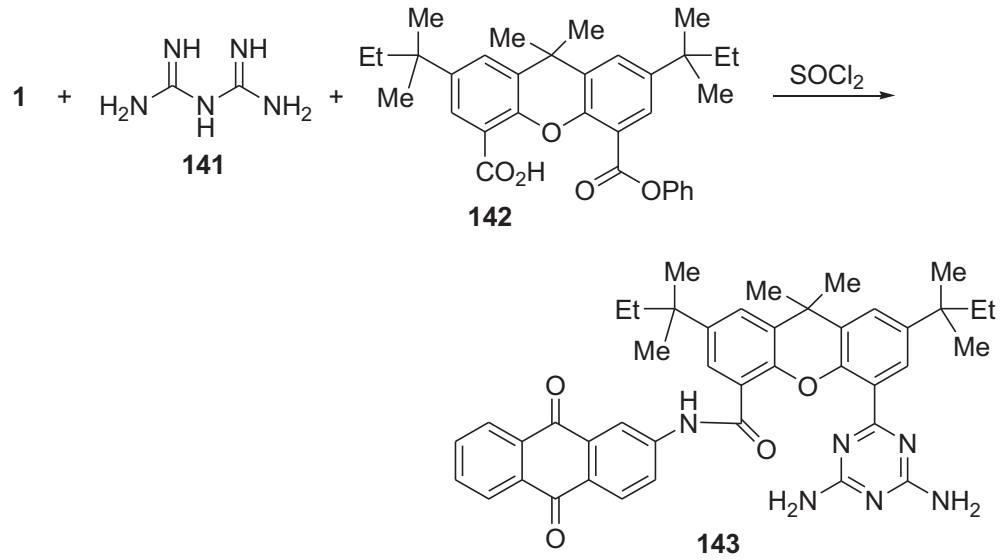
Scheme 36. One-step polymerization.

In parallel experiments, the *cis-trans* isomer **138** was converted to 1,5,7-trimethyl-2,4-dioxo-3-azabicyclo [3.3.1]nonane-7-carbonyl chloride (**139**) and then acylated with 2-AAQ (**1**) to give aromatic amine derivative **140**.[130]



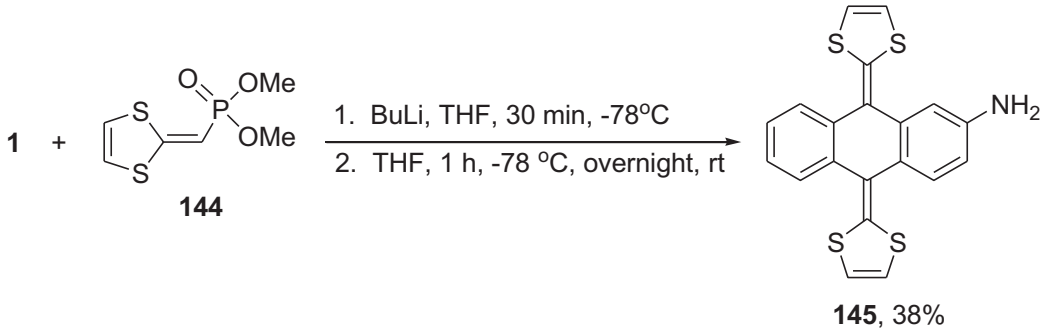
Scheme 37

Furthermore, compound **143** was achieved via 1-pot 3-component reaction of **1**, aminodiamidine **141**, and dibenzo pyrane carboxylic acid **142** in thionyl chloride.[131]



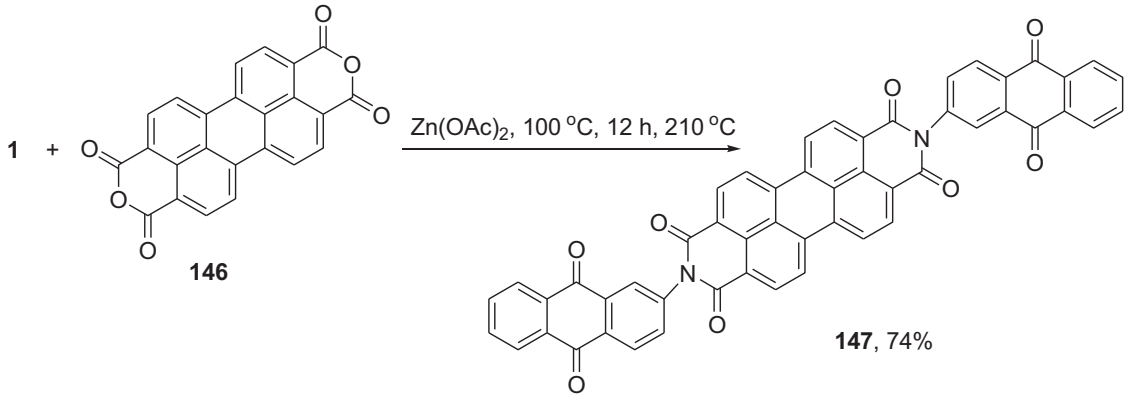
Formation of tetrathiafulvalene (TTF) derivatives

Single-walled carbon nanotubes (SWNTs) with covalently linked tetrathiafulvalene (TTF) derivatives via linkers have been synthesized and fully characterized as potential donor-acceptor nanoconjugates. Near-IR fluorescence and transient absorption measurements showed that the charge recombination dynamics is a function of the spacer linking the 2 moieties and the donor ability of the different TTF derivatives. Thus treatment of **1** with the dithole derivative **144** in tetrahydrofuran in the presence of butyl lithium afforded the corresponding tetrathiafulvalene **145**.[132]

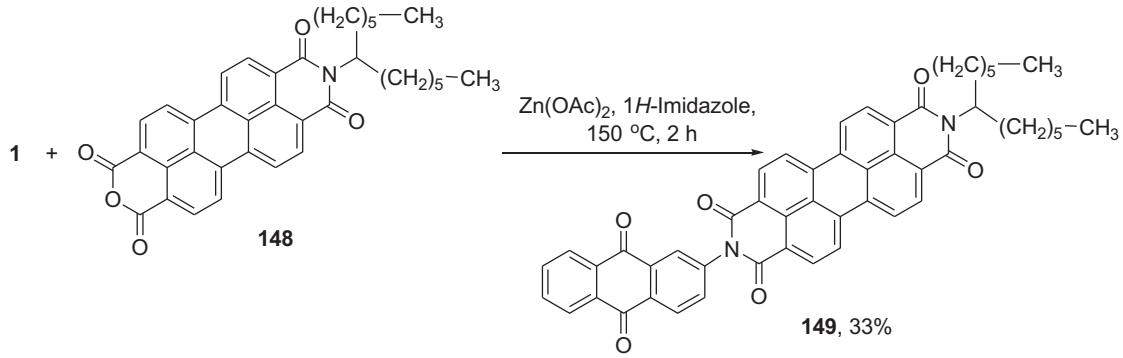


Formation of perylene dye

Perylene dye **147** was prepared by condensation of 3,4,9,10-perylenetetracarboxylic 3,4,9,10-dianhydride (**146**) with **1**.[133]

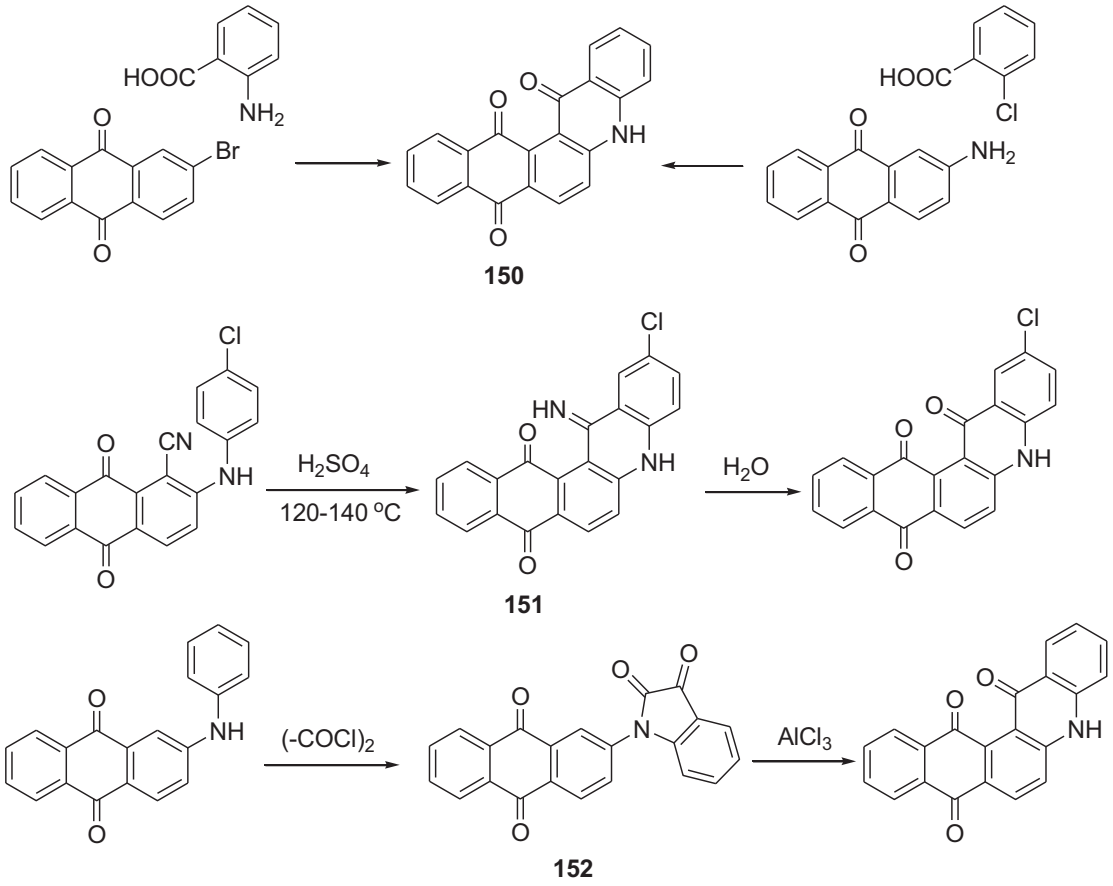


Furthermore, treatment of **1** with monoimide **148** afforded compound **149**.[133]



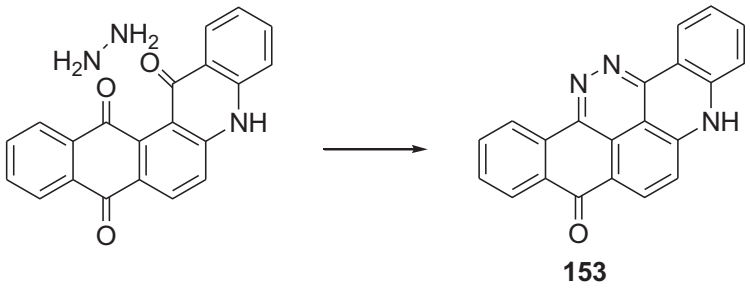
Formation of Anthraquinone-Acridones

Anthraquinone-1,2-acridone is a sparingly soluble (0.8% in boiling pyridine or nitrobenzene), orange-red substance that dissolves in alcoholic sodium hydroxide solution with a violet color. 9-Amino, 9-chloro, 9-hydroxy, and 10-hydroxy derivatives are mentioned in a patent.[134] A 6-amino derivative is said to condense with cyanuric chloride.[135] 2-Chloroanthraquinone-1,2-acridone, 7-chloro-1,2-phthaloylacridone, 5'-chloroanthraquinonyl-1,2 (*N*);1',2'(*N*)-benzeneacridone (**151**) separates from nitrobenzene as an orange-brown crystalline powder, which dyes cotton a deep orange-yellow.[136] The 10-chloro isomer is mentioned in a patent.[134,137]



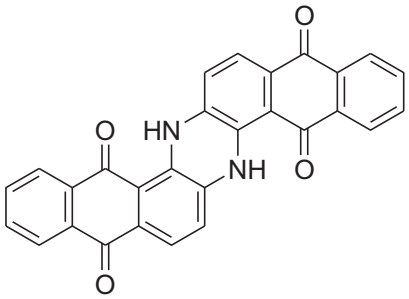
Scheme 38

Anthraquinone-1, bacridone is a 1,4-diketone, as is readily evident from its reaction with hydrazine. Two molecules of water are eliminated and anthraquinone-1,2-acridoneazine (**153**) results.[137–139]



Formation of indanthrene

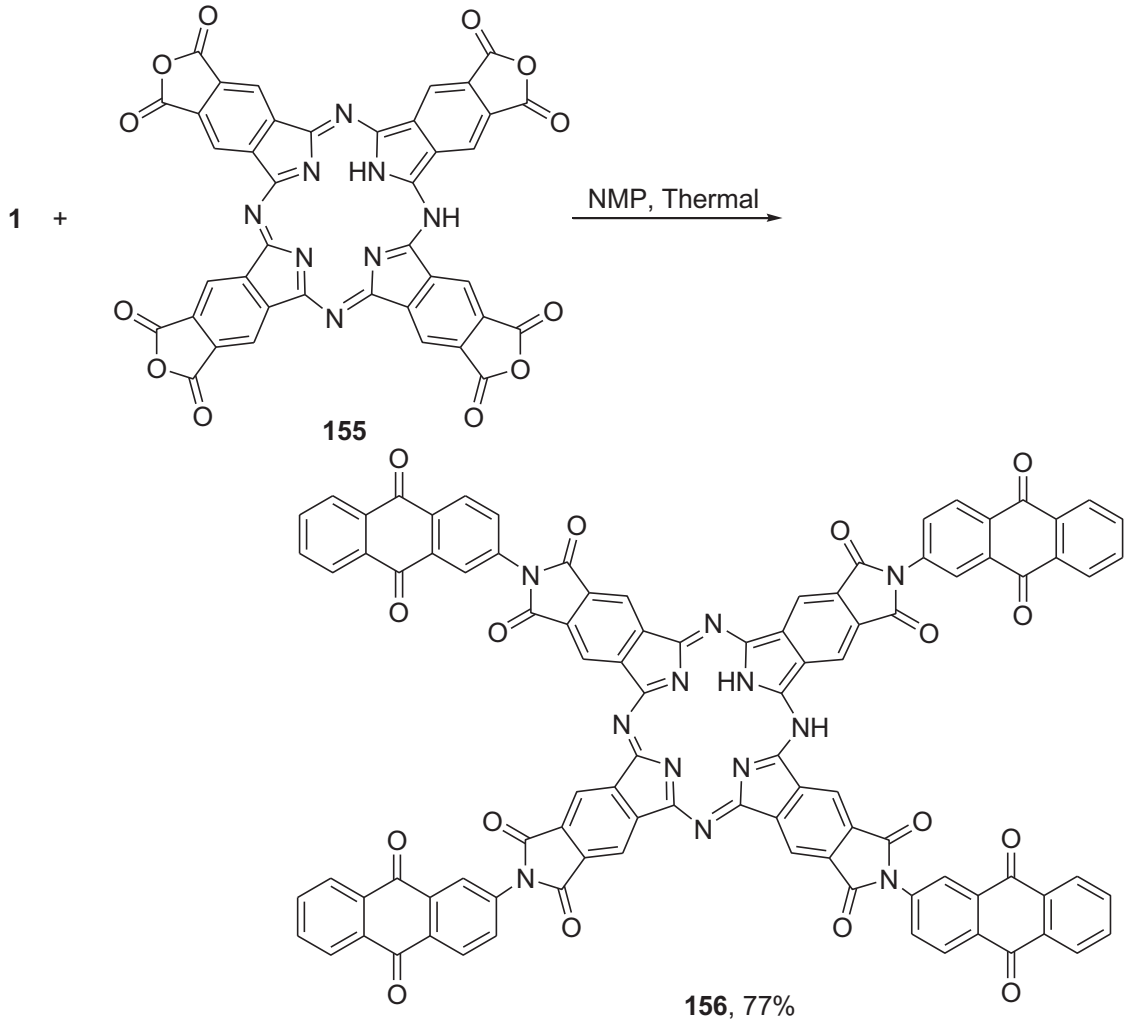
2-Aminoanthraquinone (**1**) is cyclodimerized in a melt of KOH or NaOH in the presence of NaOAc and 1.2% Fe_3O_4 catalyst, based on **1**, and the product is oxidized by $NaNO_3$ in 3 h under an inert gas at 190-225 °C to give indanthrene (**154**). The presence of Fe_3O_4 reduces byproduct formation.[140]



154

Formation of symmetrically tetra-substituted phthalocyanines

The phthalocyanine **156** was prepared by aminolysis of **155** with **1**.[141]

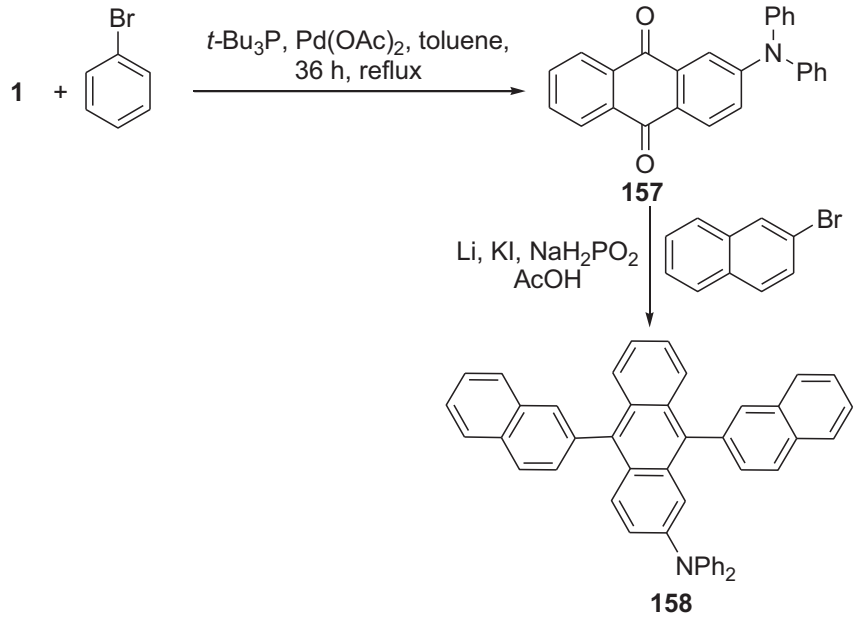


155

156, 77%

Pd-catalyzed amination

Pd-catalyzed amination of bromobenzene with 2-aminoanthraquinone in the presence of NaOBu-t, $Pd(OAc)_2$, and $(t\text{-Bu})_3P$ in refluxing toluene afforded **157**, nucleophilic addition of a lithium reagent generated in situ from 2-bromonaphthalene in THF to the latter compound, and subsequent treatment with KI and NaH_2PO_2 in acetic acid gave **158**.[142]



Scheme 39

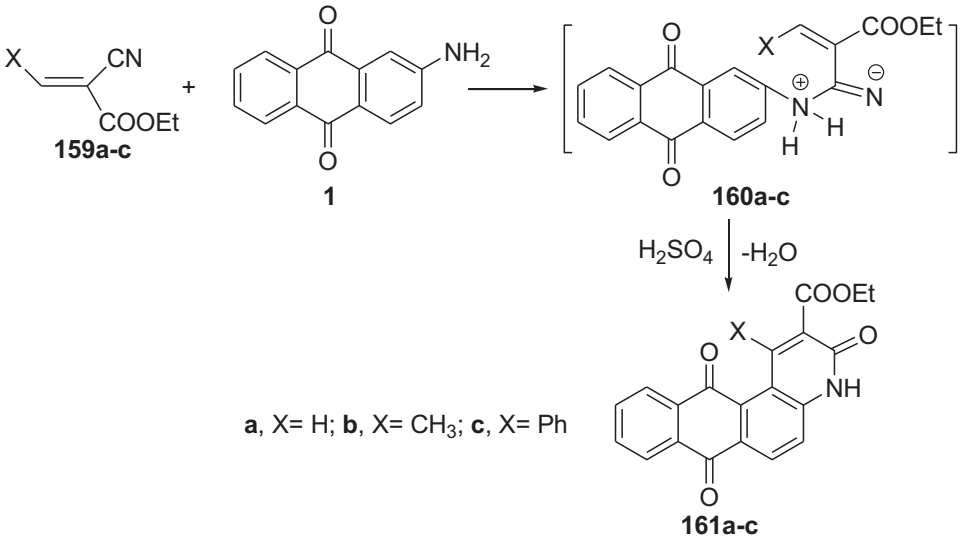
Reaction with ylidenecyanoacetates

Ylidenecyanoacetates **159a-c** reacted by fusion with 2-aminoanthraquinone to yield quinoline derivatives **161a-c**. These compounds were assumed to be formed via addition of 2-aminoanthraquinone to acrylonitriles **159a-c** yielding intermediate (zwitter ions) **160a-c** that cyclized and hydrolyzed under the reaction conditions into the final products.[143]

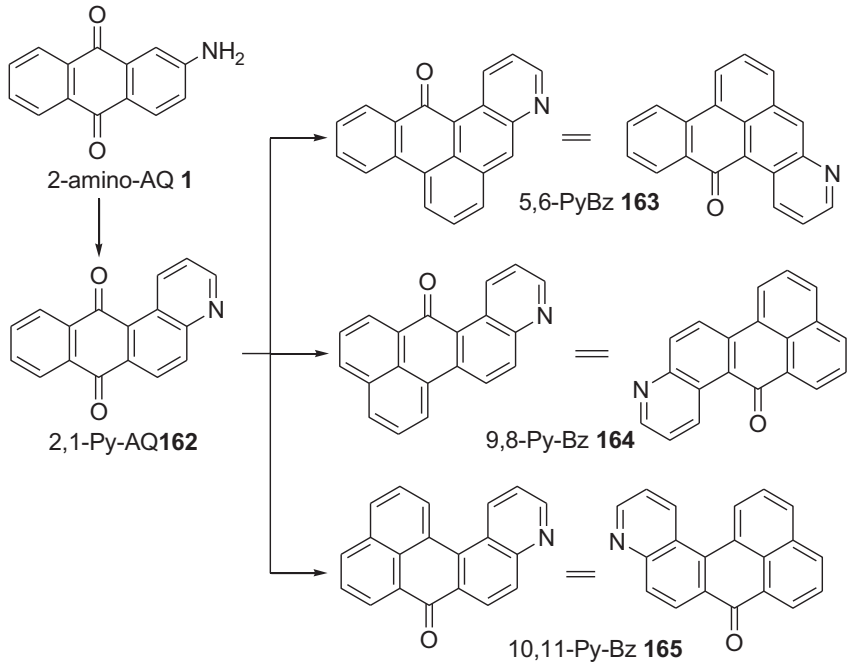
Reaction with glycerol

In 1905, Bally reported that the glycerol condensation reaction on 2-aminoanthraquinone (**1**) afforded unexpectedly a new pentacyclic ketone, pyridinobenz-anthrone (PyBz), through the actions of 2 moles of glycerol, although he attempted to prepare naphtho[2,3-f]quinoline-7,12-dione (2,1-pyridinoanthraquinone,2,1-PyAq) (**162**). This result is historically very famous since it gave him the idea to synthesize benzanthrone (Bz), an important intermediate product of polycyclic dyes. He assigned this compound as 13H-phenanthro[10,1-fg]quinolin-13-one (5,6-pyridinobenzanthrone, 5,6-PyBz) (**163**), whereas another research group proposed phenaleno[2,3-f]quinolin-13-one (9,8-pyridinobenzanthrone, 9,8-PyBz) (**164**). Pandit et al.[144] reported that glycerol condensation of 9-aminobenzanthrone gave **164**, and that it might be identical to Bally's product. Bradley

et al.[145] reported that **164** was obtained from **1** by Bally's method, but that the yields were generally low (20%∼30%). These low yields suggest that some isomers may also be produced.[146]

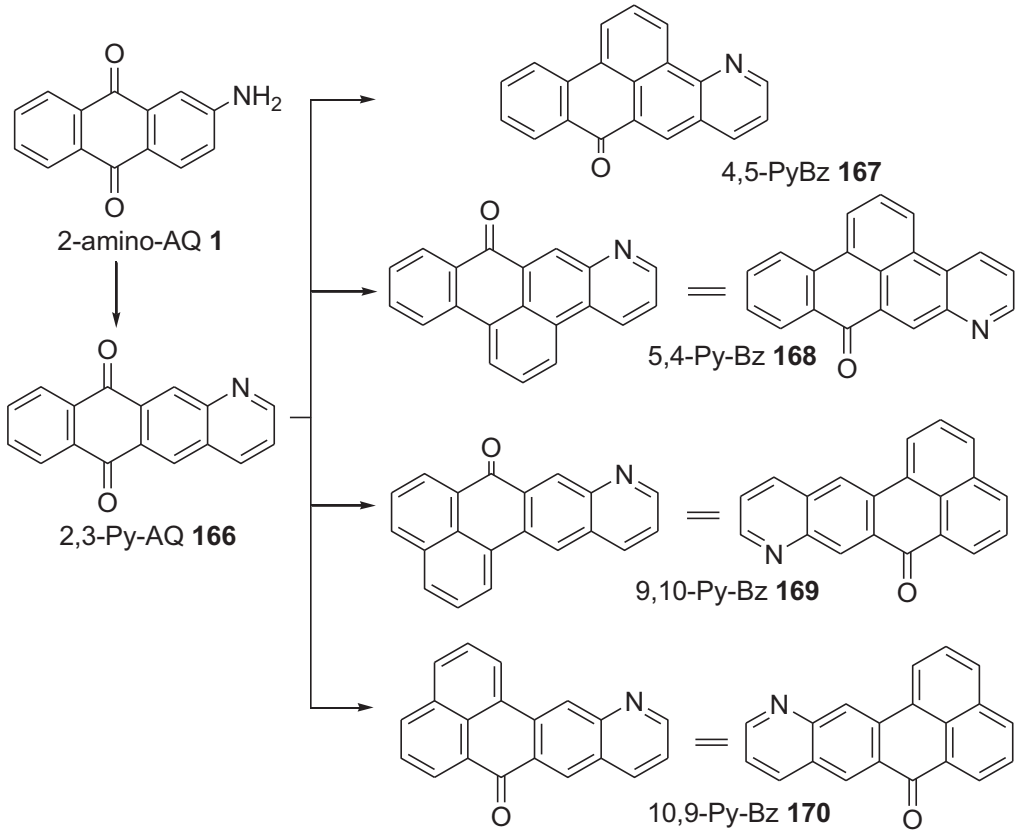


Scheme 40



Scheme 41

Generally speaking, since the action of glycerol on **1** may produce naphtho[2,3-*g*]quinoline-6,11-dione (2,3-pyridinoanthraquinone, 2,3-PyAq) (**166**) besides **162**, there is a chance that 7 kinds of pyridinobenzanthrones **163-170** may be produced. Although **164** was already prepared the others are not yet known, and the kinds of condensation products obtained from **1** and the reaction mechanism have not yet been well clarified.[146]



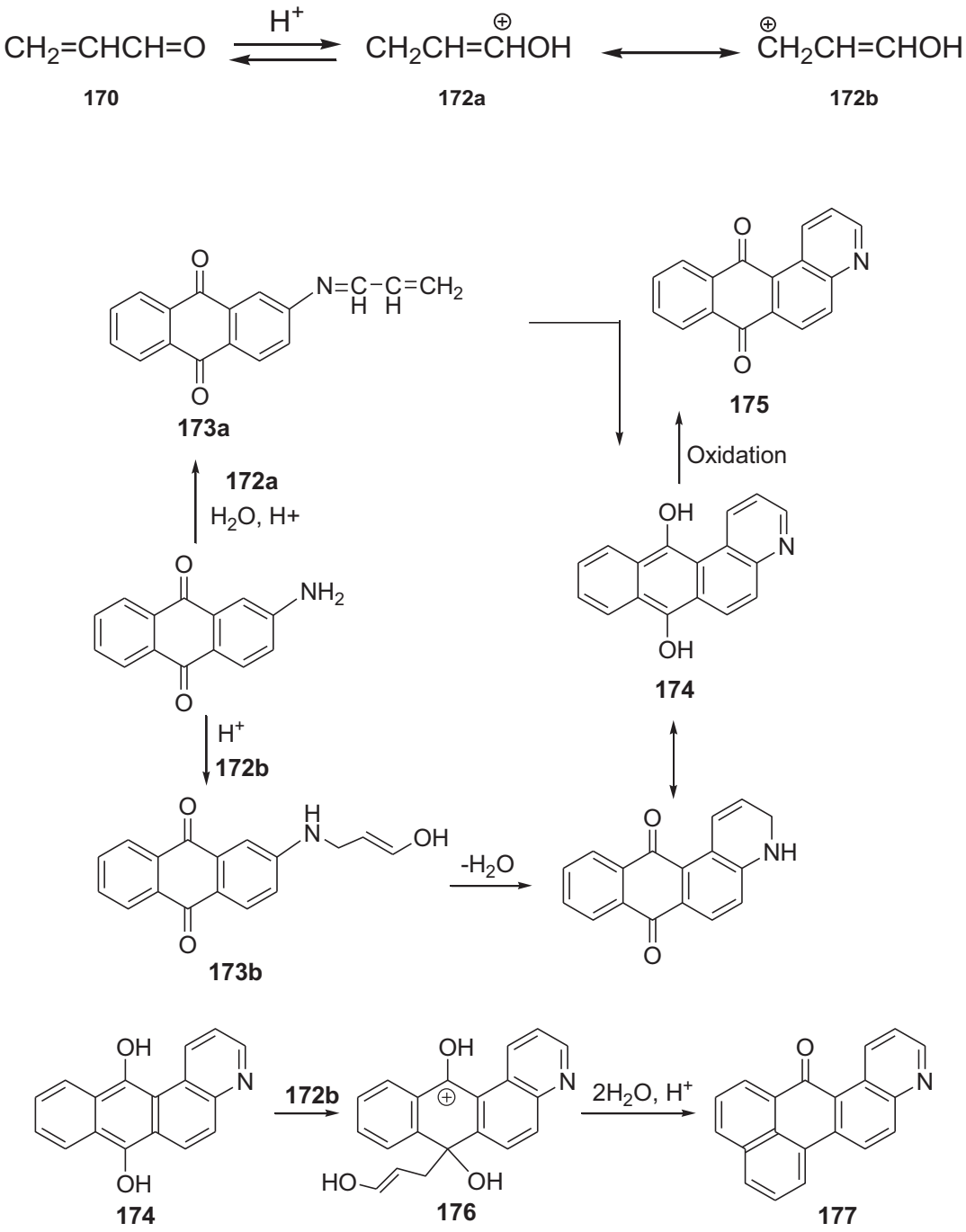
Scheme 42

First acrolein **171** produced from glycerol by the action of sulfuric acid is protonated as **172a** or **172b**. When **172a** reacts with amino group of **1**, it gives an imine **173a**, which cyclizes to form a pyridine ring, and the 2 hydrogen atoms that detached during the cyclization reaction conveniently reduce the quinone part to give **174**. On the other hand, the reaction of **172b** with **1** gives **173b**, which also cyclizes to afford **174**. Another **172b** reacts with **174** to afford **164** via **177**. In addition, the hydroquinone **174** would give **175** by an oxidizing agent.[146]

Knoevenagel condensation reaction

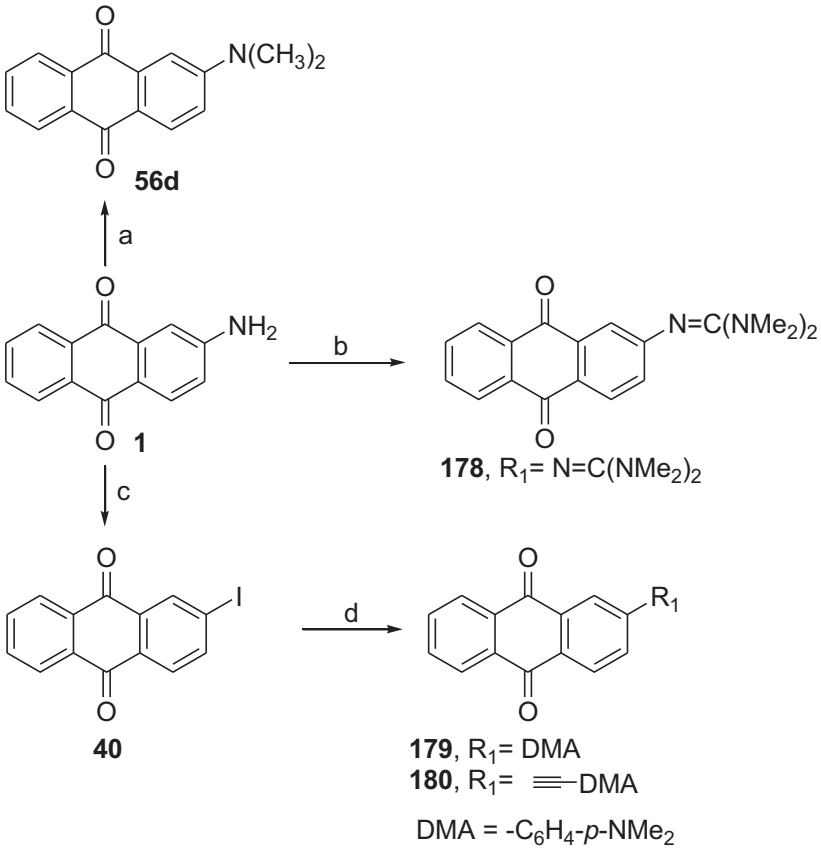
TCAQ and derivatives are conveniently accessible by Knoevenagel condensation of anthracene-9,10-dione derivatives with malononitrile, mediated by $TiCl_4$/pyridine (Lehnert reagent).[147] Therefore, various donor-substituted anthracene-9,10-diones were prepared, starting from commercially available 2-aminoanthracene-9,10-diones **1**.[148]

The Knoevenagel reaction with malononitrile, mediated by the Lehnert reagent, was first carried out on unsubstituted anthracene-9,10-dione, yielding TCAQ (**182**) in 89% yield. The other, donor-substituted anthraquinones were treated with malononitrile under the above condition as well, whereas anthraquinones **65d**, **178**, **40**, and **179** afforded the expected products **183-186**, respectively.[148]

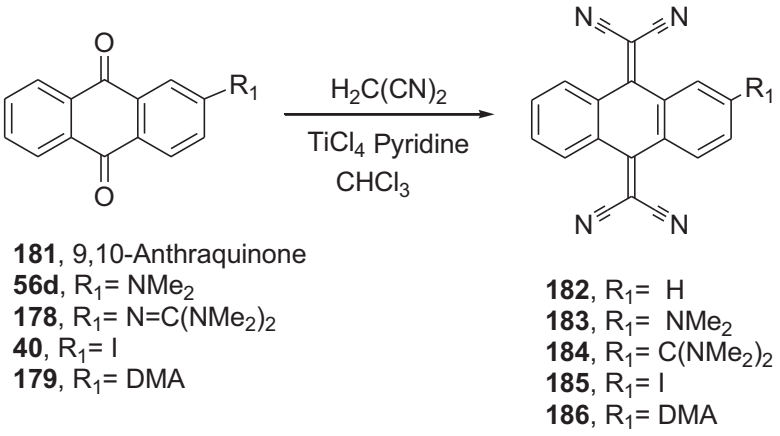


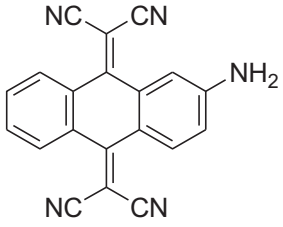
Scheme 43

Nishizawa et al. reported that 2,2'-(2-aminoanthracene-9,10-diylidene) dimalononitrile (**187**) has been prepared in high yield by direct condensation of anthraquinone and malononitrile using dry pyridine and molecular sieves.[149]



Scheme 44. Synthesis of donor-substituted anthracene-9,10-diones. **56d**: (a) KOH, Me_2SO, 20 °C, 30 min, then CH_3I; (b) *N*,*N*,*N*,*N*-tetramethylurea, $POCl_3$, benzene; (c) **40**: THF, H_2O, HCl, 40 °C, 24 h, then $NaNO_2/H_2O$, 0 °C, 10 min and KI/H_2O, 0 °C, 15 min → 20 °C, 30 min → 60 °C, 30 min, 81%; (d) **179**: [4-(dimethylamino)phenyl]boronic acid, $[PdCl_2(PPh_3)_2]$, Na_2CO_3, THF, H_2O; **180**: 4-ethynyl-*N*,*N*-dimethylaniline, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N/Et_2NH.



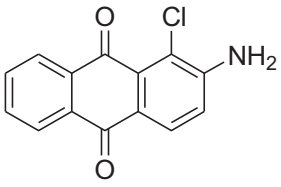


187

Halogenation

Chlorination

2-Amino-1-chloro or 2-amino-1,3-dichloroanthraquinone **188** and **189** were prepared by chlorination of 2-aminoanthraquinone with SO_2Cl_2 in an organic solvent, e.g., chlorobenzene, in the presence of DMF.[150]



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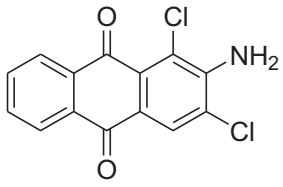
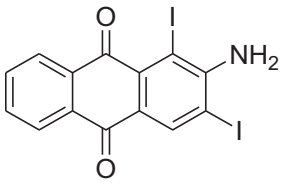


189

Iodination

Iodination of 2-aminoanthraquinone with (I_2-HIO_3) in AcOH containing H_2SO_4 at 70-75 °C gave 2-amino-1,3-diiodoanthraquinone (**190**). Diazotization and reduction of **190** gave 1,3-diiodoanthraquinone (**191**), and iodination of the intermediate diazonium salts gave 1,2,3-triiodoanthraquinone (**192**).[151]



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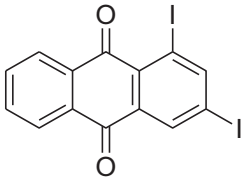

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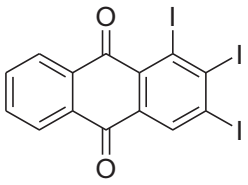
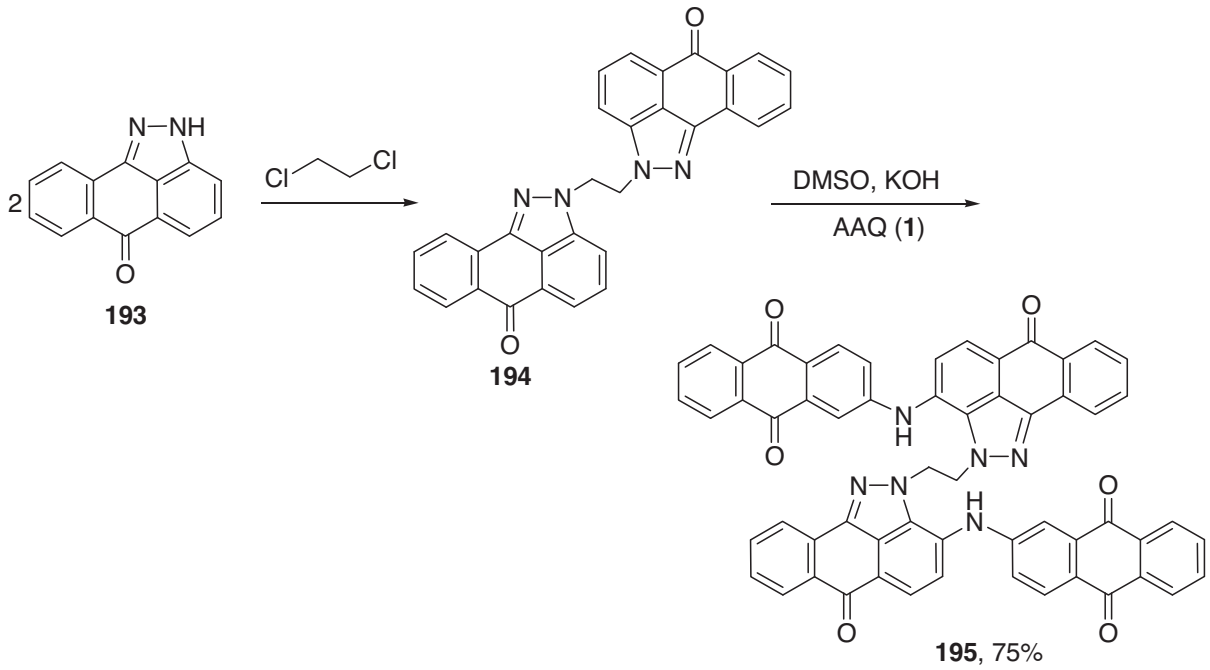


192

Nucleophilic Substitution

Reactions of 2,2'-ethylenebis(anthrapyrazolone)

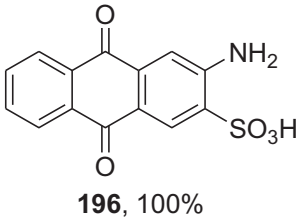
Anthra[1,9-*cd*]pyrazol-6(2*H*)-one (**193**) on alkylation with ethylene dichloride yields 2,2'-ethylenebis(anthrapyrazolone) (**194**) [nucleophilic substitution product of **194** is obtained in good yields by reacting it with 2-aminoanthraquinone and caustic potash in Me_2SO.[152]



Scheme 45

Photochemical substitution

Irradiation of 2-aminoanthraquinone with visible light in the presence of an excess of either Na_2SO_3 or Na_2S in 50% aqueous pyridine gives good yields of Na 2-aminoanthraquinone-3-sulfonate (**196**).[153]



Photolysis

Photolysis of 2-aminoanthraquinone with butan-1-amine (Bu-NH_2) in (1:1 vol./vol.) C_6H_6-EtOH at λ_{max} 300 nm and 30 °C under air for 4.5 h gave 2-amino-1-hydroxyanthracene-9,10-dione (**17**).[154]

Photodecomposition in organic solvents

2-Aminoanthraquinone was exposed to the irradiation of a xenon arc lamp in various org. solvents, and the changes in its spectra were measured. The rate of fading was markedly accelerated by substitution of the H atom of the NH_2 group by methyl or butyl groups. On exposure to light, a new absorption band in the visible

region did not develop in C_6H_6, Me_2CO, or Me_3COH, but definitely developed in the blue region ($\lambda_{max.}$ = 500 and 460 nm) in EtOH, PrOH, and *iso*-Pr-OH.[155]

Chemical Structure

The molecule of 2-aminoanthraquinone, $C_{14}H_9NO_2$, is nearly planar; with the non-H atoms exhibiting a mean distance of 0.022 Å from their best plane. The statistical disorder of the 2-aminoanthraquinone molecules is located around the centre of symmetry in space group $P2_1/c$. Weak intermolecular hydrogen bonds (N–H...N and N–H-O) link the molecules into a 3-dimensional network.

The crystal structure consists of 2 parallel sheets of planar 2-aminoanthraquinone molecules (Figure 3). The distance between 2 successive parallel planes is 3.488 (6) Å, which is slightly longer than the van der Waals distance (3.4 Å) for aromatic C atoms.[156] The angle between the planes of 2 neighboring sheets is 56.2 (5)°. The shortest intermolecular contacts between N and H, and O and H atoms are 2.36 (7) and 2.54 (7) Å, respectively (see the dashed lines in Figure 3). These values point to the existence of weak intermolecular interactions.[157]

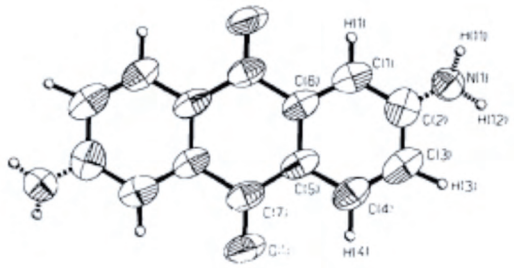
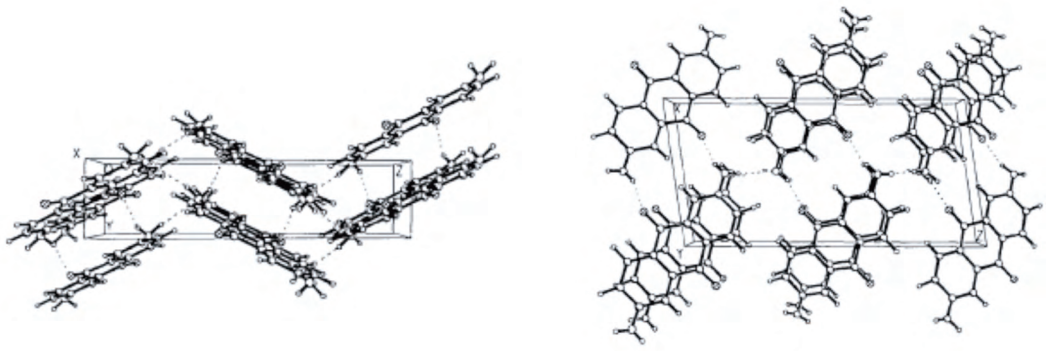


Figure 2. View of the title compound showing the numbering scheme with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary radii; atom H(2) has been omitted for clarity.



(a) (b)

Figure 3. Packing of the molecules in the unit cell shown by (a) a bc projection and (b) an ac projection.

Carcinogenicity

The parent compound anthraquinone produced liver, kidney, and urinary bladder tumors in rats. Although the mechanisms underlying anthraquinone carcinogenicity in the liver, kidney, and urinary bladder are unclear, a few modes of action have been proposed, including intercalative binding to DNA and reduction to semiquinone radicals that result in peroxidative damage. Alternatively, anthraquinone may be reduced to hydroquinones, or undergo ring hydroxylation and subsequent conjugation. Induction of hepatic cytochrome activity, demonstrated in Fischer rats fed anthraquinone,[158] suggests that cytochrome P-450 may play a role in the formation of active metabolites. Accordingly, studies examining the metabolism of anthraquinone have reported the presence of 2-hydroxyanthraquinone, 1-hydroxyanthraquinone, 9,10-dihydroxyanthracene, and 2,9,10-trihydroxyanthracene, and certain corresponding conjugates in the urine of Fischer, Chester Beatty, and another unspecified strain of rat fed anthraquinone.[159−162]

As previously shown, urinary metabolite data, although limited, provide some information on the role of substituents on biotransformation pathways of anthraquinones, which ultimately influences their carcinogenic ability. In addition to affecting biotransformation, structure–activity relationship studies demonstrated that the nature and position of substituents clearly affect binding constants and the stabilization of DNA complexes of anthraquinone compounds.[163−165] Structural factors have also been shown to influence the process of one-electron reduction of anthraquinones to semiquinones catalyzed by oxidoreductases, which ultimately results in oxygen radical formation.[166,167] It has been suggested that the determining factor governing electron transfer is the affinity of anthraquinone for the oxidoreductases, more than the redox properties of anthraquinones.[162,168]

Previous structure–activity studies, however, focused mainly on anthracycline antitumor quinones, which often contain complex side-chain substitutions with alkylating properties. Less is known about the role of single functional group substitutions on the alkylating properties or peroxidating activity of anthraquinone compounds.

One amino substitution, a potent ortho, para-directing activator, did not eliminate the carcinogenicity of anthraquinone, although it altered targets of carcinogenicity. The liver was the only organ with increased incidence of tumors in male rats exposed to 2-aminoanthraquinone. Unfortunately, 2-aminoanthraquinone was toxic to female rats, and their survival was too low to allow for analysis of late-developing tumors. Other studies with 2-aminoanthraquinone attributed the high toxicity in female Fischer rats to the renal tubule accumulation of crystals composed of 2-aminoanthraquinone and *N*-acetyl metabolites, which have low water solubility.[169] In addition to the 2-amino parent compound and the *N*-acetyl metabolite, a hydroxy-*N* acetyl and a conjugated hydroxy metabolite were also detected in the urine of Fischer rats.[169] These findings would be consistent with the activation of 2-aminoanthraquinone in the liver via *N*-hydroxylation, followed by further activation by acetylation or inactivation via conjugation. Development of liver tumors in male rats suggests that 2-aminoanthraquinone is activated, but not efficiently detoxified in the liver. The fact that the adverse kidney effects were much more severe in female rats would further suggest that male rats might have alternative pathways of hepatic detoxification of 2-aminoanthraquinone, such as sulfate conjugation, which would produce more water-soluble metabolites that could be more easily excreted. Consistent with this assumption, aromatic hydroxylamines are conjugated by aryl sulfotransferases, which are expressed at higher levels in adult male rats.[170,171] However, the various sulfotransferase isozymes have wide substrate specificities, which appear to be structurally related, and further studies are needed to investigate the role and relative contribution of

sulfotransferases on the conjugation of aminoanthraquinones. The parent compound anthraquinone induced liver tumors in male and female mice. The presence of an amino substitution in position 2, which acts as an *ortho*, *para*-directing activator, did not affect the target organs of toxicity as feeding mice 2-aminoanthraquinone also induced liver tumors. Multiple amino substitutions in positions 1, 4, 5, and 8, on the other hand, appeared to diminish the carcinogenicity of the derivative, as there were no clear carcinogenic responses following 1,4,5,8-tetraaminoanthraquinone administration. As suggested for rats, the 4-amino substitutions likely resulted in less efficient hepatic activation, or more rapid detoxification, as well as steric hindrance of intercalation and/or diminished electron transfer reactions of 1,4,5,8-tetraaminoanthraquinone. Precipitation of 1,4,5,8-tetraaminoanthraquinone was common in the urinary bladder of mice, but the incidences of nonneoplastic or neoplastic lesions of the bladder or kidney were not increased in exposed mice of either gender. These findings are consistent with urinary bladder tumors being less commonly observed in mice than rats, and further complicate the association between bladder calculi and bladder cancers.[162]

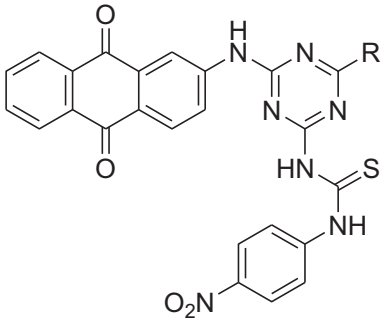
Pharmaceutical Applications

2-Aminoanthraquinone was identified as an inhibitor of glutathione reductase as a potential antimalarial drug,[172] inhibitor of xanthine oxidase,[173] inhibitor of sulfide production by sulfate-reducing bacteria,[174] in sewage,[175] oil wells, process tanks, or biomass fermentation,[176] inhibitor of sulfide production by sulfate-reducing bacteria,[177] and inhibitor of anthraquinones on bacterial collagenase.[178]

Naphtho[1,2-*d*]thiazol-2-ylamine (SKA-31) was evaluated as an activator of KCa_2 and KCa3.1 potassium channels, and potentiates the endothelium-derived hyperpolarizing factor response and lowers blood pressure.[179] Moreover, 2-anthraquinone ethacrynic acid amide was described as an antagonist of Wnt/β-catenin signaling and CLL cell survival.[180] Glycyl-L-prolyl-L-met-2-anthraquinonyl hydrazide was used for the histochemical detection of dipeptidyl peptidase IV (DPP IV),[181] and tripeptidyl peptidase (TPP I; E.C.3.4.14.9).[182] Furthermore, 2-aminoanthraquinones are well known and are widely used in the preparation of potentially effective compounds for treating lung cancer, leukemia, brain cancer, and AIDS, showing inhibition of HIV.[183,184] Moreover, many 2-aminoanthraquinone derivatives have anti-inflammatory,[185−188] antioxidant,[189] antitumor,[190] antifungal,[191] antibacterial,[191,192] and antiarrhythmic agents.[193]

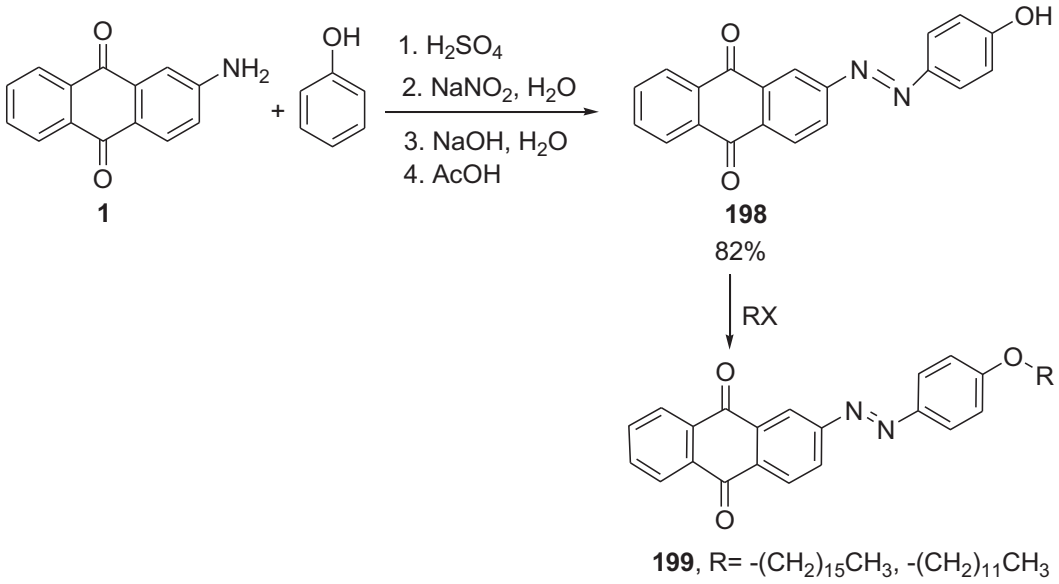
Dyestuff Applications

Park et al. have accomplished pioneering research on new dyes stuffs from 2-aminoanthraquinone.[194,195] Direct dyes **197** where R= OMe, OEt, OPr, OBu, 2-methoxyethoxy, 2-methoxyaniline, methylamine, dimethylamine, diethylamine, morpholine, and piperidine were prepared by reacting corresponding alcohols or amines with 2-(2'-anthraquinonylamino)-4-(*p*-nitrophenylthiourea)-6-dichloro-*S*-triazine. Light fastness, sublimation, and acid and alkaline perspiration of the dyed polyester fabrics were determined.[196]



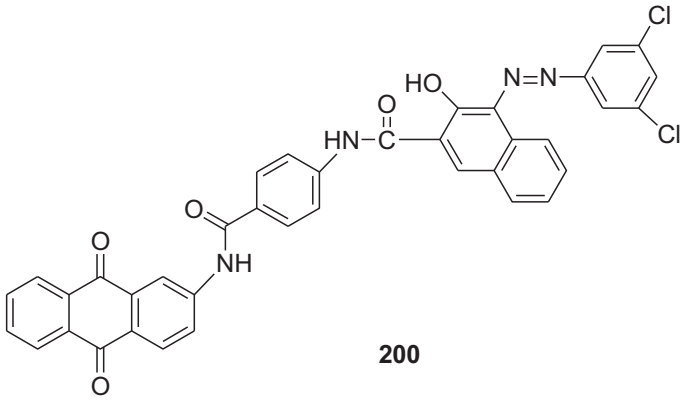
197

The synthesis of novel Langmuir-Blodgett film materials 2-(4-hexadecyloxy phenylazo)anthraquinone and 2-(4-dodecyloxyphenylazo)anthraquinone is described. These materials were obtained from 2-aminoanthraquinone by azo-coupling with phenol and followed by Williamson etherification of the phenolic hydroxyl group with alkyl bromides.[197,198]



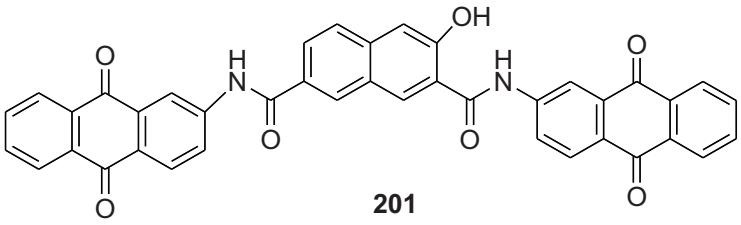
Scheme 46

2-Aminoanthraquinone was condensed with 4-[1-(2,5-dichlorophenylazo)-2-hydroxy-3-naphthoylamino] benzoyl chlorides in nitrobenzene under reflux for 8 h to yield red pigment **200**.[199]



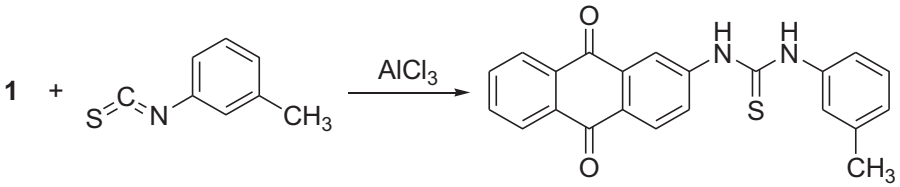
200

3,6-Dicarboxy-2-hydroxynaphthalene and 2-aminoanthraquinone in xylene at 90 °C were treated with PCl_3 followed by heating at 140 °C for 3 h to give N^2,N^7-*bis*(9,10-dioxo-9,10-dihydroanthracen-2-yl)-3-hydroxynaphthalene-2,7-dicarboxamide (**201**) can be used as raw materials for synthesis of dyes, pigments, and photosensitive materials.[200]



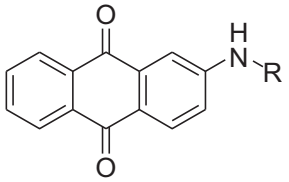
201

2-Aminoanthraquinone was treated with *m*−tolyl isothiocyanate in nitrobenzene containing $AlCl_3$ to give 2-(*m*-tolylthiocarbamido)anthraquinone, suitable as a vat dye for cotton.[201,202]



202, 75%

n-Alkyamino anthraquinones (**203**) were useful as basic dyes in coloring hair.[202]



203 R = H, Lower alkane

The waste product from purification of 2-aminoanthraquinone with 82% H_2SO_4 is utilized for the production of a vat dye by melting with S and *p*-toluidine. The resulting dye gives a dark-brown vat, insol. in Na_2S soln., and dyes cotton with a khaki tinge.[203]

Miscellaneous applications

2-Aminoanthraquinone is used as key intermediate for the synthesis of light emitting diodes,[204−208] electroluminescent materials,[209−230] switchable fluorescent systems,[231,232] and charge-transporting agents.[233] Furthermore, 2-aminoanthraquionoe is used in the preparation of thermally stable poly(amid, imide, urea),[234,235] nonlinear optical polyquinonediimine containing a di-azobenzene group in the side chain,[236] poly(2-acrylamidoanthraquinone),[237] surfactants with a hydrophilic amino group for conducting Langmuir-Blodgett films,[238] polymeric chiral stationary phases for HPLC,[239] and color paste used in making color filters for optical imaging devices.[240]

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List of Abbreviations

Aminoanthraquinone	AAQ
Multi Drug Resistance	MDR
Rotating Disk Electrode	RDE
Tetrabutylammonium Tetrafluoroborate	$TBABF_4$
Trimethylsilylacetylene	TMSA
Microwave	MW
Electron-Transporting Materials	ETMs
1-Chloro-2,3-epoxypropane	CEP
2-Methyl-aminoanthraquinone	2-MAAQ
2-Dimethyl-aminoanthraquinone	2-DMAAQ
Ionic Liquids	ILs
Trimethyl phosphite	TMP
Diethyl-aminoanthraquinone	DEAAQ
2-(1*H*-Benzo[*d*]imidazol-1-yl)-*N*-(9,10-dioxo-9,10-dihydroanthracen-2-yl) actamide	BIMANQ
2-(1*H*-Benzo[*d*]imidazol-1-yl)-*N*-(9,10-dioxo-9,10-dihydroanthracen-2-yl) hexyl actamide	HBIMANQ
Pyromellitic dianhydride	PMDA
Benzophenonetetracarboxylic dianhydride	BTDA
Hexaflouroisopropylidene diphthalic anhydride	6FDA

1,4,5,8-Naphthalene tetracarboxylic dianhydride	NDA
Benzoic acid	BA
Isoquinoline	IQ
N, *N*-Dimethylformamide	DMF
Pyridinobenzanthrone	PyBz
2,1-Pyridinoanthraquinone	2,1-PyAq
Benzanthrone	Bz
5,6-Pyridinobenzanthrone	5,6-PyBz
9,8-Pyridinobenzanthrone	9,8-PyBz
2,3-Pyridinoanthraquinone	2,3-PyAq
Lehnert Reagent	$TiCl_4$/pyridine
11,11,12,12-Tetracyano-9,10-anthraquinodimethane	TCAQ
N,*N*-Dimethylanilino	DMA
11,11,12,12-Tetracyano-9,10-anthraquinodimethane	TCAQs

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