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4,5-Dichlorophthalonitrile in the Synthesis of Macroheterocyclic Compound Precursors

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Dedicated to Corresponding Member of the Russian Academy of Sciences G.N. Vorozhtsov on the occasion of his 90th Anniversary

The first synthesis of 4,5-dichlorophthalonitrile was reported in 1992. Since then, this compound has become an indispensable building block for chemists working in porphyrazine chemistry. This is clearly evidenced by the constantly growing number of annual publications devoted to 4,5-disubstituted phthalonitriles. This review summarizes the use of this substrate in the synthesis of a wide variety of phthalonitrile derivatives. The primary goal of this work is to systematize the achievements in using 4,5-dichlorophthalonitrile as a universal precursor for constructing an extensive library of symmetric and unsymmetric 4,5-disubstituted phthalonitriles. In particular, the synthetic potential of 4,5-dichlorophthalonitrile in activated aromatic nucleophilic substitution reactions with O-, S-, and N-nucleophiles of different nature and functionality is considered. Furthermore, the review presents information on the preparation of various heterocyclic ortho-dinitriles based on 4,5-dichlorophthalonitrile. These include linked and condensed systems with 5-, 6-, 7-, and 8-membered heterocycles. Analysis of the literature leads the authors to conclude that 4,5-dichloro-phthalonitrile is a promising and multifunctional synthon. Its reactivity provides researchers with a tool for significantly expanding the range of phthalonitrile derivatives – key intermediates for the preparation of substituted phthalocyanines, subphthalocyanines, and other valuable macrocyclic structures. The presence of substituents enables fine-tuning of desired properties. The information compiled in this review is of high practical value, as it is designed to help chemists consciously choose the most efficient and selective synthetic methods to obtain target molecules with the desired architecture and, consequently, optimize their further application in materials science, medicine, catalysis, and other cutting-edge fields of science and technology.

Keywords: Dichlorophthalonitrile, disubstituted phthalonitriles, phthalocyanines, dicyano-containing heterocyclic systems, nucleophiles, binucleophiles.

4,5-Дихлорфталонитрил в синтезе предшественников макрогетероциклических соединений

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Первое сообщение о синтезе 4,5-дихлорфталонитрила датируется 1992 годом, и с тех пор это соединение прочно утвердилось в качестве незаменимого строительного блока в арсенале химиков, работающих в области порфиразиновой химии, что наглядно подтверждается постоянно растущим количеством ежегодных публикаций, посвященных 4,5-дизамещенным фталонитрилам. В статье выполнен обзор научных работ по использованию указанного субстрата в синтезе самых различных производных фталонитрила. Основное внимание в данной работе уделено систематизации достижений в использовании 4,5-дихлорфталонитрила в качестве универсального предшественника для получения обширной библиотеки 4,5-дизамещенных фталонитрилов симметричного и несимметричного строения. В частности, рассмотрены синтетические возможности 4,5-дихлорфталонитрила в реакции активированного ароматического нуклеофильного замещения с O-, S- и N-нуклеофилами различной природы и функциональности. При этом структурирована информация

о получении на основе 4,5-дихлорфталонитрила гетероциклических, связанных и конденсированных с 5-, 6-, 7- и 8-членными гетероциклическими системами разных классов орто-дикарбонитрилов. Проведенный анализ литературных данных позволяет авторам сделать обоснованный вывод о том, что 4,5-дихлорфталонитрил представляет собой перспективный и многофункциональный синтон. Его реакционная способность предоставляет исследователям инструмент для значительного расширения ассортимента производных фталонитрила – ключевых промежуточных соединений для получения замещенных фталоцианинов, субфталоцианинов и других ценных макроциклических структур, при этом наличие заместителей позволяет осуществить настройку желаемых свойств. Собранная в обзоре информация имеет высокую практическую ценность, так как призвана помочь химикам осознанно выбирать наиболее эффективные и селективные методы синтеза для получения целевых молекул с желаемой архитектурой и, как следствие, оптимизировать их дальнейшее применение в материаловедении, медицине, катализе и других передовых областях науки и техники.

Ключевые слова: Дихлорфталонитрил, дизамещенные фталонитрилы, фталоцианины, дицианосодержащие гетероциклические системы, нуклеофилы, бинуклеофилы.

Introduction

Phthalocyanines (Pcs) are widely used as pigments of blue and green shades, catalysts, molecular semiconductors, photosensitizers, elements of solar cells, and sensors.[1,2] However, their practical use is limited by extremely low solubility in organic solvents.[3] A solution to this problem has been the chemical modification of the macrocycle periphery.[1] A vivid example is the water-soluble domestic drug Photosens (sulfonated HOAlPc), approved in Russia as a clinical photosensitizer.[4]

The long-wavelength Q-band in the electronic absorption spectra is the feature most sensitive to structural changes in the Pc molecule. It has been established that the position of this band in symmetrical octa-4,5-disubstituted phthalocyanines is shifted to the red region of the spectrum compared to the position of the Q-band of tetra-4-substituted ones.[5] Furthermore, as shown in one of studies,[6] the latter turn out to be the most soluble in common organic solvents due to the presence of positional isomers.

The monograph[7] notes that carboxyl-containing metallophthalocyanine complexes MPc(3-COOH)$_4$, MPc(4-COOH)$_4$, MPc(3,5-COOH)$_8$, and MPc(4,5-COOH)$_8$ differ in their solubility in aqueous alkali solutions. Tetra-4-carboxy-substituted complexes are insoluble in water but dissolve in alkalized solutions, DMF, and DMSO, whereas their 3-isomers exhibit even lower solubility. Due to the introduction of eight carboxyl groups, MPc(3,5- or 4,5-COOH)$_8$ acquire higher solubility, including solubility in water.

Simultaneously, accumulated data on the synthesis of octa-3,6-disubstituted phthalocyanines,[8] bearing identical substituents at the nonperipheral positions of the macrocycle, have established that the Q-band of these metal complexes undergoes a bathochromic shift of approximately 50 nm compared to that of octa-4,5-disubstituted metallophthalocyanines with the same substituents.[9]

Thus, the final properties of the macroheterocycle are influenced not only by the nature and number of substituents but also by their position. To date, the most common method for the synthesis of substituted phthalocyanines is the use of phthalonitriles (Pn) containing the desired substituents.[1] Figure 1 shows commonly used dicyano-containing substrates that can be used to obtain porphyrazine precursors.

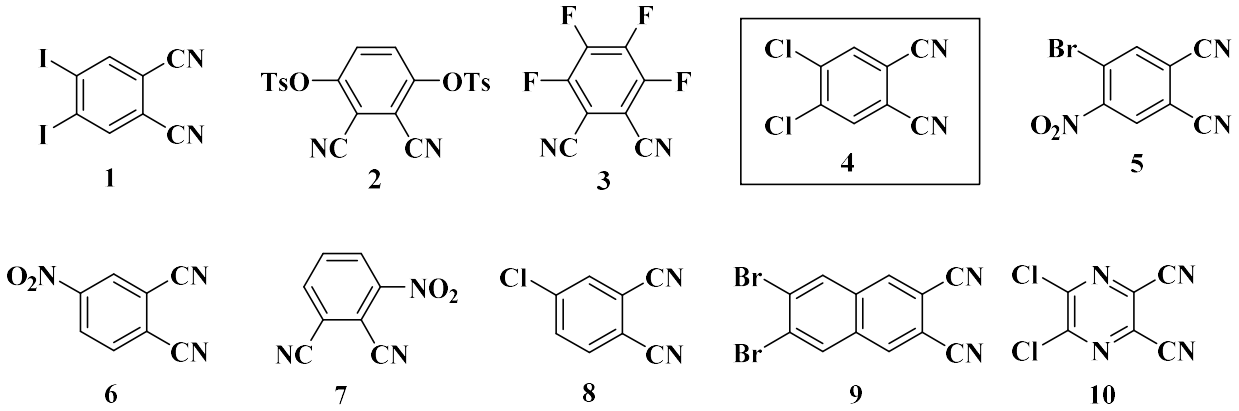


Figure 1. Commonly used porphyrazine precursors.

4,5-Diiodophthalonitrile **1** is predominantly used in cross-coupling reactions.[10] 3,6-Ditosyloxyphthalonitrile **2** can be used both in cross-coupling reactions and in nucleophilic substitution reactions to form 3,6-disubstituted Pns.[9,11,12] In turn, 3,4,5,6-tetrafluorophthalonitrile **3** allows for the introduction of two or more diverse substituents via the activated aromatic nucleophilic substitution reaction (S_NAr reaction).[12–14] The main disadvantage of this approach is the formation of complex product mixtures.[1] This review is devoted to the use of 4,5-dichlorophthalonitrile **4** (4,5-DCPN) in S_NAr reactions with various nucleophiles for the synthesis of dicyano-substituted aromatic and heterocyclic systems. Additionally, we briefly examine its applications in other transformations, particularly cross-coupling, highlighting its utility for preparing phthalocyanine precursors. These compounds serve as key intermediates for constructing macroheterocycles with a wide range of tunable, practically useful properties, which are predetermined by the substituents introduced in the initial precursors. The choice of this subject is motivated by the extensive synthetic capabilities of 4,5-DCPN and the abundance of unsystematized data in the literature.

4-Bromo-5-nitrophthalonitrile **5** (4,5-BNPN) demonstrates a synthetic potential similar to 4,5-DCPN but has fundamental differences in reactivity associated with the different nucleofugality of the bromine atom and the nitro group.[1,15] Furthermore, the literature contains exhaustive and systematized information on the preparation of heterocyclic systems based on it.[16,17] At the same time, in the case of 3- or 4-nitro-substituted[18] or chloro-substituted[19] Pn derivatives (compounds **6**, **7**, and **8**, respectively), only limited chemical modification of the molecule is possible due to the presence of only one leaving group. Therefore, despite the wide application of these compounds in both polymer chemistry and phthalocyanine chemistry, they were of much less interest to us.

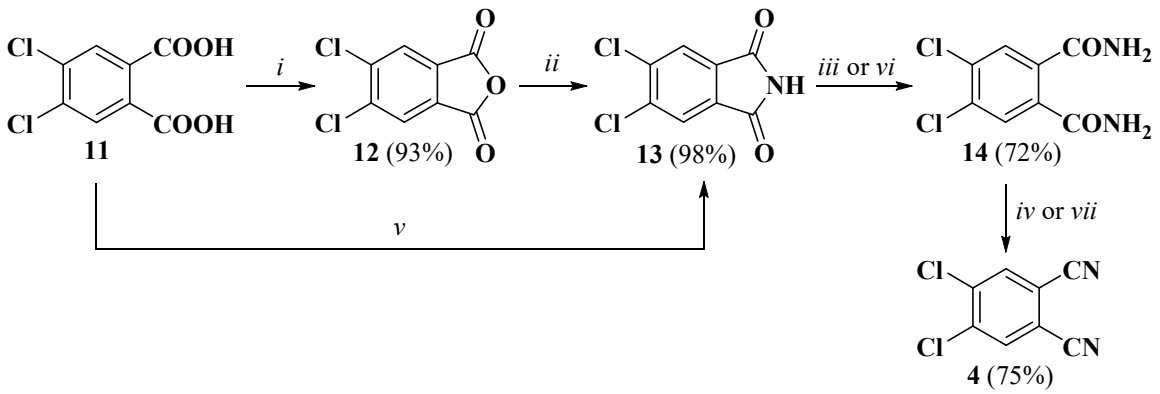
Besides phthalonitriles, other substrates are also used as precursors for macroheterocycles. Thus, based on 6,7-dibromonaphthalene-2,3-dicarbonitrile **9**, naphthalodinitriles – precursors to naphthalocyanines – can be obtained via S_NAr reaction[20,21] or cross-coupling reaction.[22,23] Their extended π-system causes a bathochromic shift (~80 nm) of the Q-band and an increased tendency for aggregation[20,23] compared to the corresponding Pcs. 5,6-Dichloropyrazine-2,3-dicarbonitrile **10**, due to the electronegative nitrogen atoms, exhibits high reactivity in S_NAr reactions proceeding under mild conditions. However, the resulting pyrazinoporphyrazines are characterized by a hypsochromic shift (~60 nm) of the Q-band relative to Pcs.[24–26]

In 1992, Wöhrle published an "elegant" method for the synthesis of 2,3,9,10,16,17,23,24-octasubstituted metal-free phthalocyanines (H_2Pc) from the corresponding 4,5-disubstituted phthalonitriles in the journal *Synthesis*.[27] The key precursor was obtained from commercially available 4,5-dichlorophthalic acid **11** via a sequence of reactions including anhydridization with acetic anhydride, subsequent imidization of the resulting anhydride **12** with formamide (which acted simultaneously as an ammonia source and solvent), amidization of the imide **13**, and finally, dehydration of the resulting 4,5-dichlorophthalamide **14** to the target 4,5-DCPN **4** with an overall yield of 49% (Figure 2).

Work[28] proposed an alternative transformation pathway. Thus, the preparation of 4,5-dichlorophthalimide **13** is possible directly from 4,5-dichlorophthalic acid **11** in a 94% yield (Figure 2, conditions *v*). Furthermore, it was possible to increase the yield of amide **14** from 72% to 78% by adding ammonium chloride during the amidization of compound **13** (conditions *vi*).

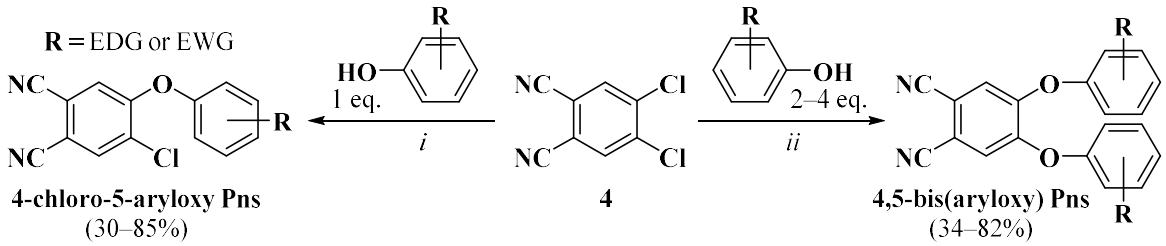
Reactions with *O*-Nucleophiles

The reactions of 4,5-DCPN with monofunctional *O*-nucleophiles have been the most extensively studied. As is known, the interaction of 4,5-dichlorophthalonitrile with phenols in an aprotic polar solvent medium usually leads to the formation of a difficult-to-separate mixture of mono- and disubstitution products.[29,30] However, the use of an excess of the nucleophile employed in the S_NAr reaction allows for chemoselective synthesis of the disubstitution products.



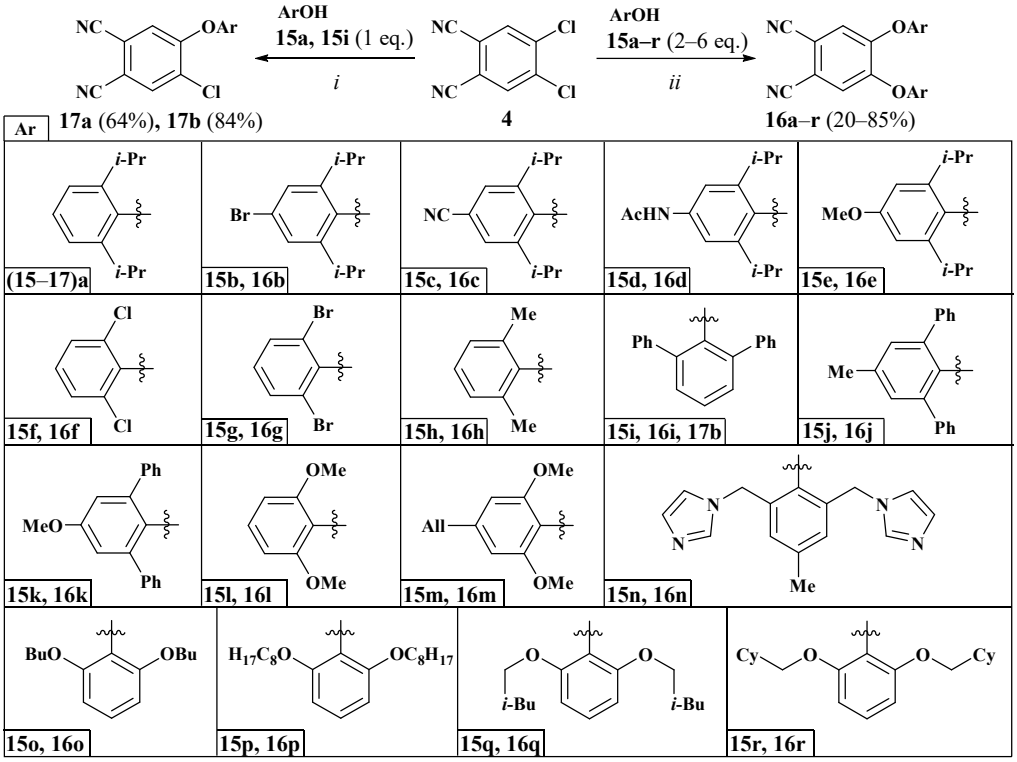
i: Ac_2O, reflux, 5 h; *ii*: $HCONH_2$, reflux, 3 h; *iii*: NH_4OH/H_2O, r.t., 48 h; *iv*: $SOCl_2$/DMF (0–5 °C), then 5 h, r.t., 24 h; *v*: $(NH_4)_2CO_3$ or NH_4OAc, AcOH, reflux, 2.5 h; *vi*: NH_4OH/H_2O, NH_4Cl, 30 °C, 2h; *vii*: $POCl_3$/DMF (0–5 °C), then <35 °C, 5 h.

Figure 2. Synthesis of 4,5-dichlorophthalonitrile.



i: K_2CO_3, DMF or DMSO or DMF/H_2O, 30–90 °C, 2–20 h; *ii*: K_2CO_3, DMF or DMSO, 45–90 °C, 3–65 h.

Figure 3. The most studied reactions involving 4,5-dichlorophthalonitrile.



i: K_2CO_3, DMF or DMF/H_2O, 30–45 °C, 1–24 h; *ii*: K_2CO_3 or CsF, DMF or DMSO or MeCN, 70–110 °C, 1.5–166 h.

Figure 4. Interaction of 4,5-DCPN with 2,6-disubstituted phenols.

Today, 4,5-DCPN is primarily employed to access a wide variety of 4,5-bis(aryloxy)phthalonitriles (Figure 3), which serve as precursors for the synthesis of corresponding octasubstituted Pcs. Study[31] established that octa-substituted ZnPcs bearing phenoxy fragments with electron-withdrawing substituents on their periphery exhibit improved photostability due to enhanced aggregation in solutions.

In contrast, 4-chloro-5-aryloxyphthalonitriles have only recently begun to attract researchers' attention. Based on available data, it has been determined that the presence of chlorine atoms in addition to aryloxy groups in H_2Pc leads to inhibition of aggregation in DMSO due to increased NH-acidity of the molecule,[32,33] enhanced photooxidative stability,[21] and photosensitizing activity. This often, though not always, results in a bathochromic shift of the absorption maximum,[34] which is important in the fields of nonlinear optics and photodynamic therapy (PDT). Studies[35,36] note that chlorine atoms not only serve an auxochromic function but also prevent the self-association of phthalocyanine cores.

To date, 4-chloro-5-aryloxyphthalonitriles are typically obtained by separating the mixture of mono- and disubstitution products into individual components using column chromatography.[30] However, in some cases, it is possible to halt the reaction at the formation of 4-chloro-5-aryloxyphthalonitriles. This can be achieved by conducting the S_NAr reaction under mild conditions[37] or by using a binary DMF-water solvent system[38] (in both cases, a 1:1 ratio of 4,5-DCPN to phenols is used). It should be noted that in the latter case, all components of the reaction mixture are dissolved, resulting in the S_NAr reaction proceeding under homogeneous conditions. After some time, the forming monosubstitution product is removed from the reaction zone by precipitating and thus does not participate in further transformations. It is noteworthy that, unlike the reaction with a twofold excess of *para*-hydroxybenzoic acid under anhydrous conditions (conditions *ii*, Figure 3), which yields the disubstitution product,[31] under the specified conditions (DMF/H_2O), the reaction of 4,5-DCPN with a

twofold excess of *para*-hydroxybenzoic acid proceeds selectively to form the monosubstitution product.

Currently, peripherally octasubstituted phthalocyanines containing both electron-withdrawing chlorine atoms and electron-donating aryloxy substituents are being intensively studied. Detailed data on the properties of phthalocyanines obtained from 4-thymoxy-5-chlorophthalonitrile are presented in studies.[33,39,40]

We have identified the most promising directions for the synthesis of aryloxyphthalonitriles from 4,5-DCPN, where the phenolic reagents are 2,6-disubstituted derivatives, fluorinated phenols, phenols with hydrophilic groups, as well as phenols containing heteroaromatic, macroheterocyclic, and macrocyclic fragments.

Studies[24,37,41–44] note that the introduction of 2,6-diisopropyl-, 2,6-dihalogen-, 2,6-dimethoxy-, and 2,6-dimethylphenoxy fragments is not only effectively inhibits aggregation but also significantly enhances the solubility of various types of macroheterocycles in common organic solvents due to the steric bulk of these groups.

The nature of the substituent in the 4-position of 2,6-diisopropyl- and 2,6-diphenylphenols (**15a–e** and **15i–k**, respectively) does not significantly affect the yield of the corresponding Pns (Figure 4). However, using acetonitrile as a solvent instead of DMF reduces the yield and prolongs the reaction time (for comparison: η(**16l**, DMF, 48 h) = 85%, η(**16m**, MeCN, 166 h) = 36%). The presence of an additional methyl or methoxy group imparts to the Pc the ability to dissolve in toluene,[45] while the presence of an acetylamino group, in turn, decreases solubility.[41] At the same time, the presence of halogens in the 2- and 6-positions of the phenol complicates the S_NAr reaction. Thus, the authors succeeded in synthesizing Pns **16f** and **16g** in the presence of cesium fluoride as a base, but the temperature and reaction time had to be significantly increased. However, a similar reaction with 2,6-difluoro(iodo)phenols proved unsuccessful[42]. In the conclusion of their study, the authors state that aggregation is impossible due to steric hindrance, as the presence of a 2,6-dichloro(bromo)-phenoxy fragment leads to an orthogonal arrangement of the phenoxy group relative to the planar Pc core.

Study[45] demonstrates the potential of the electron-donating 2,6-diphenylphenoxy group as a key structural fragment for improving the efficiency of solar cells based on zinc phthalocyanine.

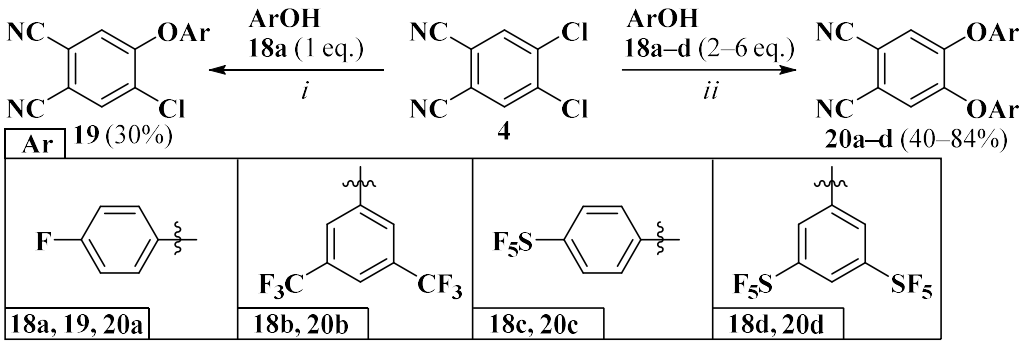
X-Ray structural data[46,47] has revealed that the bulky 2,6-diphenylphenoxy and 2,6-diisopropylphenoxy substituents, combined with a chlorine atom in the molecules of 4-chloro-5-aryloxyphthalonitriles **17a,b**, cause a perpendicular orientation of the phenoxy groups relative to the plane of the phthalocyanine macrocycle. This creates significant steric strain near the Pc core, effectively suppressing its cofacial self-association. It is also shown that the simultaneous presence of four chlorine atoms and four 2,6-diisopropylphenoxy fragments on the periphery of the phthalocyanine not only increases its oxidative stability compared to an analogue containing eight diaryloxy substituents but also enhances solubility, which is explained by the formation of randomers.

The authors of work[48] synthesized a series of MPcs to evaluate their antibacterial activity. The study showed that the cobalt complex containing eight 2,6-dimethoxy-4-allylphenoxy substituents and obtained from phthalonitrile **16m** exhibits antibacterial activity against Gram-negative bacteria.

Japanese chemists[49,50] studied the influence of the alkyl chain length in 2,6-dialkoxyphenoxy fragments on the properties of sensitized solar cells based on ZnPc. The authors found that increasing the length of the alkyl chain, as well as its branching, negatively affects the efficiency of the solar cell and the density of dye adsorption on the titanium dioxide surface. A cobalt-phthalocyanine-sensitized solar cell[49] was fabricated based on Pn **16o**, converting solar energy into electricity with a record (according to the authors) efficiency of 6.4%.

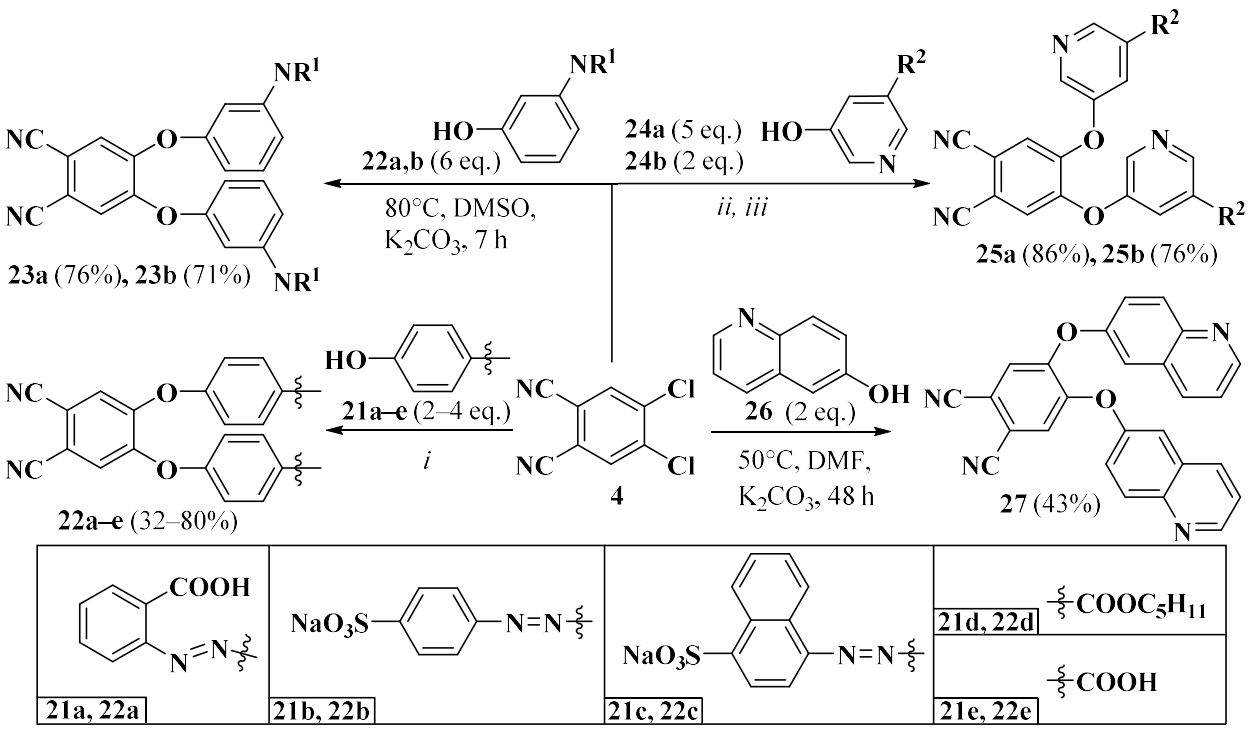
It is known that fluorine-containing substances have become increasingly relevant in pharmaceutical chemistry recently.[51] Fluorinated metallophthalocyanines demonstrate exceptionally good solubility in various solvents and possess antibacterial properties[52]. Furthermore, the introduction of a fluorine atom into the structure significantly affects the photochemical activity of phthalocyanines. For example, fluorine-containing MPcs (M = ClGa, ClIn), obtained from Pn **20a** (Figure 5), exhibit high singlet oxygen generation quantum yields (Φ_Δ = 0.90 and 0.84, respectively).[53] At the same time, MPcs (M = Zn, ClIn), synthesized based on Pn **20b**, are, according to the authors, potential candidates for the role of photosensitizers (Φ_Δ = 0.64 and 0.84, respectively).[54]

The methodology we developed for the synthesis of 4-(4-fluorophenoxy)-5-chlorophthalonitrile **19** (Figure 5) in a DMF–water system[38] provides access to new derivatives of fluorine-containing MPcs.



i: K_2CO_3, DMF/H_2O, 80 °C, 3 h; *ii*: K_2CO_3, DMF or DMSO, 90–120 °C, 1–3 h.

Figure 5. Interaction of 4,5-DCPN with fluorinated phenols.



22a, **23a**: R^1 = Me; **22b**, **23b**: R^1 = Et; **24a**, **25a**: R^2 = H;
24b, **25b**: R^2 = 4-*t*-BuC_6H_4–
i: Na_2CO_3 or K_2CO_3, DMF or DMSO, 20–90 °C, 3–45 h; *ii*: K_2CO_3, DMF, 80 °C, 3 h; *iii*: K_2CO_3, DMF, 125 °C, 100 MW, 0.5 h.

Figure 6. Synthesis of 4,5-disubstituted precursors of water-soluble Pcs.

In another study,[55] aiming to investigate mesomorphic properties, Pns **20c** and **20d** containing both electron-withdrawing and bulky pentafluorosulfanyl substituents (Figure 5) were synthesized, and based on them, highly soluble CuPcs were obtained. It was shown that the complex with *meta*-substituted SF_5 groups exhibits mesomorphism, while its *para*-substituted analogue does not possess this ability.

Phthalocyanines are known for their hydrophobicity and tendency to form aggregates in water, which reduces their efficacy as sensitizers by causing a fluorescence quenching effect.[56] To prevent this phenomenon, the periphery of the phthalocyanine must bear groups that simultaneously enable the macrocomplex to dissolve in water and inhibit the formation of supramolecular ensembles. Currently, the range of water-soluble macroheterocycles is being expanded by utilizing the S_NAr reaction during the phthalonitrile synthesis stage.

In the study,[57] researchers synthesized a 4,5-disubstituted Pn **22d** (Figure 6), containing pentoxycarbonyl groups that are easily hydrolyzable in the presence of base. After cyclotetramerization followed by hydrolysis of the ester groups, a water-soluble ZnPc was obtained. This complex enables applications not only in bioimaging of living organisms in the near-infrared range but also in inhibiting the formation of amyloid beta-fibrils, thereby reducing the risk of Alzheimer's disease.

Water-soluble ZnPcs incorporating additional chromophores–specifically arylazo groups–have also been prepared from carboxy-[58] and sulfo-substituted[56] phthalonitriles **22a–c** (Figure 6).

Macroheterocycles containing anionic charged groups typically exhibit enhanced water solubility. The authors of study[59] employed a different approach to synthesizing water-soluble phthalocyanines. Thus, based on Pns **23a,b**, ZnPcs containing 4-*N*,*N*-dimethyl- and 4-*N*,*N*-diethylamino groups in the phenoxy substituents were obtained. These amino groups were successfully quaternized with methyl iodide to form cationic charged complexes. The authors noted that these ZnPcs possess antibacterial properties against both Gram-positive and highly resistant Gram-negative bacteria.

A similar approach was used to obtain cationic water-soluble zinc phthalocyanine complexes containing quinoline[60] and pyridine fragments.[61,62] Notably, the cationic ZnPc obtained from Pn **27** exhibits reduced fluorescence quantum yield (Φ_F) and Φ_Δ compared to non-ionic ZnPc.[60]

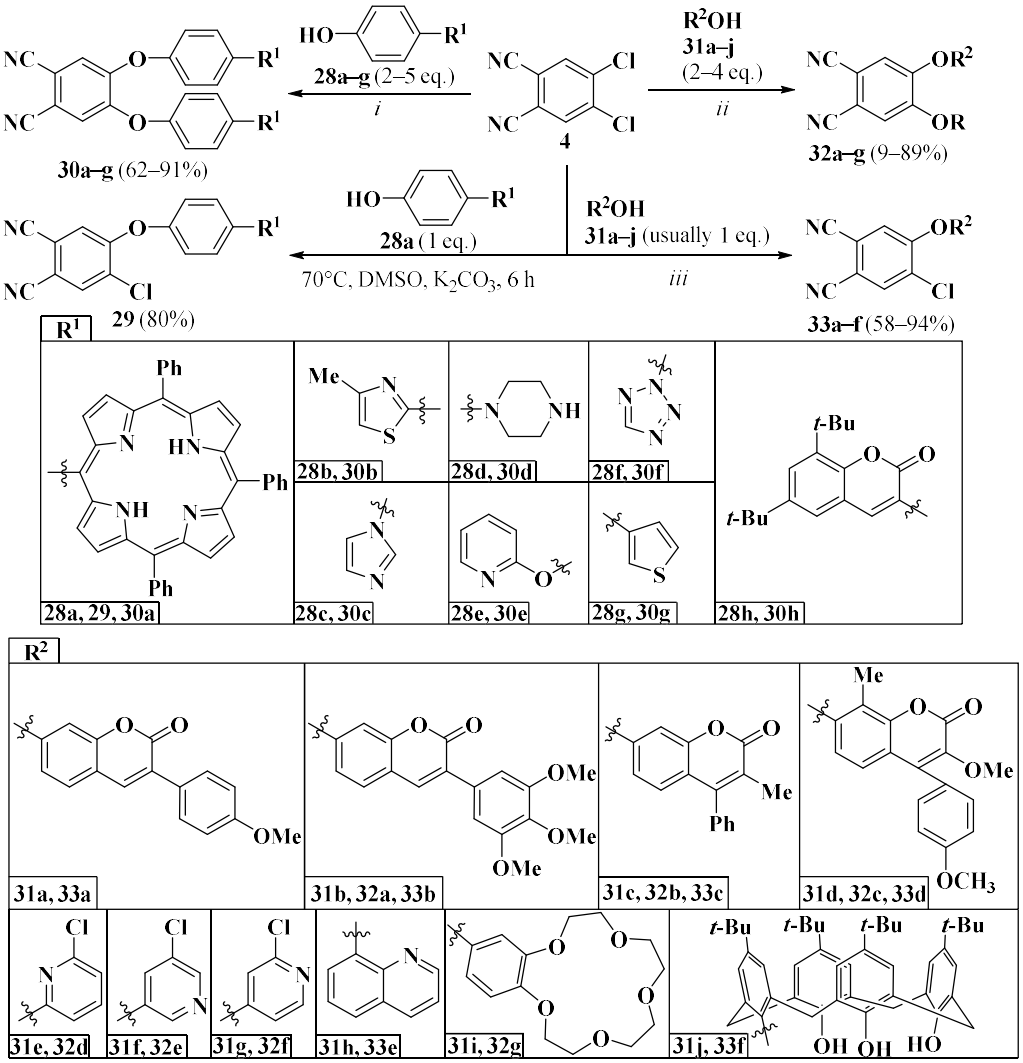
In the context of photodynamic therapy for cancer, study[61] determined the ability of a quaternized zinc and silicon phthalocyanine complex, obtained from Pn **25a**, to localize in lysosomes and induce a phototoxic effect. The investigation revealed that even after quaternization with methyl iodide, aggregation of the cationic ZnPc could not be suppressed. However, the presence of bulky axial ligands on the silicon atom not only effectively prevents self-association but also increases the fluorescence quantum yield compared to analogous zinc complexes. In another study,[62] the strong electron-accepting properties of a zinc complex with quaternary pyridinium groups, obtained from Pn **25b**, allowed the role of single-walled carbon nanotubes

in the hybrid system to be altered: they transitioned from electron acceptors to electron donors.

Based on the porphyrin-containing phenol **28a** and 4,5-DCPN **4**, 4-aryloxy-5-chlorophthalonitrile **29**[21] and 4,5-disubstituted phthalonitrile **30a**[63] were obtained (Figure 7). It was noted that the presence of electronegative chlorine atoms improves the stability of the macroheterocyclic pentad synthesized from Pn **29a** and its nonlinear optical properties.[21] At the same time, the combination of a zinc phthalocyanine complex fragment with eight covalently linked porphyrin fragments leads to $\Phi_F = 1$.[63]

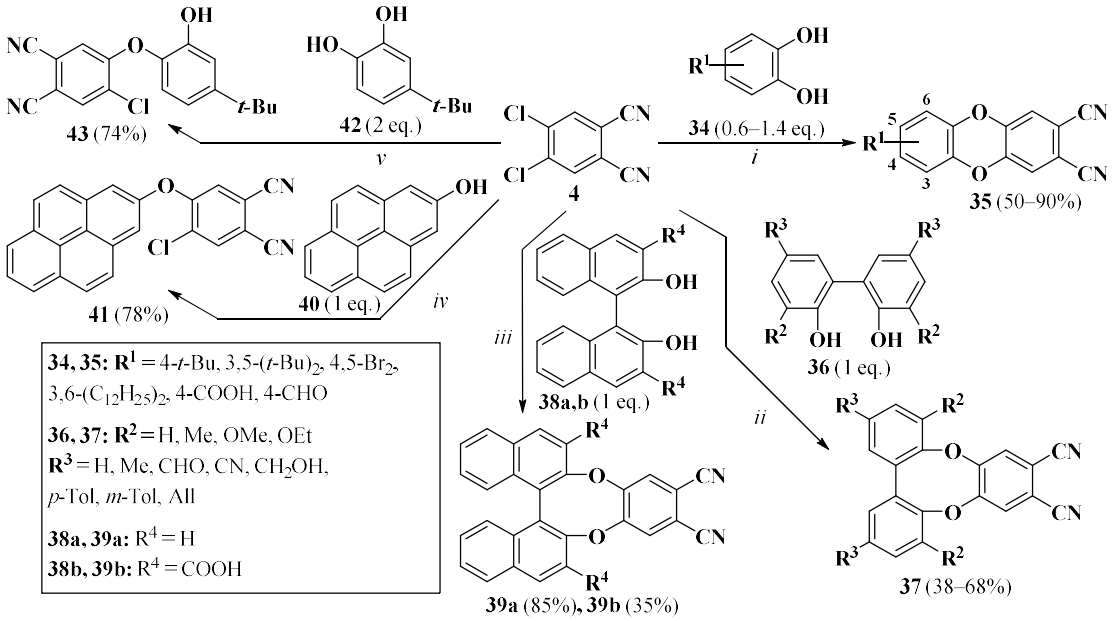
Study[64] reported the synthesis of 4,5-disubstituted Pns **30b–f**, containing various nitrogen-containing heterocycles. Turkish chemists[65,66] were the first to obtain 4-thiophen-3-yl- and coumarin-containing *ortho*-dicarbonitriles **30g** and **30h**, respectively. Phthalocyanines derived from these compounds exhibited reduced aggregation tendency and enhanced organosolubility. It was noted that 4-thiophen-3-yl-containing macroheterocycles, according to electrochemical testing results, may find applications in electrochemical fields,[65] while compounds combining phthalocyanine and coumarin fragments are promising photosensitizers for PDT.[66]

The literature also contains examples of phthalonitriles linked to a heterocyclic system directly via an oxygen bridge. Turkish chemists investigated the influence of the number and position of coumarin substituents in MPc molecules (where M = AcOIn[67] or Zn[29,68]) on their photophysical properties and aggregation behavior in DMF. They found that the presence of a chlorine atom in the structure of coumarin-containing MPc can either increase[67] or decrease[68] Φ_F compared to other coumarin-containing MPcs, while maintaining a high Φ_Δ value. It was established that MPcs synthesized from Pns **32b**, **33a**, and **33c** can be used as type II photosensitizers.[67,68] Furthermore, the coumarin-containing Pns **32a** and **33b** themselves demonstrate a high Stokes shift (135 nm) and possess properties of organic chemosensors for Fe^{3+} ions[69]. Interestingly, the S_NAr reaction could not be conducted chemoselectively to form only the chlorine-containing phthalonitrile **33d**. This compound was isolated from the mixture of mono- and disubstitution products using column chromatography.[29]



i: K_2CO_3, DMF or DMSO, 20–90 °C, 6–120 h; *ii:* K_2CO_3, DMF or DMSO, 20–100 °C, 1.5–240 h; *iii*: K_2CO_3, DMF, 20–70 °C, 24–240 h.

Figure 7. Preparation of phthalonitriles containing heterocyclic, macroheterocyclic and macrocyclic fragments.



i: K_2CO_3, DMF or DMSO, 20–90 °C, 1.5–168 h; *ii*: K_2CO_3, DMF, 80–120 °C, 1.5–4 h; *iii*: K_2CO_3, DMF, 80 or 90 °C, 6 or 6.5 h; *iv*: LiOH, DMSO, 25 °C, 24 h; *v*: K_2CO_3, DMF, r.t., 24 h.

Figure 8. Synthesis condensed *ortho*-dicarbonitriles.

The literature also describes phthalonitriles linked via an oxygen bridge to other heterocycles, particularly pyridine and quinoline. The authors of work[70] studied in detail the bromination reaction of 8-hydroxyquinoline and chlorophthalonitrile **33e** to compare the selectivity of the electrophilic aromatic substitution reaction. Japanese scientists[71] studied the influence of the nitrogen atom position in the pyridyloxy group on the mesomorphic properties of the compounds. They found that CuPc obtained from Pn **32f** forms stable mesophases over a wide temperature range, whereas CuPc obtained from Pn **32d** exhibits mesomorphic properties only at 325 °C. According to the authors, the complete absence of mesomorphism in CuPc obtained from **32e** is due to the presence of intra- and intermolecular N…Cl bonds. It should be noted that the reactivity of isomeric hydroxypyridines **31e–g** in the S_NAr reaction decreased in the expected order: **31f** (*meta*-) > **31g** (*para*-) > **31e** (*ortho*-).

Phthalonitriles containing macrocyclic fragments are also reported. Thus, study[72] reported the synthesis of Pn **32g**, containing two benzo-15-crown-5 polyether fragments, via the reaction of 4,5-DCPN and 4'-hydroxybenzo-15-crown-5 **31i**. A series of octa(benzo-15-crown-5)-substituted MPcs was obtained based on it. The authors of study[73] required a calixarene-substituted Pn **33f** for the synthesis of a new phthalocyanine-calixarene conjugate. They managed to obtain it selectively by performing the S_NAr reaction between 4,5-DCPN **4** and 4-*tert*-butylcalix[4]arene **31j** at a stoichiometric reagent ratio of 1:1. Notably, under the reaction conditions (excess deprotonating agent – K_2CO_3) an intramolecular nucleophilic substitution of the second chlorine atom in compound **4** did not occur, despite the proximity of activated *O*-nucleophilic centers in the molecule **33f**.

A series of dicyanodibenzo[1,4]dioxins was obtained via an S_NAr reaction between 4,5-DCPN **4** and pyrocatechol derivatives **34** (Figure 8). The presence of a *tert*-butyl group in Pn **35** (R = 4-*t*-Bu), combined with the dibenzo[1,4]-dioxin system, enables the synthesis of highly soluble metalloporphyrazines based on it.[74] Photophysical studies established that the zinc complex obtained from this Pn possesses a high Φ_Δ value of 86%. The presence of an additional *tert*-butyl group in the structure of Pn **35** (R = 3,5-*t*-Bu_2) leads to a significant increase in the solubility of the corresponding zinc porphyrazine in *n*-hexane[75]. It should also be noted that the authors of the aforementioned work synthesized Pn **35** (R = 4,5-Br_2), from which dibenzo[1,4]-dioxine-2,3,7,8-tetracarbonitrile **35** (R = 4,5-$(CN)_2$) was synthesized under Rosenmund–Braun reaction conditions. A green, hyperbranched polymer that does not soften up to its decomposition temperature (>300 °C) was obtained based on the latter. Recently, dibenzo[1,4]dioxin **35** (R = CHO), containing a formyl group, was obtained.[76] This group is more stable toward air oxidation to a carboxylic group compared to the previously described 4-formylphenoxyphthalonitrile.[77]

Russian chemists provide an equally probable forecast regarding the manifestation or absence of mesomorphism in metalloporphyrazines obtained from *ortho*-dicarbonitrile **37** ($R^2 = R^3 = H$), as such a structure is characteristic of discotic mesogens.[78] A study by foreign chemists[79] showed that a zinc porphyrazine annulated with a tribenzo[1,4]dioxocin fragment ensures efficient singlet oxygen generation and is a promising photosensitizer for PDT of oncological diseases (Φ_Δ = 0.612). Furthermore, there are reports on azadipyrromethene boron complexes containing a tribenzo[1,4]dioxocin fragment and exhibiting optical activity extending into the near-IR range.[80]

Using derivatives of biphenyl-2,2'-diol and 4,5-DCPN in an S_NAr reaction, we were the first to obtain *ortho*-dicarbonitriles **39** containing various substituents on the periphery of the tribenzo[1,4]dioxocin fragment.[81] Using a similar methodology with compound **4** and carboxyl-

containing binaphthol **38b**, we obtained *ortho*-dicarbonitrile **39b**[76].

Study[82] reports the reaction of the condensed phenol **40** with 4,5-DCPN **4** in DMSO medium in the presence of lithium hydroxide as a deprotonating agent. Aggregation and electrochemical studies revealed that the newly obtained pyrene-containing MPc does not aggregate in $CHCl_3$ and possesses, according to the authors, good electrochemical properties.

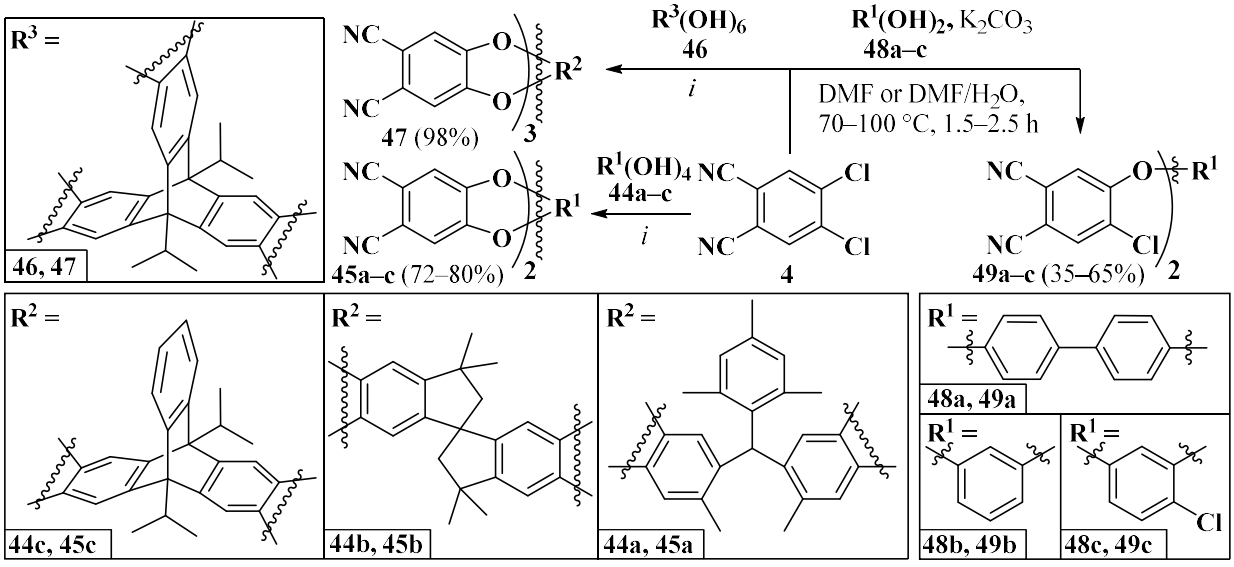
Study[83] deliberately synthesized the chlorine-containing Pn **43** via an S_NAr reaction between 4,5-DCPN and 4-*tert*-butylcatechol **42**. It was found that this compound possesses excellent chelating ability towards Fe^{2+}, not inferior to EDTA. Furthermore, the corresponding CuPc has the ability to bind to circulating tumor DNA.

The literature describes examples of obtaining diphthalonitriles based on 4,5-DCPN using bi- and tetrafunctional *O*-nucleophiles. Derivatives of pyrocatechol linked by various fragments, such as arylidenyl **44a** or spiro nonanyl **44b**, are used as the latter (Figure 9). Compound **45a** is an intermediate in the synthesis of a monomer (diphthalic anhydride), which was used to prepare intrinsically microporous polyimides,[84] while the spiro derivative **45b** was used for the synthesis of a network cobalt phthalocyanine polymer – a potential heterogeneous catalyst for oxidation reactions of cyclohexenone and hydroquinone.[85]

Triptycene-containing polyimides have attracted researchers' attention[86,87] due to their microporous structure and potential for use in highly efficient gas separation membranes. The synthesized polymers demonstrated a combination of permeability and selectivity significantly surpassing modern polymeric materials for key gas separation processes. Outstanding efficiency was observed in the separation of hydrogen (H_2/N_2, H_2/CH_4) and air components (O_2/N_2). Diphthalic anhydride obtained from diphthalonitrile **45c** via the standard hydrolysis and anhydridization scheme was used as monomers for the synthesis of these polyimides. Meanwhile, triphthalic anhydride based on triphthalonitrile **47** was used in the synthesis of a three-dimensional polyimide framework with high specific surface area and thermal stability.[88] This polymer is a potential candidate for CO_2 capture, H_2 storage, and gaseous hydrocarbon separation.

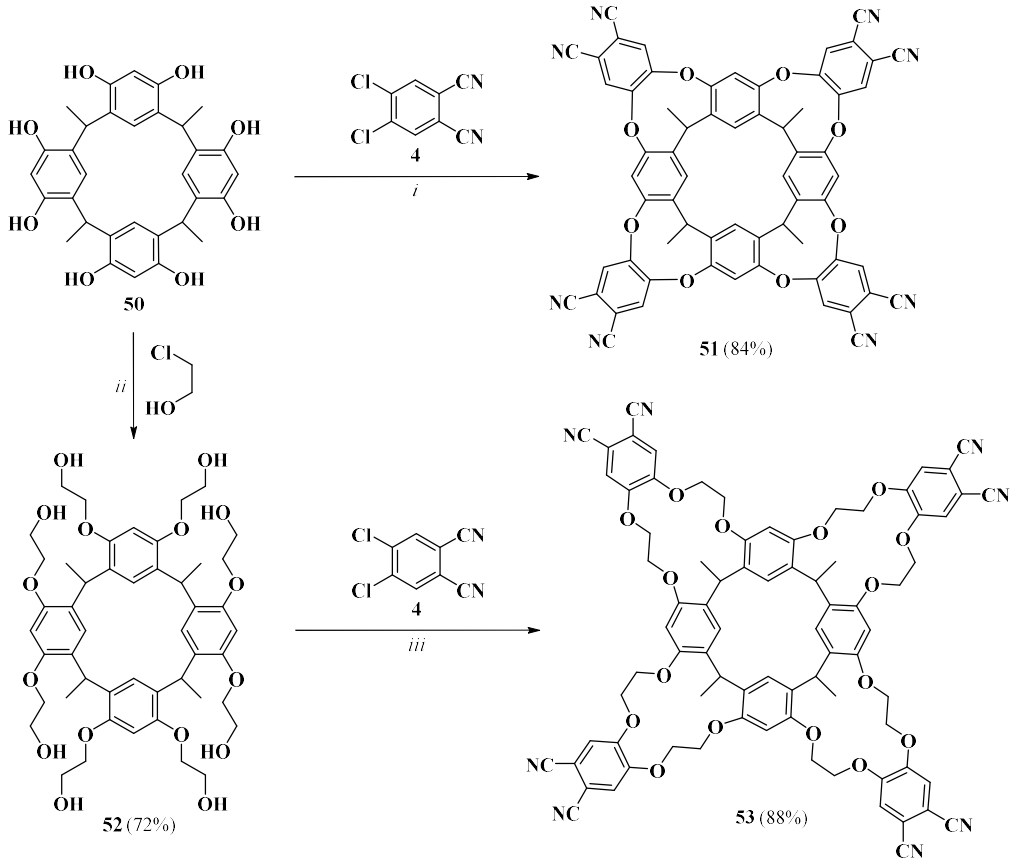
Compounds **49a–c** represent another type of diphthalonitrile. A feature of these compounds is that two phthalonitrile fragments are linked by an arylenedioxy bridge, while two chlorine atoms are retained in the molecule.[89] These diphthalonitriles can be further used to obtain the corresponding diphthalic anhydrides – promising monomers for the synthesis of polyetherimides.[90] As known, chlorine-containing polyimides possess good transparency, a high refractive index, as well as good thermal stability and mechanical resistance.[91]

The literature describes examples of synthesizing tetraphthalonitriles based on 4,5-DCPN. They have found application in the synthesis of metallophthalocyanine polymers. Thus, study[92] reported the synthesis of a dioxonine-containing tetraphthalonitrile **51** based on resorcinarene **50**, and research[93] described compound **53**, containing four tetraoxa-containing 15-membered macroheterocycles (Figure 10). It should be noted that both reactions were conducted under microwave irradiation, which reduced the reaction time to 10–20 minutes and afforded the target compounds in high yield. The resulting metallophthalocyanine polymers derived from tetraphthalonitrile **53** exhibited higher solubility in organic solvents than those obtained from compound **51**.



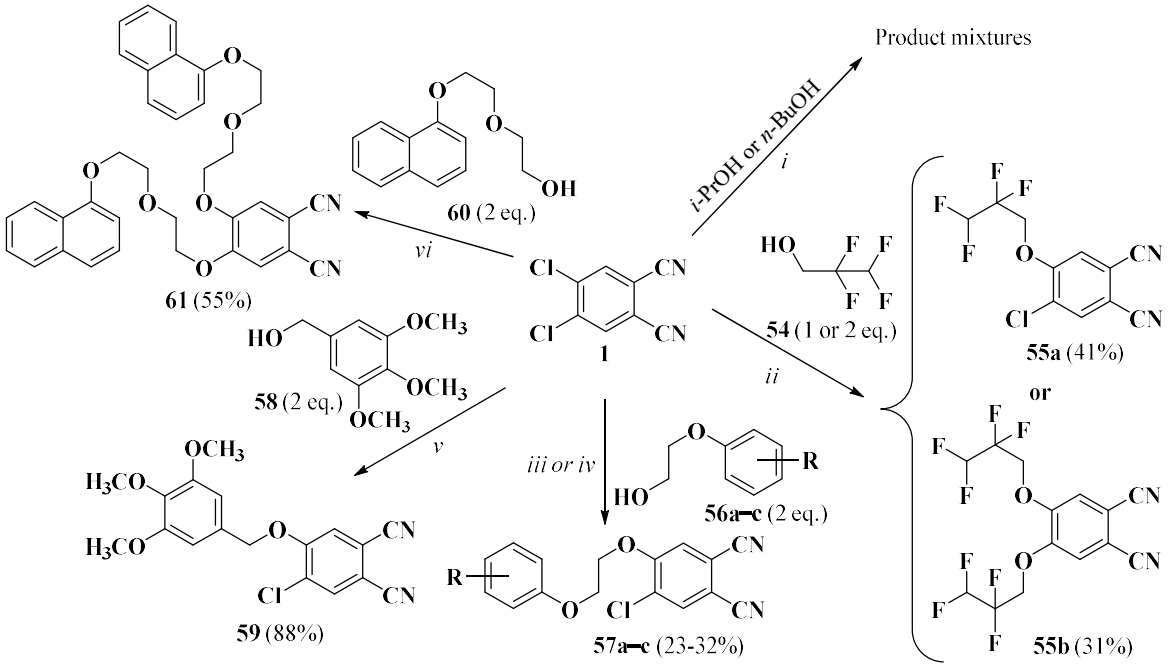
i: K_2CO_3, DMF, 80 °C, 3–10 h.

Figure 9. Obtaining precursors of polyimides and polyphthalocyanines.



i–*iii*: K_2CO_3, DMF, 360 W, 10–20 min.

Figure. 10. Interaction of 4,5-DCPN with resorcinarenes.



56a, **57a**: R = 1,2,3,4,5-H_5; **56b**, **57b**: R = 1,2,3,4,5-F_5;
56c, **57c**: R = 2-OMe, 4-All

i: different bases (NaH, CsF, K_2CO_3, NaOH), strictly anhydrous conditions; *ii*: K_2CO_3, DMSO, 20 °C, 24 h; *iii*: K_2CO_3, DMF, 60 °C, 48 h; *iv*: K_2CO_3, MeCN, 82 °C, 168 h; *v*: K_2CO_3, DMF, r.t., 24 h; *vi*: K_2CO_3, DMF, 50 °C, 72 h.

Figure 11. Interaction of 4,5-DCPN with aliphatic *O*-nucleophiles.

Study[27] established that 4,5-DCPN reacts with *n*-C_3H_7OH in the presence of *n*-C_3H_7ONa even at 0 °C, forming several reaction products, in particular, an alkoxyimino-1*H*-isoindole with partial substitution of chlorine atoms. At the same time, a group of Czech scientists notes[94] that all attempts to synthesize 4,5-di(*n*-butoxy)phthalonitrile directly from 4,5-DCPN and *n*-C_4H_9OH using various deprotonating agents (NaH, CsF, K_2CO_3, NaOH), elevated temperatures, and strictly anhydrous conditions were also unsuccessful. Currently, this type of compound is obtained in three stages from pyrocatechol.[94,95]

Conversely, the authors of study[96] successfully achieved the mono- and disubstitution reaction of chlorine atoms in 4,5-DCPN using 2,2,3,3-tetrafluoro-1-propanol **54** (Figure 11) as the *O*-nucleophile in DMSO in the presence of K_2CO_3 as a base. Based on the results of photophysical and aggregation studies, it was found that zinc phthalocyanine complexes obtained from phthalonitriles **55a,b** have the potential to act as type II photosensitizers.

Research[97,98] has shown that 4,5-dichlorophthalonitrile reacts with a twofold excess of *O*-aryl-substituted monoethylene glycol derivatives **56(a–c)** to form chlorophthalonitriles **57(a–c)** (Figure 11). Based on X-ray diffraction analysis (XRD) data, it was established that chlorophthalonitrile **57b**, unlike chlorophthalonitrile **57a**, adopts a thermodynamically unfavorable conformation due to intramolecular interactions between the chlorine atom and the OC_6F_5 fragment.

Study[99] reported the synthesis of chlorophthalonitrile **59** via the reaction of 4,5-DCPN **4** with a twofold excess of benzyl alcohol **58**. Turkish chemists noted that the introduction of 3,4,5-trimethoxybenzyloxy[99] and eugenoxyethyleneoxy[98] fragments into the phthalocyanine structure solves the solubility problem and inhibits aggregation, preventing the molecules of the corresponding MPcs from associating.

At the same time, according to study,[100] elongation of the ethyleneoxy groups also increases the solubility of metallophthalocyanines. Thus, based on the 4,5-disubstituted phthalonitrile **61**, obtained from the reaction of 4,5-DCPN with a twofold excess of *O*-substituted diethylene glycol derivative **60**, the synthesis of metallophthalocyanine complexes with enhanced solubility in organic solvents was accomplished.

Reactions with *S*-Nucleophiles

The interaction of 4,5-DCPN with aliphatic *S*-nucleophiles leads to the formation of 4,5-bis(alkylsulfanyl)-phthalonitriles, which are reported in the literature much more frequently than their oxygen-containing analogues.

Czech chemists synthesized the corresponding 4,5-disubstituted Pns **63** from 4,5-DCPN and aliphatic thiols **62** (R = *t*-Bu, C_8H_{17}) (Figure 12). Photophysical studies showed that both long-chain and sterically bulky substituents effectively inhibit aggregation. The low yield of Pn **63** (R = *t*-Bu), initially 25%,[25] served as an incentive to optimize the methodology, which allowed it to be increased to 65%.[101] During the optimization of conditions, it was discovered that at 170 °C, a mixture of benzo- and phthalonitriles (**64** and **65**) is formed.

Earlier, Wöhrle[27] demonstrated that the reaction of 4,5-DCPN with *n*-propanethiol proceeds under mild conditions, forming 4,5-bis(*n*-propylthio)phthalonitrile. Kumru and colleagues,[12] applying this methodology, synthesized Pn **63** (R = *t*-Bu) in 86% yield, confirming its advantage over the NaH/Cu_2O approach, even in its optimized version[101]. It is interesting to note that the S_NAr reaction of 4,5-DCPN with aliphatic thiols can proceed efficiently in ionic liquids.[13]

Subsequent research has focused on the influence of the nature of the alkyl substituent on the photophysical properties of macroheterocycles. Within these works, a series of phthalonitriles **63** with various substituents (R = C_2H_5 – $C_{10}H_{21}$, Bn, Bzh, Ph) were synthesized, after which the corresponding MPcs were obtained.[102,103] It was found that the length of the alkyl chain does not significantly affect the position of the Q-band in the absorption spectra. The benzyl substituent, due to the presence of a methylene bridge separating the sulfur and phenyl ring, confers spectral properties similar to those of alkyl derivatives. In contrast, the phenyl substituent directly linked to the sulfur atom exhibits pronounced electron-donating properties, causing a significant bathochromic shift of the Q-band. This effect was confirmed in study.[26]

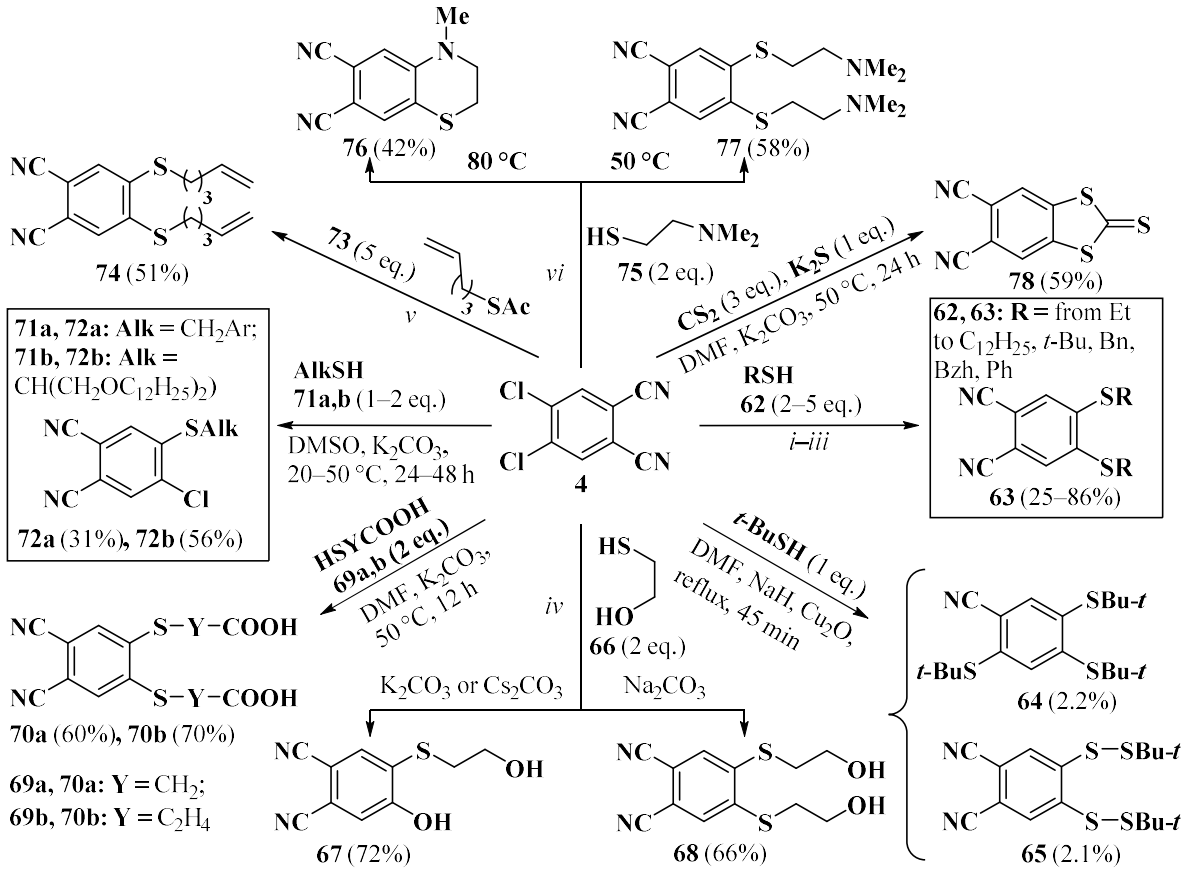
The choice of base can drastically influence the course of the S_NAr reaction (Figure 12). Thus, the reaction of substrate **4** with the *O*,*S*-binucleophile **66** in DMF in the presence of Na_2CO_3 leads to the formation of Pn **67**. However, carrying out the reaction in the presence of K_2CO_3 or Cs_2CO_3 as a base results in the unsymmetrical Pn **68** being the major product.[104,105] When using nucleophile **69b**, which differs from nucleophile **66** by the presence of a carboxylic group instead of a hydroxyl group, the S_NAr reaction proceeds smoothly in the presence of K_2CO_3.[106] Studies of the properties of the obtained complexes showed that tetrasubstituted ZnPcs can in some cases form more efficient sensitizers for solar cells than octasubstituted ones.

4-Alkylsulfanyl-5-chlorophthalonitriles are rarely reported in the literature. According to photophysical testing,[107] ZnPc based on Pn **72a** is a promising photosensitizer due to its increased organosolubility, photostability, and high Φ_Δ value. Also, liquid crystalline CuPcs stable over a wide temperature range were obtained based on chlorophthalonitrile **72b**.[108]

The authors of study[109] used ZnPc obtained from Pn **74** to modify polyvinylidene fluoride to impart semiconductor properties to the polymer. Notably, in the S_NAr reaction, the *S*-nucleophile is formed *in situ* from the *S*-acetylated thiol **73** (Figure 12).

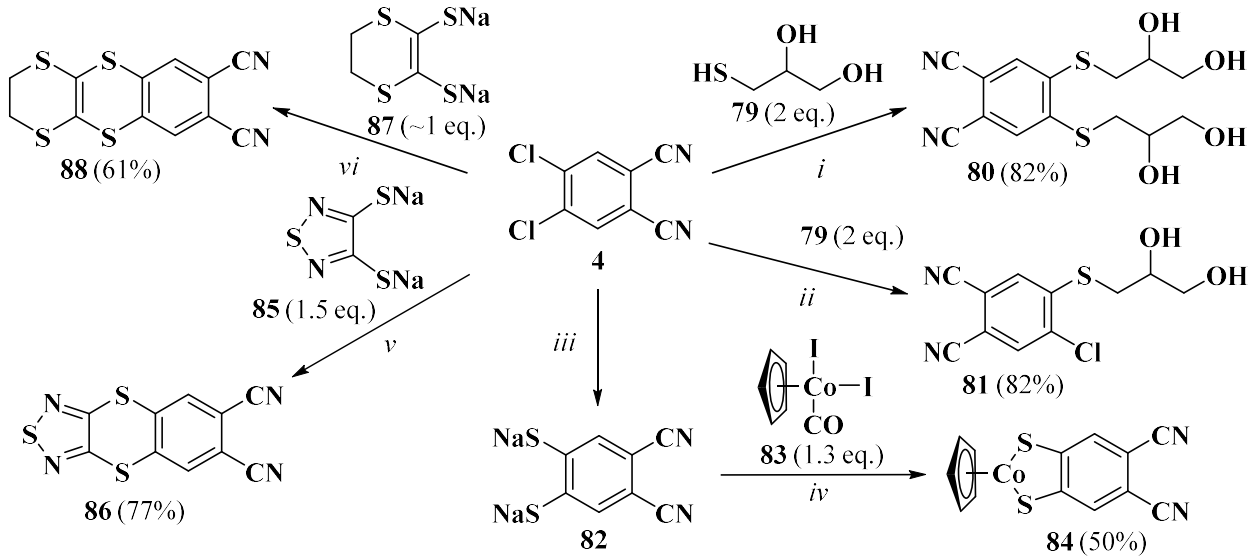
The authors of study[110] found that under mild conditions, the S_NAr reaction yields product **77**. However, when the temperature is raised to 80 °C, the *S*-nucleophile **75** used acts as a bifunctional *S*,*N*-nucleophile, resulting in the formation of benzothiazine **76** (Figure 12).

Potassium trithiocarbonate, obtained *in situ* from carbon disulfide and potassium sulfide in DMF, can be used as an *S*-nucleophile.[111] According to X-ray diffraction analysis (XRD) data, compound **78** is planar.



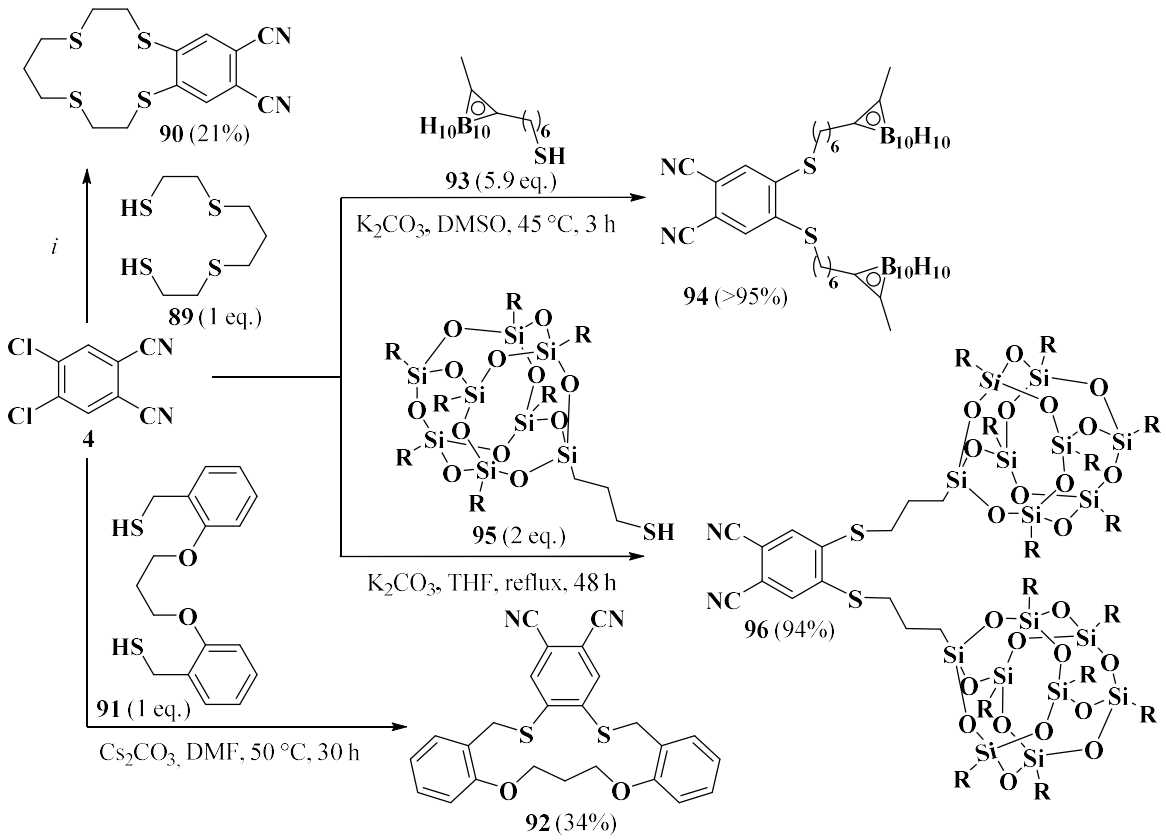
i: NaH, Cu_2O, DMF, 90 °C, 30 min; *ii*: K_2CO_3, DMF or DMSO or THF, 20–50 °C, 12–14 h; *iii*: 100 °C, K_2CO_3, Bu_4NBr, 16 h; *iv*: DMF, 40 or 50 °C, 48 h; *v*: K_2CO_3, DMSO, reflux, 24 h; *vi*: K_2CO_3, DMSO, 24 h.

Figure 12. Interaction of 4,5-DCPN with aliphatic *S*-nucleophiles.



i,*ii*: K_2CO_3, THF, reflux, 8–12 h; *iii*: $Na_2S{\bullet}9H_2O$, Me_2CO, r.t., 4 h; *iv*: Me_2CO, r.t., 20 h; *v*: DMF, r.t., 8 h; *vi*: THF, r.t., 12 h.

Figure 13. Dihydroxyalkylthiols and dithiolates as *S*-nucleophiles.



i: Na_2CO_3, DMSO, 40 °C, 54 h.

Figure 14. Preparation of macrocyclic and cluster-containing *ortho*-dicarbonitriles based on aliphatic *S*-nucleophiles.

Another example of a polyfunctional nucleophile is 3-mercapto-1,2-propanediol **79** (Figure 13). The reaction of 4,5-DCPN with it can be carried out chemoselectively with the participation of only the *S*-nucleophilic center. Both disubstitution **80** and monosubstitution **81** products are known. It was shown[112] that phthalocyanines based on the 4,5-disubstituted Pn **80** can be used for the detection of noble metals (Ag^+ and Pd^{2+} ions). The authors of study[113] obtained the chlorinated Pn **81** and a series of ionophoric metallophthalocyanines based on it. The 2,3-dihydroxypropylsulfanyl fragments not only increase the solubility of MPcs in protic solvents but can also serve as binding sites for various metal ions. Nomura *et al.*[114] developed a one-pot method for the synthesis of organometallic complexes of 4,5-benzene-1,2-dithiolate with cobalt, rhodium, and iridium. In the first stage, both chlorine atoms were replaced by sulfide ion under the action of sodium sulfide in acetone to form Pn **82**. Subsequent reaction, for example, with the η^5-pentamethylcyclopentadienyl cobalt complex **83**, led to the corresponding dithiolate complex **84**. Dithiolates have also found application as *S*-binucleophiles in the S_NAr reaction with 4,5-DCPN. Studies[115,116] utilized 1,2-dithiolates, which are derivatives of heterocycles, enabling the assembly of 1,4-dithiin-containing binuclear heterocyclic structures **86**, **88** (Figure 13).

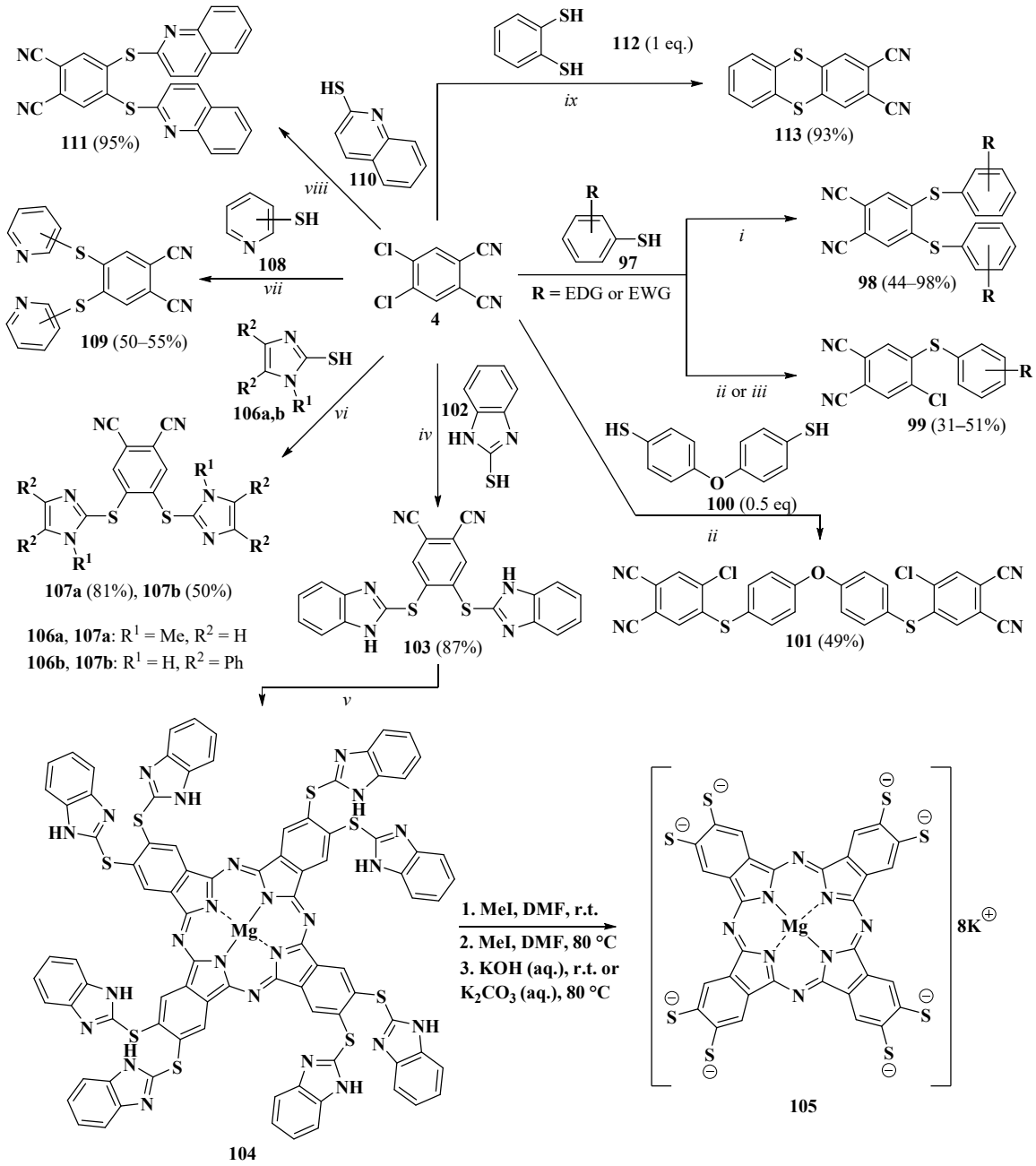
The literature also contains examples of the synthesis of macroheterocyclic compounds via the reaction of 4,5-DCPN **4** with bis-*S*-nucleophiles (Figure 14). Thus, study[117] reported the synthesis of a tetrathiadecane **90** annulated with a phthalonitrile fragment in low yield (21%). A series of phthalocyanines was obtained based on it to investigate the possibility of metal ion complexation using donor thioether bridges; however, it turned out that all these phthalocyanines are characterized by low solubility, unlike their tetraoxa- and tetraaza analogues. Turkish scientists[118] obtained a 15-membered dioxa-dithia macrocycle **92** using a benzyl-type bisthiol **91**. A zinc phthalocyanine based on Pn **92** was used to develop a quartz microbalance sensor for chloroform detection.

Italian chemists[119] synthesized a 4,5-disubstituted phthalonitrile **94** containing dicarba-*closo*-dodecaborane fragments from 4,5-DCPN. The carborane clusters were incorporated into the structure of **94** via a mercaptohexyl substituent, introduced in several steps, containing an *S*-nucleophilic center. Based on compound **94**, the corresponding octasubstituted ZnPc and its polyanionic *nido*-analogue (obtained by treating the former with cesium fluoride in EtOH/THF) were prepared. *In vitro* boron neutron capture therapy experiments revealed that the latter can accumulate boron in specific cancer cell lines, indicating potential for bimodal or multimodal anticancer therapy. Another interesting example[120] is the synthesis of Pn **96** with POSS (polyhedral oligomeric silsesquioxanes) substituents. A similar strategy was used to introduce siloxane clusters: incorporation of a mercaptoalkyl substituent containing a highly reactive thiol group capable of readily undergoing an S_NAr reaction with compound **4**. A copper phthalocyanine based on **96** is a promising candidate as an optical limiting material.

The literature notes that replacing aryloxy bridges with aryl sulfide bridges in the peripheral positions of

phthalocyanines not only preserves their key advantages – high solubility and suppression of aggregation – but also provides an additional bathochromic shift of the absorption band by ~30 nm.[26,121,122] However, replacing an oxygen bridge with a sulfide bridge can reduce the efficiency of solar cells, as observed for ZnPc obtained from Pn **98** (R = 2,6-Ph_2, Figure 15).[123] Numerous studies[26,122–124] demonstrate that, unlike the synthesis of 4,5-bis(aryloxy)phthalonitriles, the preparation of sulfur-containing analogues Pn **98** proceeds with higher yields and under milder conditions, requiring lower temperatures and shorter reaction times. It is important to note that even when using bifunctional nucleophiles, such as 2-aminothiophenol[124] or hydroxythiophenols,[121,125] the S_NAr reaction with 4,5-DCPN **4** proceeds chemoselectively at the sulfur atom.

We previously noted that the solubility of phthalocyanine derivatives strongly depends on their degree of substitution. Thus, tetrasubstituted Pcs demonstrate better solubility than octasubstituted Pcs with the identical substituents (using 4- and 4,5-disubstituted Pns obtained from thiophenol **97** (R = 2,4-Cl_2, Figure 15) as phthalocyanogens). The authors of study[6] explain this empirical fact by the presence or absence of randomers.



i: 2–3 eq. **97**, K_2CO_3, DMF or DMSO or THF, 20–100°C, 1.5–48 h; *ii*: 1 eq. **97** (R = 2-COOH, 4-NHAc, 4-Cl), K_2CO_3, DMF/H_2O, 70–90 °C, 2–3 h; *iii*: 2 eq. **97** (R = 2-NH_2), Cs_2CO_3, THF, reflux, 12 h; *iv*: K_2CO_3, DMF, r.t., 18 h; *v*: $Mg(OEt)_2$, 1-octanol, 160 °C, 10 min; *vi*: K_2CO_3, DMF, 80 °C, 24 h (a); Na_2CO_3, DMSO, r.t., 7 days (b); *vii*: K_2CO_3, DMF, r.t., 3.5–16 h; *viii*: K_2CO_3, DMF, r.t., 26 h; *ix*: Na_2CO_3, DMF, 50 °C, 24 h (glass tube)

Figure 15. Interaction of 4,5-DCPN with aromatic *S*-nucleophiles.

Study[122] is a continuation of the investigation into columnar mesomorphism. During the research, CuPcs were synthesized from phthalocyanogens **98** (R = 2-, 3- or 3,4-OMe), and their physicochemical characteristics were studied. It was found that all obtained macrocycles exhibit a columnar mesophase only at high temperatures in an inert atmosphere. Based on the aforementioned Pn **98** (R = 3,4-OMe), the researchers in study[126] synthesized MPcs with tunable properties, highlighting their potential in electrochemistry and catalysis. Thus, manganese, iron, and cobalt complexes can be used as cathode materials in fuel cells and metal-air batteries, replacing expensive platinum catalysts.

Study[125] discovered the phenomenon of aggregation-induced emission in phthalonitriles **98** (R = 2-OH, R = 3-OH and R = 4-OH). As the authors note, all compounds exhibit emission from blue to blue-green when excited by UV light (λ = 365 nm).

Article[127] describes not only the synthesis of new fluorinated MPcs (M = Co, Zn) containing 4-(trifluoromethoxy)thiophenyl groups but also the results of investigating their biological activity, including antioxidant activity (ability to chelate iron ions). It was found that MPcs obtained from Pn **98** (R = 4-OCF_3) exhibit reduced aggregation tendency, high organosolubility, and positive antibacterial activity against a number of pathogenic microorganisms, including both Gram-positive and Gram-negative bacteria.

Information on the preparation of unsymmetrical octasubstituted phthalocyanines from 4,5-DCPN containing aryl sulfanyl substituents and chlorine atoms simultaneously is practically absent in the literature, which is likely due to the lack of suitable phthalocyanogens. It was first reported in 2002[128] that the S_NAr reaction outcome in the synthesis of 4-arylsulfanyl-5-chlorophthalonitrile depends on the base used. Thus, the monosubstitution product **51** (R = 2-NH_2) was synthesized in 39% yield by conducting the S_NAr reaction in THF in the presence of Cs_2CO_3 (the product was isolated by separating the reaction mixture using preparative HPLC). In our DMF-water system, we synthesized analogous derivatives **51** (R = 2-COOH, 4-NHAc, 4-Cl) and demonstrated the use of the bifunctional *S*-nucleophile **100** in the reaction with 4,5-DCPN **4** for the synthesis of diphthalonitrile **101** (Figure 15).

Study[129] noted that due to the electron-withdrawing influence of chlorine, the oxidation potential of MPcs shifts to a more positive region, enhancing their catalytic activity in oxygen reduction reactions. Unlike less stable bromine-substituted analogues, chlorinated Pcs demonstrate high chemical stability and increased electrical conductivity. Hybrid systems combining the electron-withdrawing chlorine with electron-donating aryl sulfanyl substituents are particularly interesting. Using the synthesis of MPcs (M = AcOMn, 2H) from Pn **99** (R = 4-OCH_3) as an example, it was shown that such a combination creates a balanced electron density distribution, enabling fine control over optical and redox properties. The authors emphasize that such hybrid structures, containing opposing substituents within a single aromatic core, form a new promising class of phthalocyanine derivatives with tunable spectral and redox properties.

Heterocyclic compounds containing a sulfanyl group as a substituent are commonly employed as *S*-nucleophiles. The authors of research[130] required the octathiolated phthalocyanine complex $K_8[S_8PcMg]$ **105** for coordination studies. To obtain it *in situ*, they developed a strategy based on the synthesis of an octasubstituted phthalocyanine **104** containing 1-*H*-benzimidazol-2-ylsulfanyl residues, its subsequent exhaustive methylation (carried out in two stages to reduce byproducts), and cleavage of the benzimidazolium groups under the action of a base. It should be noted that the key precursor in the synthesis of **105** was the disubstituted Pn **103**, which is readily available from the reaction of 4,5-DCPN with 2-mercaptobenzimidazole **102** (Figure 15).

There are also examples of non-benzannulated 2-mercaptoimidazoles (**106a,b**) being used as *S*-nucleophiles. The reaction of 4,5-DCPN **4** with compound **106b**, like the reaction with benzimidazole **102**, proceeds chemoselectively with the participation of only the *S*-nucleophilic center.

A study[131] utilized 2-mercaptoquinoline **110** to synthesize the corresponding 4,5-bis(heteroarylsulfanyl)-phthalonitrile, while articles[132, 133] used isomeric 2- and 4-mer-captopyridines **108**. The presence of a pyridine nitrogen atom in MPcs based on compounds **109** allowed the synthesis of quaternized water-soluble complexes (using MeI or Me_2SO_4 as alkylating agents, Figure 15).

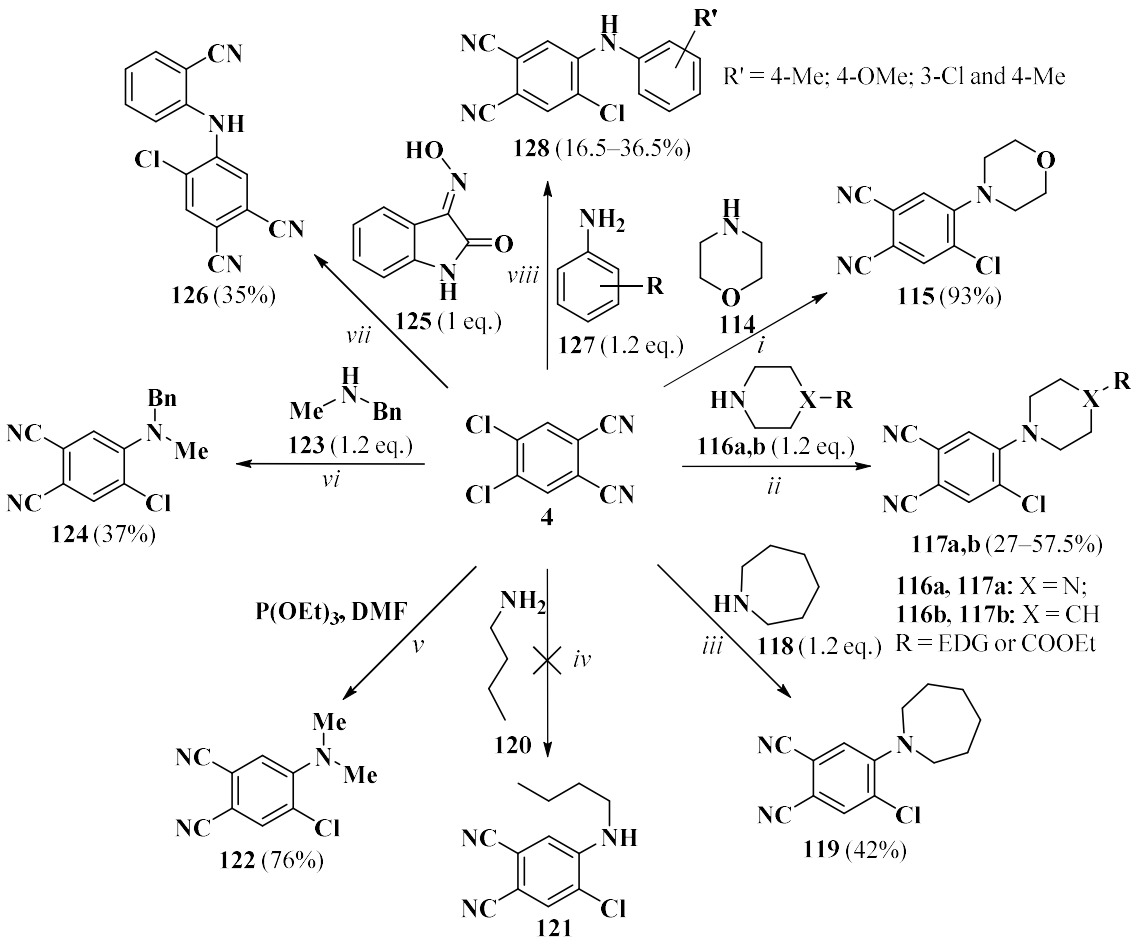
Researchers in study[134] demonstrated the possibility of obtaining a thianthrene system based on 4,5-dichlorophthalonitrile by using benzene-1,2-dithiol **112** as a bis-*S*-nucleophile (Figure 15). The resulting compound **113** exhibited fluorescence both in solution and in the solid state. Compared to the oxathiane analogue (compound **176**), a bathochromic shift of the absorption maximum was observed. This indicates a conjugation effect, which can be explained by the lower electronegativity and higher π-polarizability of sulfur compared to oxygen.

Reactions with *N*-Nucleophiles

Previous work has shown that 4,5-dichlorophthalonitrile reacts with morpholine **114** in an inert atmosphere at room temperature[135] (Figure 16). In this case, compound **114** acts simultaneously as a nucleophilic reagent, base, and solvent. Recently, we obtained a series of 4-piperidino- and 4-piperazino-5-chlorophthalonitriles **117a,b**;[28] however, in the reaction, we used 1.2 equivalents of the *N*-nucleophilic reagent, while the roles of base and solvent were performed by triethylamine or potassium carbonate and DMF, respectively. Similarly, Pn **119** was obtained by reacting **4** with azepane **118**. All these examples relate to the use of secondary alicyclic amines in the reaction with 4,5-dichlorophthalonitrile.

In the case of primary *n*-butylamine **120**, as the authors of study[135] claim, the formation of a complex and inseparable mixture of seven compounds occurs. It should be noted that an attempt to carry out the reaction between compounds **4** and **120** under Buchwald-Hartwig reaction conditions also failed to yield phthalonitrile **121** (Figure 16).

Research[14] demonstrated that 4-(dimethylamino)-5-chlorophthalonitrile **122** can be obtained in good yield by generating dimethylamine through the decomposition of DMF under the action of triethyl phosphite under harsh conditions upon heating in a glass tube at 160 °C. The use of alkali metal carbonates as a base instead of triethyl phosphite proved to be a much less effective.



i: r.t., 24 h; *ii*: Et_3N or K_2CO_3, DMF, 100-110 °C, 1.5-6 h; *iii*: K_2CO_3, DMF, 90 °C, 4 h; *iv*: r.t., 24 h; *v*: 160 °C, 6 h (glass tube); *vi*: K_2CO_3, DMF, 120 °C, 1.5 h; *vii*: K_2CO_3, DMF, 95 °C, 24 h; *viii*: Bu_3N, DMF, 140 °C, 8.5–26 h.

Figure 16. Interaction of 4,5-DCPN with various *N*-nucleophiles.

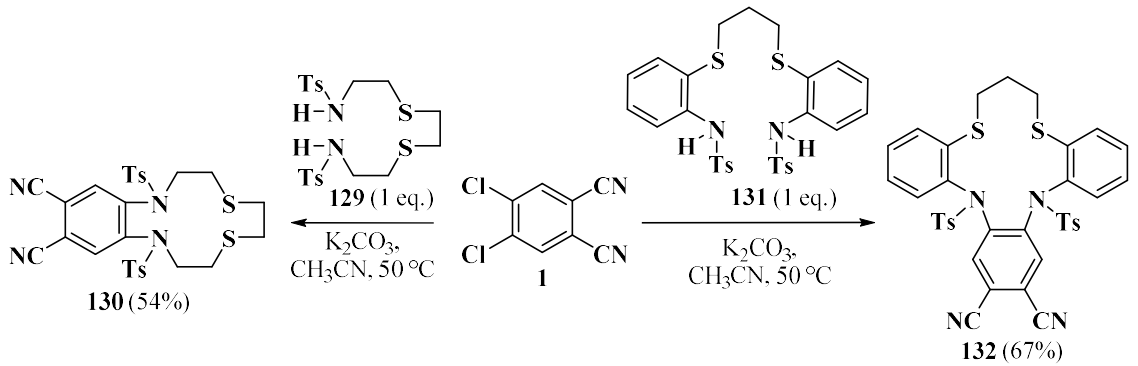


Figure 17. Interaction of 4,5-DCPN with *N*-binucleophiles.

The reaction of 4,5-DCPN with a benzyl-type amine **123** proceeds with low yields upon heating in DMF in the presence of potassium carbonate.[28] The S_NAr reaction between 4,5-DCPN **4** and isatin-3-oxime **125** was shown to proceed via an unexpected rearrangement, leading to the formation of diphenylamine **126**[76] (Figure 16).

We were the first to demonstrate the possibility of direct substitution of the chlorine atom in 4,5-dichlorophthalonitrile with an arylamino fragment under the action of arylamines **127** as *N*-nucleophiles. However, the reaction could only be carried out under harsh conditions with multihour heating at 140 °C with tributylamine in DMF.[28]

Turkish scientists[136] obtained a phthalonitrile **130** annulated with a 12-membered diazadithiamacrocycle in 54% yield (Figure 17). The reaction proceeded in dry acetonitrile medium in the presence of anhydrous potassium carbonate

as a templating agent. The authors suggest that compound **130**, as well as metalloporphyrazine complexes based on it, can find application for the selective extraction of alkali, alkaline earth, and transition metal cations. Study[137] describes a 13-membered analogue **132**, containing two additional annulated benzene rings.

The literature contains a number of examples of the interaction of 4,5-dichlorophthalonitrile with *N*-nucleophiles of a heterocyclic nature (Figure 18). Thus, study[138] describes the reaction of 4,5-DCPN **4** with unsubstituted imidazole **133a**. The disubstitution product **134a** was used to obtain an A_3B type porphyrazine, based on which, through sequential quaternization and complexation with $Pd(OAc)_2$, a new catalyst for the Suzuki reaction was developed. Research[139] reported the synthesis of 4,5-dipyrazolylphthalonitriles **134b** functionalized at the 3-position. The activated aromatic nucleophilic substitution reaction was carried out in the complete absence of moisture in absolute DMSO under an inert atmosphere in the presence of K_2CO_3/DIPEA as a base. It should be noted that the arylation of pyrazoles **133b** proceeded regioselectively at the less sterically hindered *N*-1 nitrogen atom.

According to other researches[140,141] 4,5-dicarbazolylphthalonitriles **134c** were synthesized in 75–80% yields using cesium fluoride as a base (Figure 18). It is likely that during the reaction, 4-fluoro-5-chloro- and 4,5-difluorophthalonitriles are formed *in situ*[142], which are more reactive than 4,5-DCPN **4**. Thus, CsF in this case acts not only as a base but also as a nucleophilic catalyst. Phthalocyanines obtained from Pn **134c** possess not only excellent photophysical (Φ_Δ reaches 0.81) but also electrochemical properties. Carbazole-containing phthalocyanines are of particular interest for various applications, such as PDT and solar cells. For further exploration of this direction, we recommend referring to a recently published review[143].

Heterocyclic *N*-nucleophiles such as triazolones can also be used.[144] The authors compared traditional S_NAr methodology with the microwave method; the use of the latter not only reduces the reaction time from 48 hours to 10 min but also increases the yield of **134d** from 42% to 75%.

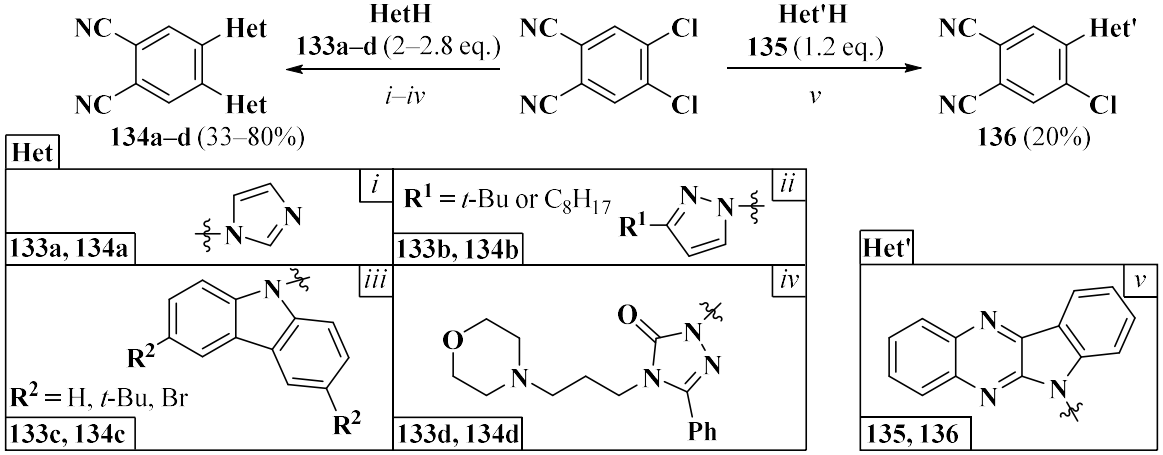
The examples described above illustrate the possibility of obtaining symmetrical 4,5-disubstituted derivatives based on *N*-containing heteroaromatic compounds and substrate **4**. However, the synthesis of the corresponding unsymmetrical 4-*R*-5-chlorophthalonitriles represents a much more challenging task. Previously, we[28] obtained phthalonitrile **136** based on **4** and 6*H*-indolo[2,3-*b*]quinoxaline **135** (Figure 18). This reaction proceeded in only 20% yield using a 1:1.2 reagent ratio and K_2CO_3 as a base.

Non-symmetric substitution

Recently, researchers have shown significant interest in unsymmetrical phthalocyanines containing different functional substituents in the isoindole units. Such compounds find applications in nonlinear optics, photodynamic therapy, and are interesting materials for Langmuir-Blodgett films, highly ordered ("stacked") polymers, and liquid crystals. However, the synthesis and isolation of such compounds remain a challenging problem for synthetic chemists. This subsection covers the literature on the synthesis of 4,5-disubstituted unsymmetrical phthalonitriles obtained using 4,5-dichlorophthalonitrile.

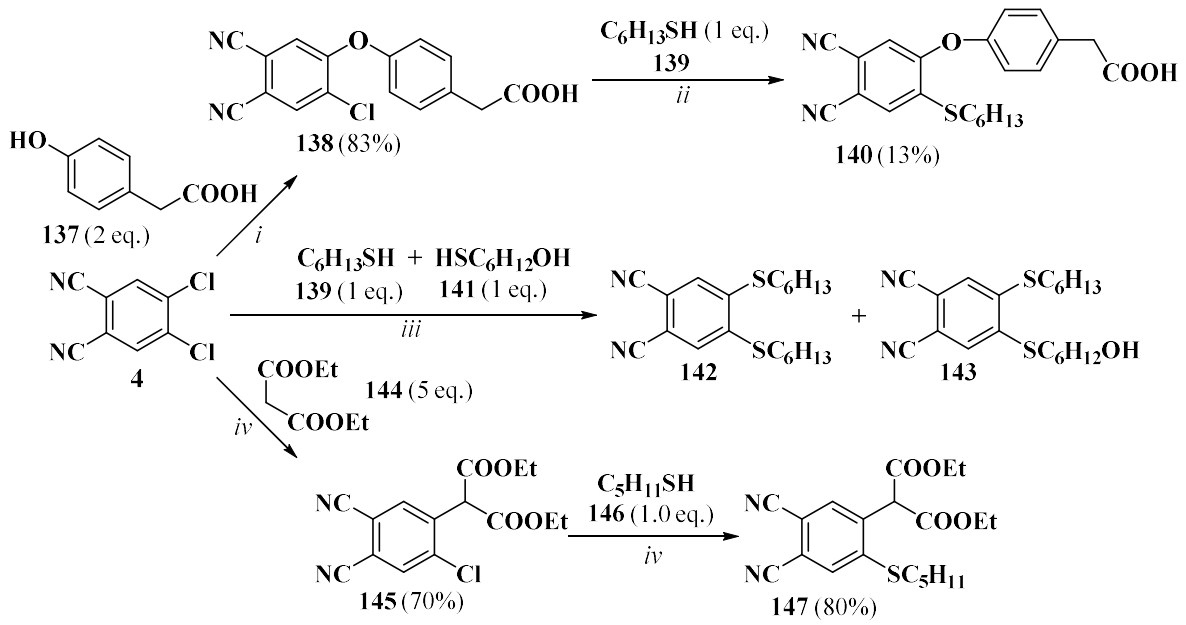
Chlorinated phthalonitrile **138** was obtained in study[145] via an S_NAr reaction between 4,5-DCPN **4** and a twofold excess of 4-hydroxyphenylacetic acid **137** in the presence of K_2CO_3 as a base (Figure 19). The authors noted that using the weaker base Na_2CO_3 in this reaction results in a mixture of mono- and disubstitution products. The remaining chlorine atom in compound **138** was substituted using *n*-hexanethiol at room temperature over one week with a 13% yield.

Turkish chemists[5] developed and experimentally implemented the synthesis of unsymmetrical phthalonitrile **143** via a one-pot method by introducing 4,5-DCPN **4** into a mixture of *S*-nucleophiles **139** and **140** (4,5-DCPN:**139**:**140** = 1:1:1). Based on this, an A_3B-type phthalocyanine was obtained through statistical tetramerization with 4,5-bis(*n*-hexylthio)phthalonitrile.



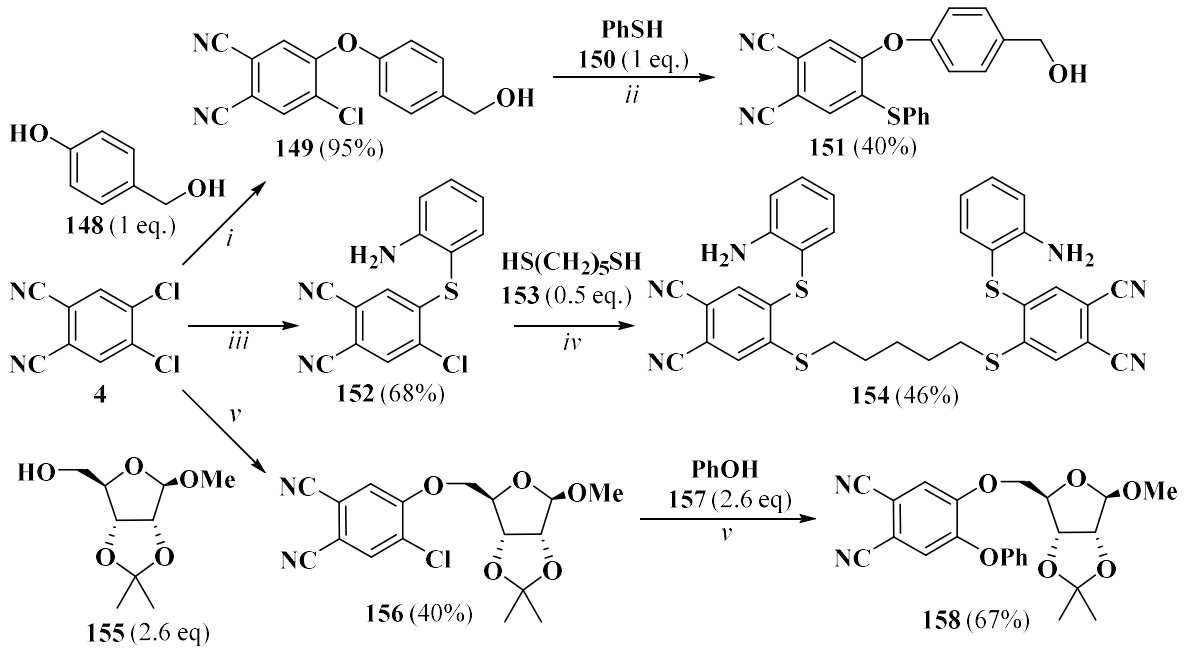
i: K_2CO_3, DMF, r.t.; *ii*: K_2CO_3/DIPEA, absolute DMSO, protection from light, 90–110 °C, 2h; *iii*: CsF, DMF, 75–90 °C, 24 h; *iv*: K_2CO_3, DMF, 60 °C, 48 h or 800 W, 10 min; *v*: K_2CO_3, DMF, 80 °C, 19.5 h.

Figure 18. Synthesis of *N*-heterylphthalonitriles based on 4,5-DCPN.



i: K_2CO_3, DMF, r.t., 144 h; *ii*: K_2CO_3, DMF, r.t., 168 h; *iii*: K_2CO_3, DMF, r.t., 48 h; *iv*: K_2CO_3, DMF, 50 °C, 48 h

Figure 19. Synthesis of unsymmetrical 4,5-disubstituted phthalonitriles using aliphatic *S*-nucleophiles.



i: K_2CO_3, acetone, reflux, 24h; *ii*: Et_3N, acetone, r.t., 24 h; *iii*: K_2CO_3, THF, 70 °C, 4 h; *iv*: K_2CO_3, THF, reflux, 24 h; *v*: K_2CO_3, DMSO, 90 °C, 3 h.

Figure 20. Synthesis of unsymmetrical 4,5-disubstituted phthalonitriles.

Malonate ester **144** can act as a *C*-nucleophile in the reaction with 4,5-DCPN **4** under standard S_NAr conditions due to its enhanced C–H acidity.[146] All attempts to substitute the second chlorine atom in compound **145** by increasing the excess amount of *C*-nucleophile, reaction time, and temperature were unsuccessful. The second chlorine atom was successfully substituted using an aliphatic *S*-nucleophile **146**.

Article[147] describes a method for obtaining Pn **151**, containing a hydrophilic hydroxymethyl phenoxy group and a hydrophobic phenylsulfanyl fragment, conferring amphiphilicity to this phthalonitrile (Figure 19). Such a combination of substituents allows for the modulation of solubility and biological activity of phthalocyanines. Unfortunately for the authors, all attempts to isolate an individual product from the statistical cyclization of compound **151** and 4,5-bis(phenylsulfanyl)phthalonitrile were unsuccessful.

Article[148] is devoted to the synthesis and study of a new bisphthalonitrile **154**, obtained from pentanedithiol **153**

(Figure 20), and its polymeric phthalocyanine complexes. The polymeric ZnPc was found to be effective for the extraction of heavy metals and is particularly effective in recovering Ag^+ ions. The authors also propose a modified version of the synthesis method for chlorophthalonitrile **152**, increasing the yield from 39% to 68%.

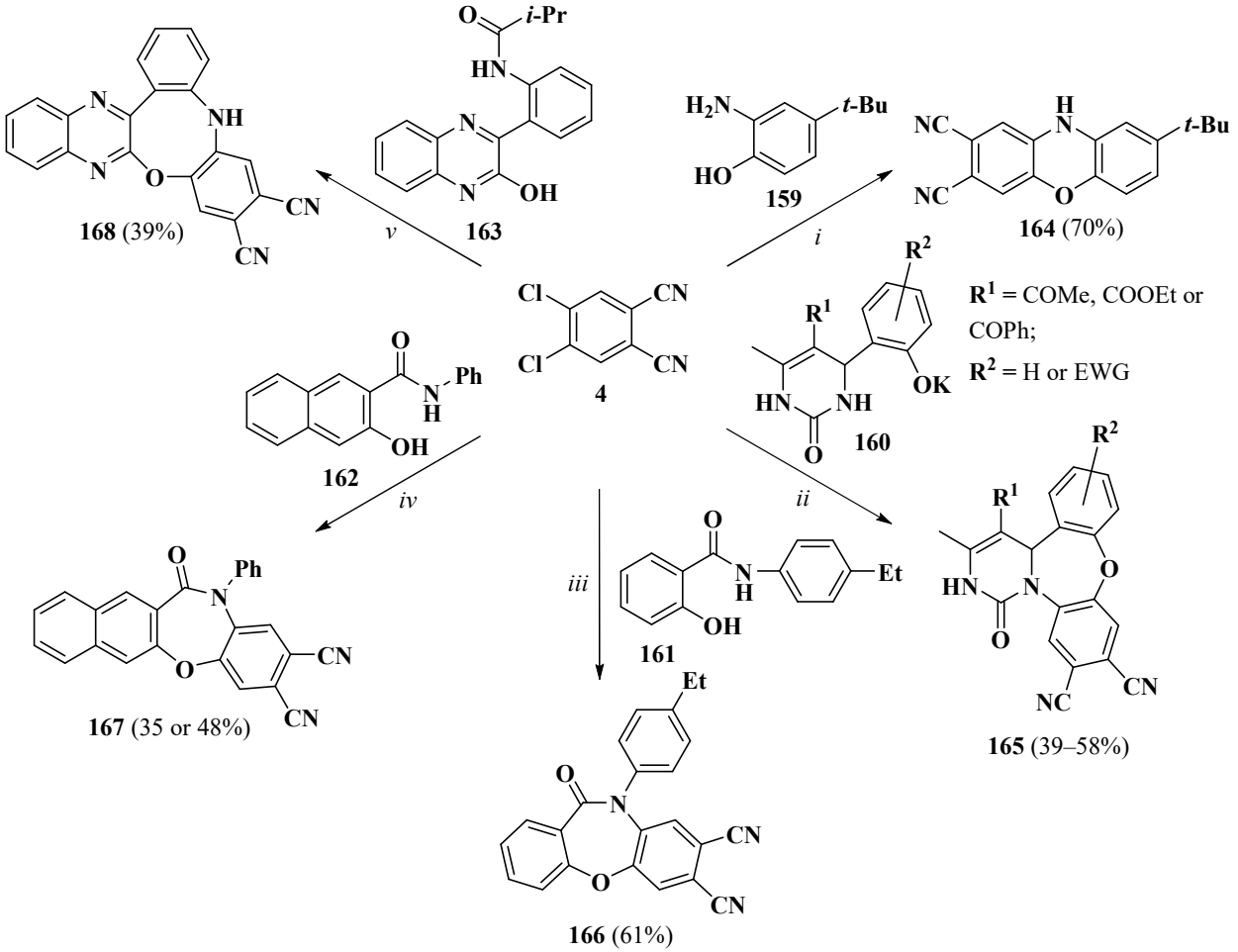
Based on 4,5-DCPN **4** with sequential use of different types of *O*-nucleophiles in the S_NAr reaction, a hybrid unsymmetrical **158** was obtained, combining a polar carbohydrate fragment of ribose and a hydrophobic phenoxy group.[149] The synthesis of this compound highlights the advantage of unsymmetrical systems over symmetrical ones, which lies in the possibility of fine-tuning properties through diverse substituents. It is noteworthy that at the stage of obtaining chlorophthalonitrile **156**, the authors used an excess of ribose **155** (Figure 20); however, due to steric hindrance, the disubstitution product could not be obtained.

Currently, there is no full-fledged one-pot method for the synthesis of 4,5-disubstituted phthalonitriles of unsymmetrical structure. An alternative approach to the synthesis of these compounds is to replace the substrate with 4,5-BNPN **5**, based on which a wider range of such phthalonitriles can be created. Nevertheless, the mono-substitution product will still have to be isolated from the reaction mixture. In other words, replacing the substrate helps expand the assortment of unsymmetrical phthalonitriles, but the problem of the two-stage synthesis remains unresolved.

Heterocycle annulation

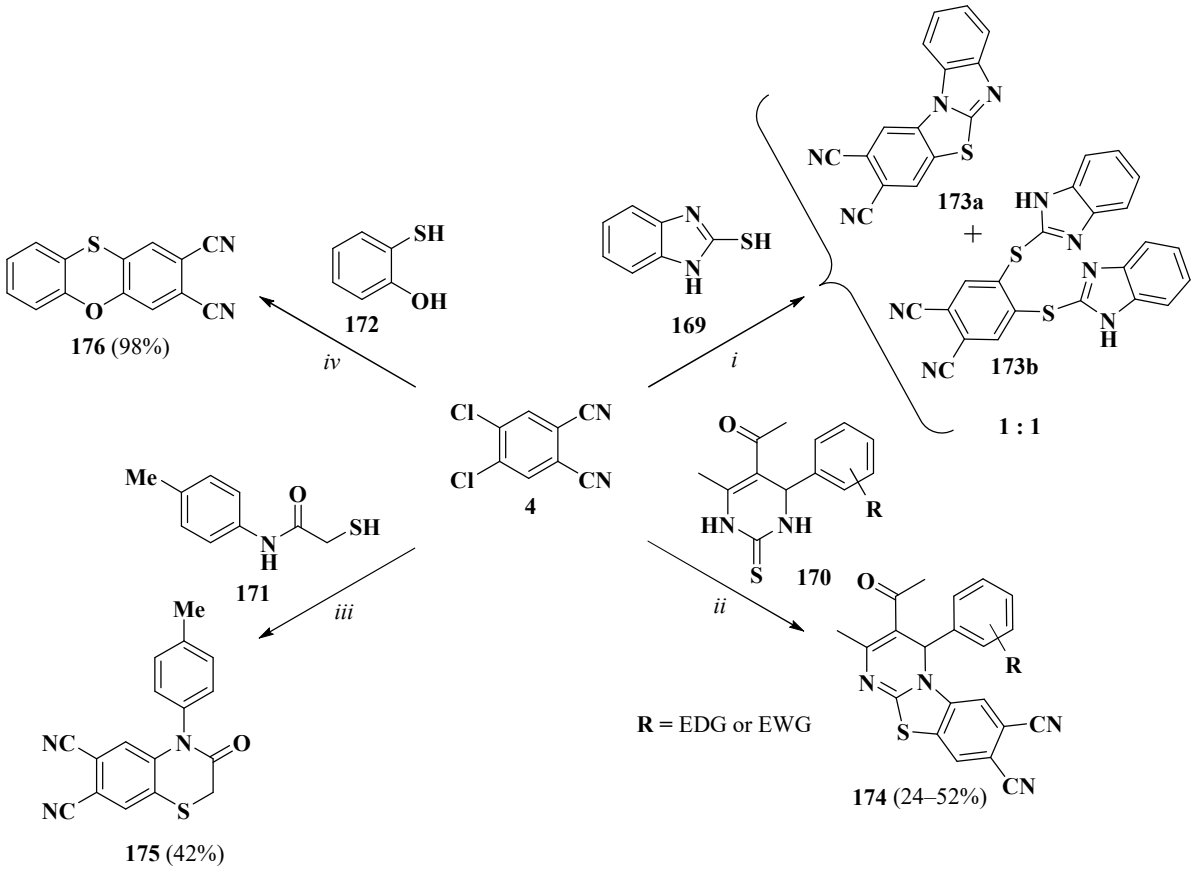
This section will discuss the synthesis of heterocyclic compounds containing two different heteroatoms using 4,5-dichlorophthalonitrile as a key substrate.

The synthesis of heterocycles with identical heteroatoms (O, S, or N) was previously described in the sections: *O*-nucleophiles, *S*-nucleophiles, and *N*-nucleophiles, respectively. Figure 21 provides examples of syntheses of heterocycles based on 4,5-DCPN **4** and *O*,*N*-binucleophiles **159–163**. In our studies,[76,150] derivatives of oxazine **164**, oxazepine **165**, **166**, and oxazocine **168** were obtained. Additionally, oxazepine **167** is known in the literature.[151] It should be noted that the presence of a heterocyclic fragment in the initial nucleophilic reagent enables the assembly of binuclear heterocyclic systems. Thus, the use of hydroxyl-containing products of the Biginelli reaction in the S_NAr reaction provides access to pyrimido[1,6-*d*][1,4]oxazepines **165**, which are promising from the perspective of pharmaceutical chemistry. Meanwhile, the reaction with 2-hydroxy-3-(*o*-acylaminophenyl)quinoxaline leads to the



i: K_2CO_3, DMF, 90 °C, 2.5 h; *ii*: K_2CO_3, DMF, 80–90 °C, 1.5–3 h; *iii*: K_2CO_3, DMF, 80 °C, 4 h; *iv*: K_2CO_3, DMF, 75 °C, 48 h or K_2CO_3, microwave 350 W, 10 min; *v*: K_2CO_3, DMF, 90°C, 13.5 h.

Figure 21. S_NAr Reaction between 4,5-DCPN and *O*,*N*-binucleophiles.



i: K_2CO_3, DMF, 80 °C, 28 h; *ii*: K_2CO_3, DMF, 70–90 °C, 3–7.5 h; *iii*: K_2CO_3, DMF, 90 °C, 4 h; *iv*: K_2CO_3, DMF, 50 °C, 24 h (glass tube).

Figure 22. S_NAr Reaction between 4,5-DCPN and *O*,*S* or *N*,*S*-binucleophiles.

formation of pyrazino[2,3-*g*][1,4]oxazocine **168**. Typically, the synthesis of heterocyclic compounds based on 4,5-DCPN **4** employs a standard S_NAr reaction protocol (prolonged heating with K_2CO_3 in DMF), with yields rarely exceeding 50%. However, the authors of study[151] demonstrated that the use of microwave irradiation not only increases the yield of oxazepine **167** from 35% to 48% but also reduces the reaction time from 48 h to 10 min.

Figure 22 illustrates the reactions of 4,5-dichlorophthalonitrile **4** with bifunctional *N*,*S*- and *O*,*S*-nucleophiles **169–172**. We have shown[76] that the reaction of compound **4** with 2-mercaptobenzimidazole **169** proceeds non-selectively, yielding a mixture of imidazo[2,1-*b*]thiazole **173a** and 4,5-disubstituted phthalonitrile **173b**. This outcome results from the competition between intramolecular cyclization and substitution of the remaining chlorine atom by the *S*-nucleophilic center of a second molecule of **169**. In contrast, the reaction of 4,5-DCPN with Biginelli reaction products proceeds smoothly to form benzo[4,5]thiazolo[3,2-*a*]pyrimidines **174**, albeit with modest yields.[152] Examples of 1,2-bifunctional nucleophiles include thioglycolic acid amide **171** and 2-mercaptophenol **172**. Their reactions with 4,5-DCPN yield dicyano-containing derivatives of benzothiazine **175**[76] and phenoxathiin **176**,[134] respectively.

Miscellaneous transformations

As previously demonstrated, an S_NAr reaction can create a C–C bond (Figure 19, compound **145**). Figure 23 demonstrates alternative approaches for forming carbon-carbon bonds.

The cyano groups in 4,5-DCPN can exhibit reactivity not only in templated cyclotetramerization but also in [3+2]-cycloaddition reactions. For example, the corresponding arylimidazole **178** was obtained from compound **4.**[154] In this case, an unstabilized azomethine ylide, generated *in situ* from hemiaminal **177**, was used as the dipolar reagent, and one of the cyano groups of 4,5-DCPN acted as the dipolarophile. The initially formed imidazoline was oxidized under mild conditions using $KMnO_4$ on silica gel. Study[155] reported the synthesis of phthalonitrile functionalized with phosphonate groups **180**. The cross-coupling of 4,5-DCPN **4** with triethyl phosphite **179** was catalyzed by tetrakis(triphenylphosphine)-palladium under harsh conditions, heating to 230 °C in a microwave reactor under pressure of approximately 7 atmospheres. Japanese scientists demonstrated the possibility of substituting chlorine atoms in 4,5-dichlorophthalonitrile **4** with diphenylphosphino groups using diphenyltrimethylsilylphosphine **181.**[156] Both mono-substitution **182** and di-substitution **183** products were obtained.

Suzuki-Miyaura[22,23,157,158] and Sonogashira[159–162] reactions are most commonly used to form C–C bonds. Notably, the presence of cyano groups in 4,5-dichlorophthalonitrile **4** activates this compound for oxidative addition, enabling the reaction to proceed without additional specialized ligands.[23] 4,5-Diarylphthalonitriles **184** are typically synthesized with a reagent ratio (compound **4** and arylboronic acid) of 1:2,[157,158] although in some cases, a four-fold[22] or even six-fold[23] excess of arylboronic acid is required. 4-Alkynyl-5-chloro- and 4,5-dialkynylphthalonitriles (compounds **186** and **187**) can be easily obtained under standard Sonogashira reaction conditions with yields of 25–52%. The synthesis of the latter requires reagent ratios of 1:4 or 1:6. Study[94] provides an example illustrating the low efficiency of the Negishi reaction for modifying substrate **4**. Thus, monosubstitution **189** and disubstitution **190** products were obtained in only 11% and 28% yields, respectively, after chromatographic separation.

Conclusions

The analysis of literature data unequivocally confirms that 4,5-dichlorophthalonitrile has firmly established itself as a key building block and universal precursor in the synthetic chemistry of phthalocyanines. Its unique reactivity, primarily manifested in aromatic nucleophilic substitution reactions with diverse *O*-, *S*-, and *N*-nucleophiles, as well as in cross-coupling reactions, provides researchers with a powerful tool for creating extensive libraries of 4,5-disubstituted phthalonitriles. This approach is particularly valuable for synthesizing a wide range of heterocyclic systems annulated with the phthalonitrile fragment. The introduced substituents enable fine-tuning of the physicochemical properties of the resulting macrocycles – phthalocyanines and subphthalocyanines.

Thus, this review not only demonstrates the vast synthetic potential of 4,5-dichlorophthalonitrile but also serves as a guide for researchers in selecting the most efficient and selective strategies to obtain precursors for macroheterocycles with tailored architectures. This, in turn, paves the way for the targeted design of new functional materials with applications in materials science, medicine, catalysis, and other advanced fields of science and technology.

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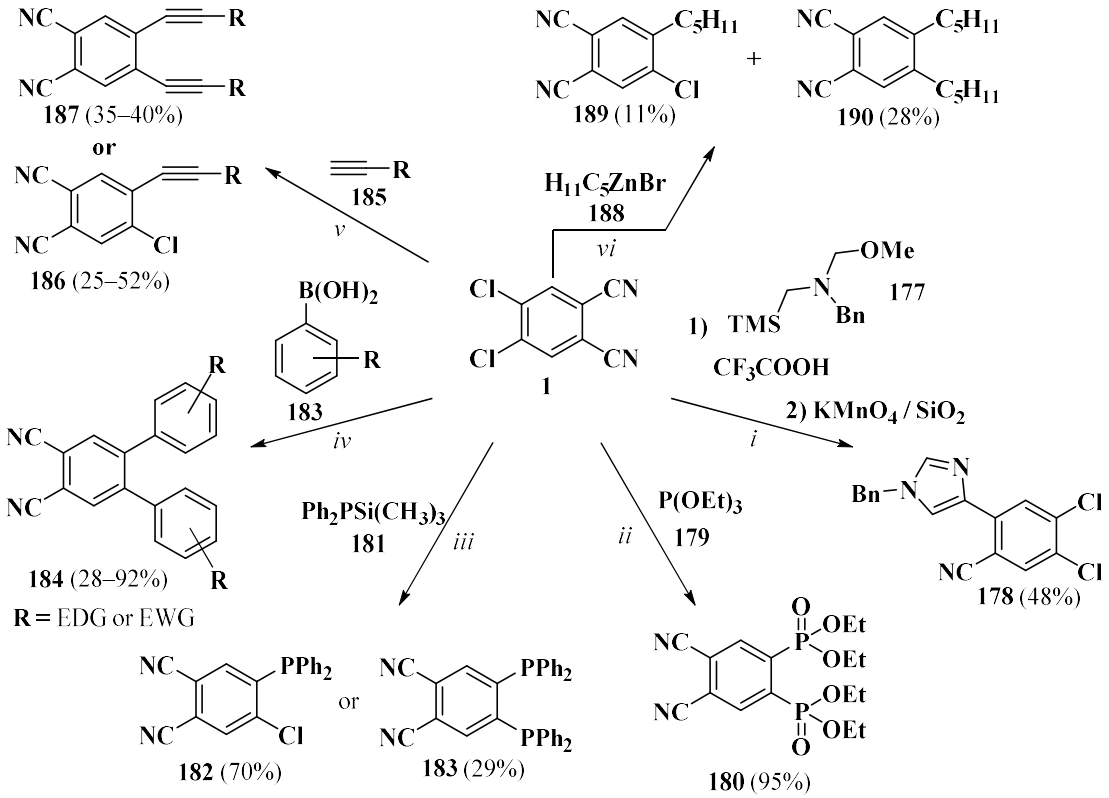

i: 1) 0 °C to r.t., 16 h; 2) r.t. 16 h; *ii*: $Pd(PPh_3)_4$, 230 ºC, 100 PSI, 120 W, 45 min; *iii*: 1) toluene, 110 °C, 48 h (for **115**); 2) toluene, 110 °C, 120 h (for **116**); *iv*: $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$, K_3PO_4 or NaBr, K_2CO_3, 1,4-dioxane, 90 °C, ; *v*: $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 90 °C, 24-48 h (for disubstitution); $Pd(PPh_3)_2Cl_2$, Et_3N–THF, CuI, 80 °C, 12 h (for monosubstitution); *vi*: $Ni(PPh_3)_2Cl_2$, PPh_3, LiCl, $H_{11}C_5ZnBr$, r.t.

Figure 23. Less common reactions involving 4,5-DCPN.

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