Synthetic approaches to asymmetric phthalocyanines and their analogues

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Dedicated to Professor Evgeny A. Luk'yanets on the occasion of his 75th anniversary and to Professor Özer Bekaroğlu on the occasion of his 80th anniversary

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Abstract
This review summarizes synthetic strategies for the preparation of asymmetric phthalocyanines and their analogues. Cross-condensation between two phthalonitrile components, cross-condensation between one phthalonitrile and one non-nitrile component, targeted synthesis of AABB-type compounds, the subphthalocyanine ring-expansion method, as well as post-modification approaches on pre-formed symmetric and asymmetric systems, are discussed. Methodologies for targeted preparation of specific types of asymmetric phthalocyanines and their analogues are also briefly overviewed.

Keywords: Asymmetric phthalocyanines and their analogues, subphthalocyanine, substituted phthalonitriles, synthesis

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1. Introduction

Although the formation of a deep blue-colored phthalocyanine macrocycle was reported about hundred years ago, comprehensive investigation of this class of compound did not start until the 1930s, when Linstead and co-workers conducted extensive chemical and crystallographic studies on these fascinating macrocycles.[1-7] Initially after their discovery, phthalocyanines were predominantly used as pigments and dyes in the textile and paper industries because of their chemical, photochemical, and thermal stabilities.[8,9] In more recent decades the chemistry of substituted phthalocyanines has undergone tremendous growth,[10-12] and, in addition to traditional applications, substituted and unsubstituted phthalocyanines have found potential applications in industrial catalysis,[13-18] photosensitizers for photodynamic cancer therapy,[16,19-26] markers for bio-imaging,[27,28] antibacterial composites,[29-32] materials for ink-jet printing,[33] chemical sensors,[34-37] semiconductors,[38,39] functional polymers and liquid crystals,[40-43] light-harvesting modules for dye-sensitized solar cells and organic photovoltaics,[44-51] nanotechnology,[52-56] and non-linear optics.[57-63]

Many of these new applications require pinpoint modification of the phthalocyanine macrocycle, which is achieved in asymmetric phthalocyanine analogues (Figure 1). For instance, in order to achieve selective surface functionalization, one needs to design an asymmetric phthalocyanine with a single anchor group, while preparation of nano-scale supramolecular assemblies demands disubstituted phthalocyanine platforms. Similarly, asymmetric-shaped phthalocyanines are desired for ideal Langmuir-Blodgett film formation, while targeting non-linear optic properties in phthalocyanine require preparation of push-pull types of asymmetric macrocycles.[64-69] In order to satisfy this demand, over the last few decades numerous research groups have made great strides in the preparation of asymmetric phthalocyanines and their analogues including triazole-, thiadiazole-, and hemiporphyrazines.[64-74]

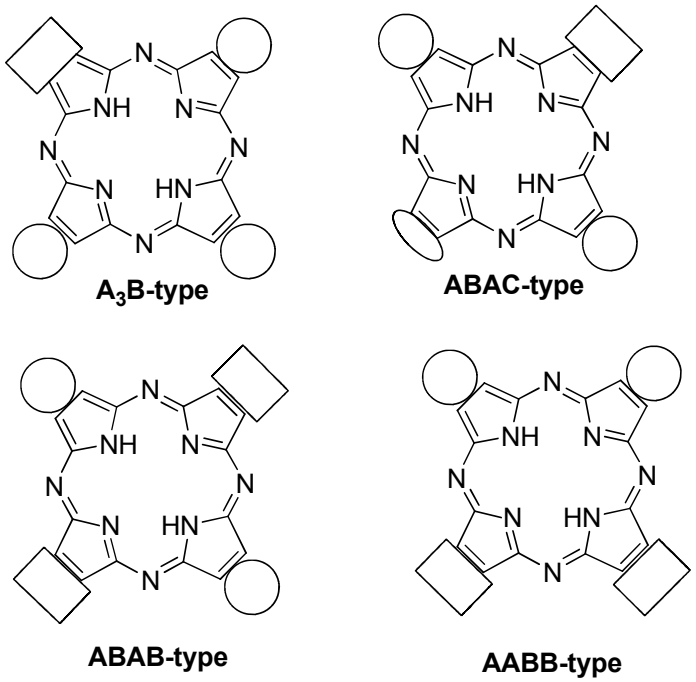


Figure 1. General types of asymmetric phthalocyanines and their analogues.

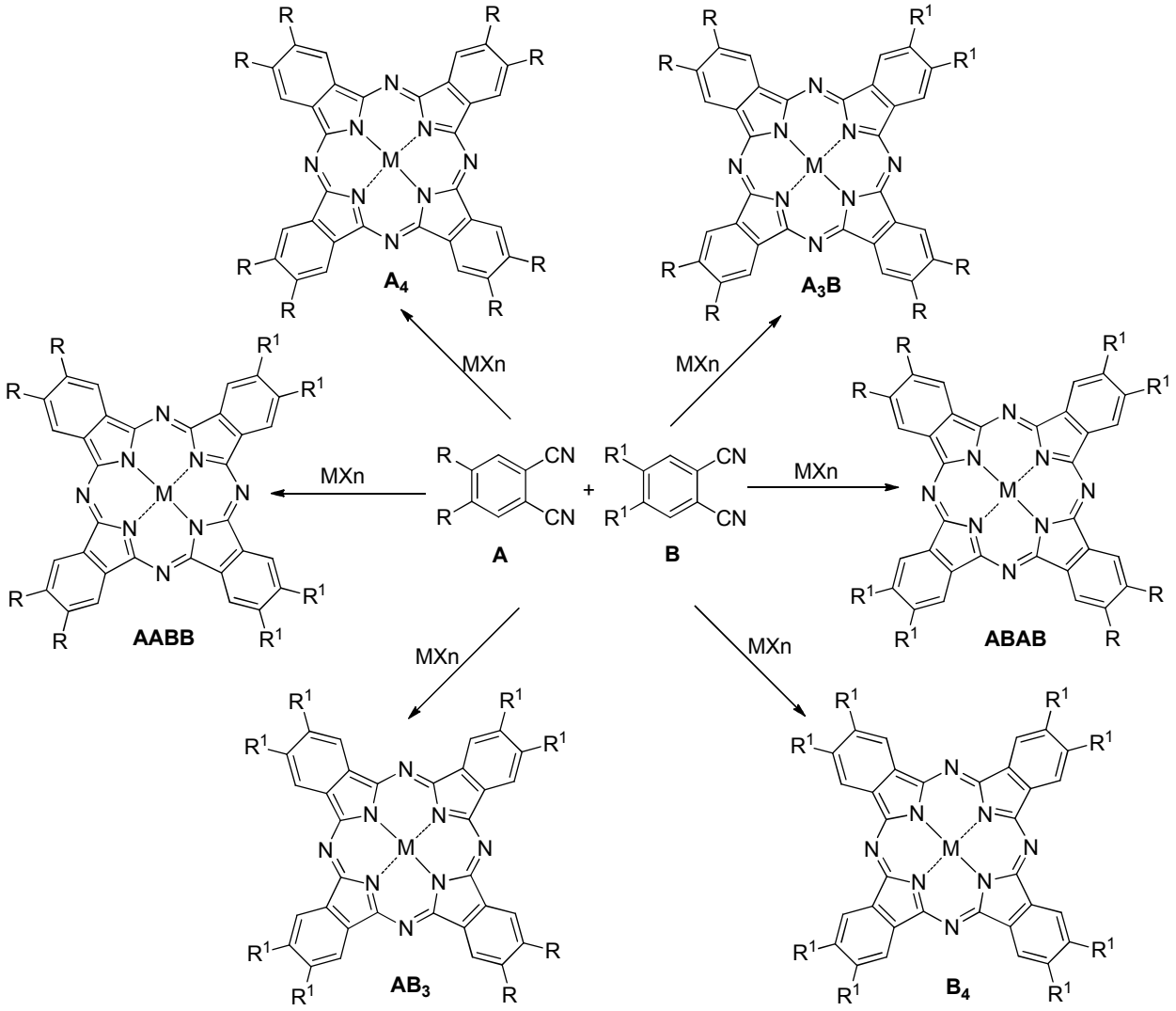
The chemistry of asymmetric phthalocyanines had a slow start. The first report on an asymmetric phthalocyanine analogue by Linstead and co-workers dates back to 1955,[75] followed by work of Luk'yanets and co-workers in 1979.[76] These two initial publications were finally followed by a group of key reports between 1982 and 1995 on the preparation of asymmetric phthalocyanines and their analogues.[77-100] After that time, the number of reports on the preparation of asymmetric phthalocyanines and their analogues increased almost exponentially. Moreover, during the last decade several reviews on asymmetric phthalocyanines have become available.[67-69,101-107] In this review, we highlight the state-of-the-art approaches for preparation of asymmetric phthalocyanines and their analogues. Rather than focusing on the preparation of specific types of asymmetric macrocycles, we would like to provide reaction-based synthetic strategies for preparation of low-symmetry systems.

2. Cross Condensation Between Two Different Dinitrile or 1,3-Diimino-isoindoline Components

2.1 Statistical condensation

The statistical condensation method is the oldest synthetic method[75,76] for the preparation of asymmetric phthalocyanines and is still the most popular for the preparation of the 3:1 (A_3B type) compounds (Scheme 1). In general, statistical condensation method is non-selective and it could be expected that if the reactivity of the dinitrile A and dinitrile B are similar and these

dinitriles are taken in equimolar quantities, all six possible products (Scheme 1) would be formed in statistical proportions (*i.e.* A_4 (8.33%), A_3B (25%), AABB (25%), ABAB (8.33%), AB_3 (25%), and B_4 (8.33%)). Taking into consideration the well-known aggregation properties of phthalocyanines, preparative scale separation of such reaction mixtures by conventional chromatographic methods could be very challenging. As a result, the statistical condensation approach has never been used for targeting all six possible products. On the contrary, this method is predominantly used for preparation of the A_3B asymmetric phthalocyanine analogues and, in several cases, for the preparation of *opposite* ABAB and *adjacent* AABB compounds. Metal-free compounds could be prepared using direct cross condensation method, while the metal-ion template approach results in the formation of the corresponding phthalocyanine metal



Scheme 1. General method for preparation of asymmetric phthalocyanines by the statistical condensation approach.

complexes. The dinitrile component could be a substituted or unsubstituted phthalo-, 1,2-naphthalo- or 2,3-naphthalo-nitrile, along with derivatives of fumaro- and maleo-nitriles. In some cases, substituted phthalonitriles could be part of another macrocycle and thus a cross-condensation reaction would result in the formation of di- or tri-macrocyclic systems such as, for example, phthalocyanine-triazolephthalocyanine hybrids **1** and **2** (Figure 2).[108]

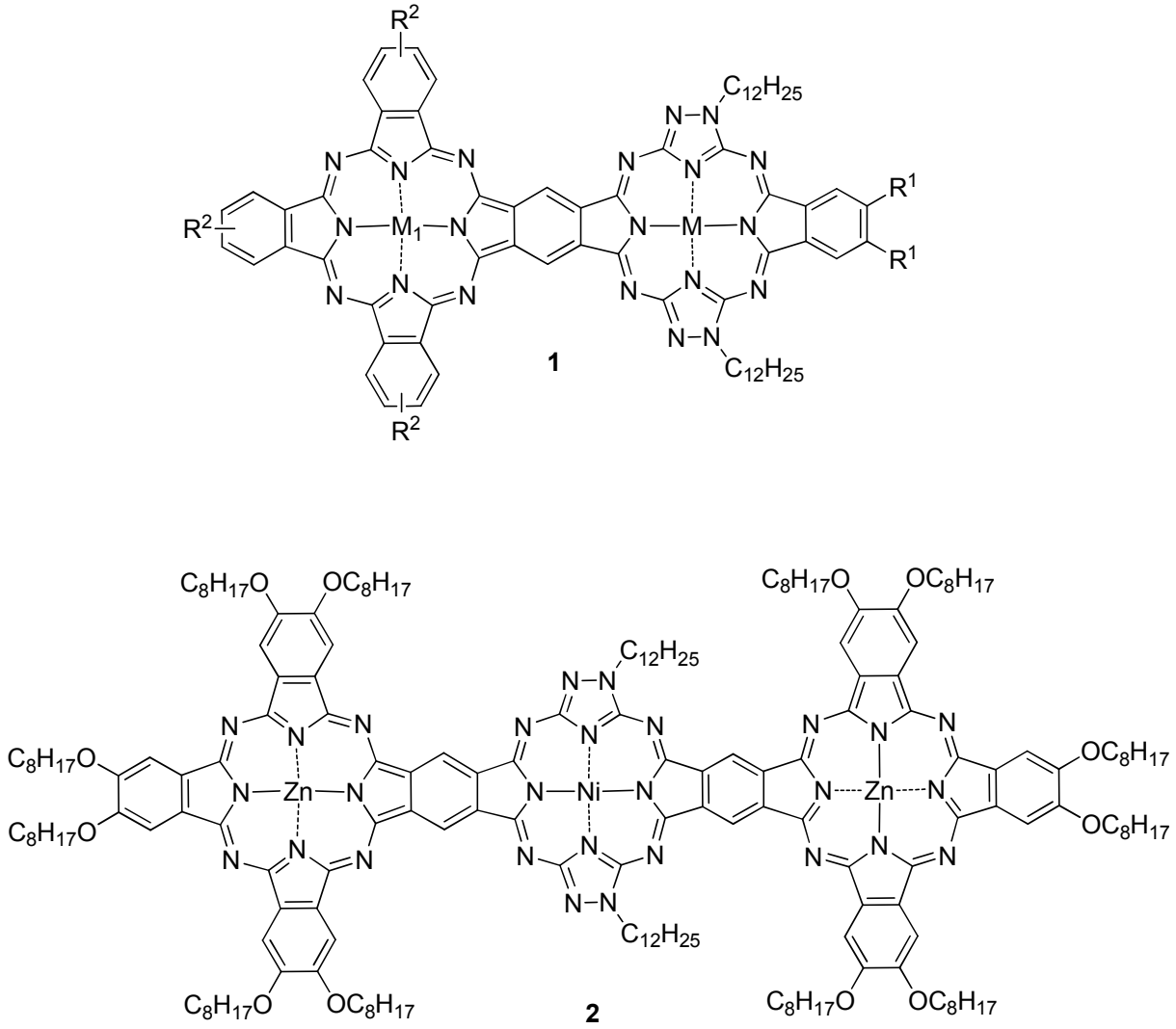


Figure 2. Examples of phthalocyanine-triazolephthalocyanine hybrids.[108]

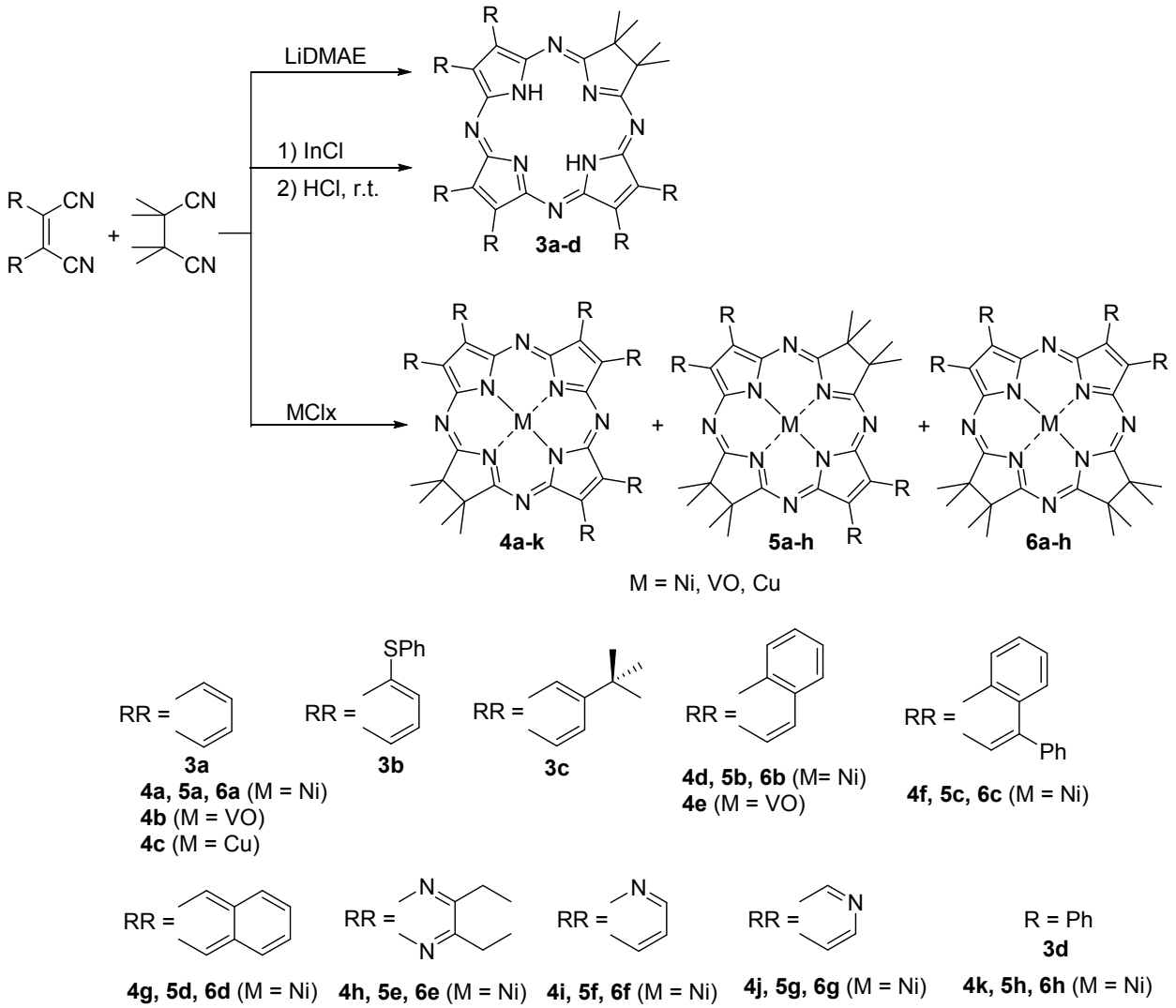
When an A_3B asymmetric phthalocyanine is targeted, the stoichiometry and reactivity of the dinitriles or 1,3-diiminoisoindolines involved in the cross condensation are two key factors that need to be considered. If the reactivities of two dinitriles involved in the cross condensation are similar, then the simple 3:1 ratio of the nitrile A and B should lead to the formation of the symmetric A_4 compound (33%), the target asymmetric A_3B phthalocyanine as a major product (44%), and the remaining A_2B_2, AB_3, and B_4 compounds as minor products (23%). Although

experimental yields were found to be between 10 and 20% for the A_3B phthalocyanine, the presence of all possible reaction products complicates the purification of the desired compound by conventional methods. In order to suppress formation of the unwanted A_2B_2, AB_3, and B_4 compounds, a 9:1 (dinitrile A to B) or higher ratio has been recommended and successfully used by several research groups.[67-69,103,104] In this case, symmetric A_4 phthalocyanine and asymmetric A_3B compound, essentially are the only reaction products, and thus separation of the reaction mixture is less complicated. Another useful tip for the preparation of asymmetric A_3B systems was introduced by Cook and co-workers.[89-92,109-111] This research group found that introduction of the substituents into the 3,- and 6-positions of the phthalonitrile facilitates separation of the symmetric A_4 from the asymmetric A_3B system using conventional chromatography methods, apparently because of the lower aggregation ability of such phthalocyanines. Although the influence of electronic effects in the phthalonitrile on its reactivity is not clearly understood, it was suggested that a high A : B molar ratio should be used when the phthalonitrile B is more reactive than phthalonitrile A, while a close or even inverted A : B ratio should be used when the phthalonitrile B is significantly less reactive than phthalonitrile A.[67] This synthetic strategy is advantageously used to prepare functionalized phthalocyanines with moieties of biological relevance, such as carbohydrates[113-116] or chalcones[117] for medicinal applications.

An interesting variation of the cross-condensation method was recently developed by Luk'yanets and co-workers (Scheme 2).[118-125] In this approach, one unsaturated or aromatic dinitrile was reacted with a simple tetramethylsuccinonitrile to target formation of the A_3B tetraazachlorin-type macrocycles **3** and **4**. In early attempts, metal-free compounds **3** were prepared using the lithium salt of *N,N*-dimethylaminoethanol,[118-122] but it was shown very recently that yields of such A_3B tetraazachlorins **3** could be significantly improved when indium was used for template condensation followed by demetalation of the macrocycle with hydrochloric acid.[124,125] The use of nickel ions as a template in this reaction results in the formation of the A_3B type nickel tetraazachlorins **4**, ABAB type tetraazabacteriochlorins **5**, and AABB type tetraazaisobacteriochlorins **6** (Scheme 2).[118-123] A similar strategy was applied by Kobayashi and co-workers for the synthesis of a fullerene-containing tetraazachlorin derivative.[126-130]

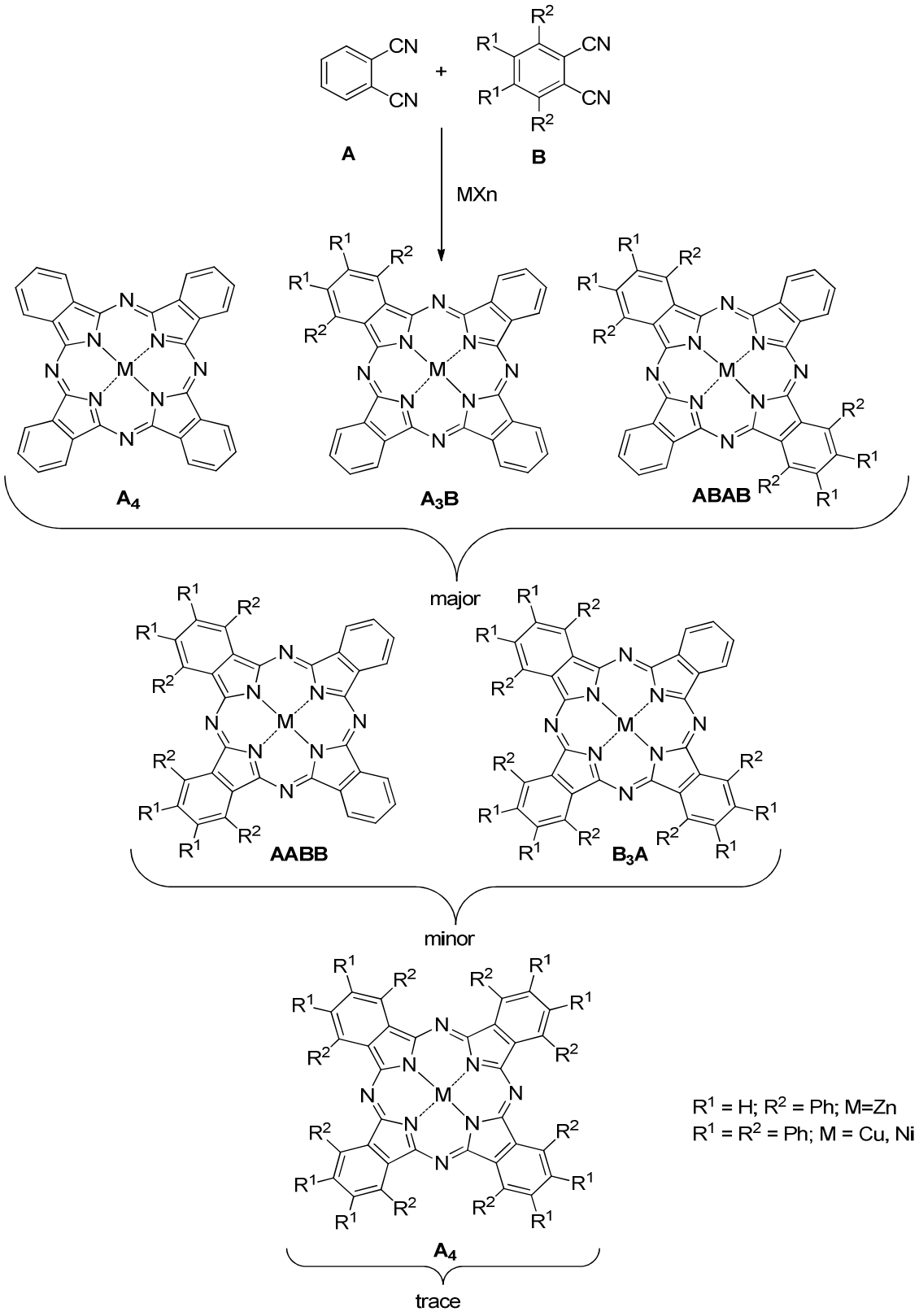
2.2 Sterically driven cross condensation

An interesting modification of the statistical cross condensation method was developed and implemented by several research groups between 1990 and 2000.[80,82,83,85-87,131] In this approach, one of the dinitriles or 1,3-diiminoisoindolines (say reactant B) should have bulky rigid groups at 3,6-positions. In this case, because of the steric hindrance between the bulky groups in close vicinity, formation of the sterically strained *adjacent* AABB, as well as AB_3, and B_4 compounds is significantly suppressed, while the formation of the less sterically crowded A_4, A_3B, and



Scheme 2. General synthetic strategies for preparation of tetraazachlorins, tetraazabacteriochlorins, and tetraazaisobacteriochlorins.

opposite ABAB compounds is favored even at a 1:1 ratio of the reactants A and B (Scheme 3). So far, phenyl and *tert*-butyl groups have been proposed as the rigid substituents in this approach, and such phthalonitriles are relatively easy to prepare. For instance, 3,4,5,6-tetraphenylphthalonitrile can be prepared from the commercially available 2,3,4,5-tetraphenylcyclopentadienone and chlorofumaronitrile.[132] Another significant advantage of this method is that bulky rigid substituents at the 3 and 6-positions simplify the chromatographic separation of the target compounds. With more conformationally flexible substituents such as *n*-alkyl groups at the 3,6-positions, the corresponding phthalonitriles are not sterically crowded enough to prevent the formation of *adjacent* AABB, AB_3, and B_4 products.



Scheme 3. Sterically driven cross-condensation reaction approach for preparation of asymmetric phthalocyanines.

2.3 Polymer support-based approach

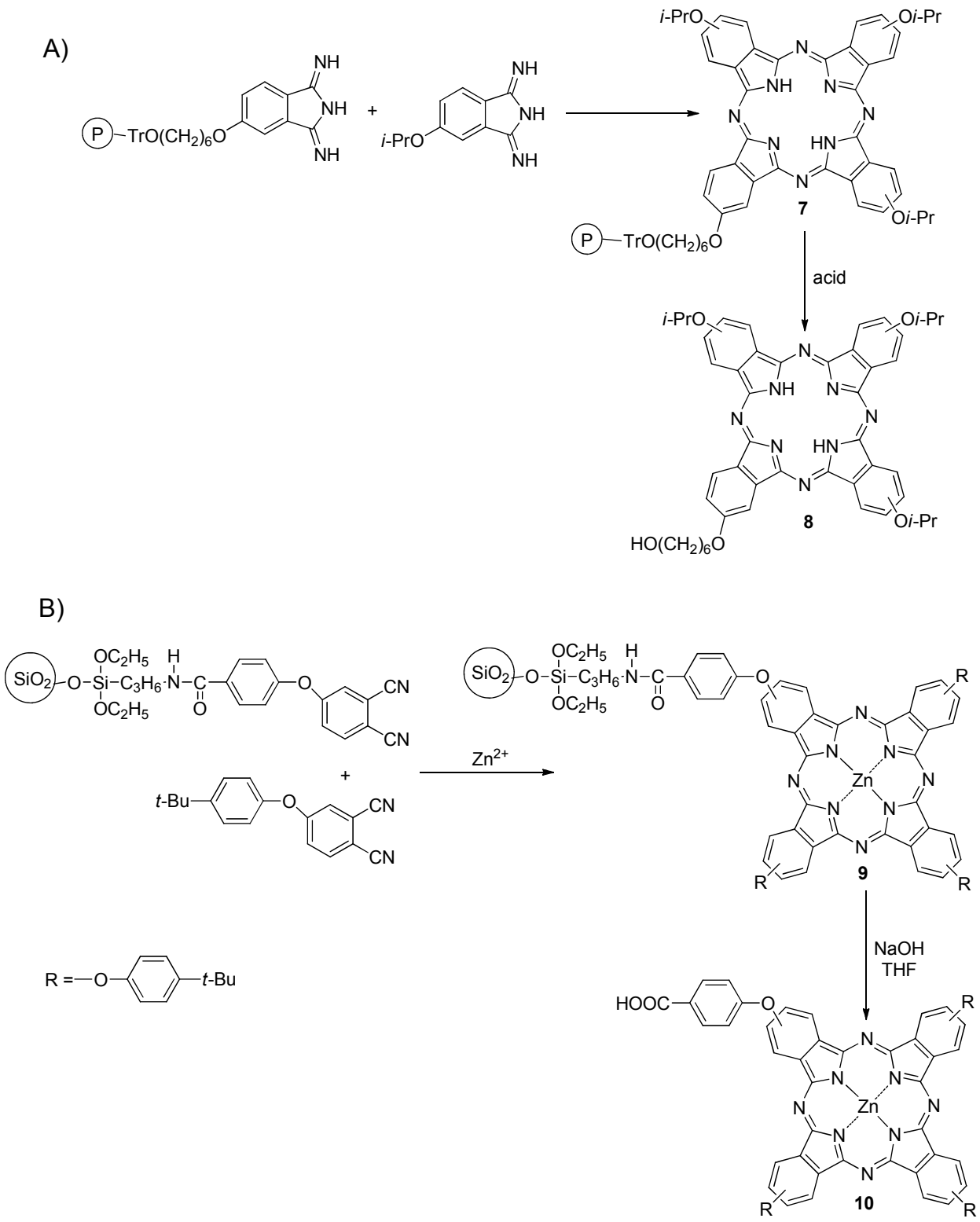
A polymer support-based approach for preparation of asymmetric phthalocyanines was pioneered by Leznoff and co-workers in 1982.[93,94] Because of the nature of this synthetic strategy, it used exclusively for preparation of the A_3B type of phthalocyanines (Scheme 4A). In this approach, a 4-substituted phthalonitrile or 1,3-diiminoisoindoline (B) is first coupled, usually using ether bond formation, to an appropriately functionalized polymer. Such phthalonitrile or 1,3-diiminoisoindoline containing polymer then reacted with a large excess of second phthalonitrile or 1,3-diiminoisoindoline (A) in appropriate solvent, which solubilize A but not polymer-supported B.[93-95] Symmetric phthalocyanine A_4, which is the major reaction product could be removed by simple washing of the reaction mixture with organic solvent, while polymer-bound asymmetric A_3B compound **7** remains insoluble. Further treatment of the polymer-bound asymmetric A_3B phthalocyanine with an acid cleaves polymer backbone and liberates the target A_3B compound **8** into solution, which can be filtered from the remaining insoluble polymeric support. The typical yields of the asymmetric A_3B phthalocyanines in this method were observed around 20%.

In a different variation of this synthetic strategy, Wöhrle and co-workers used functionalized silica gel supports to couple substituted phthalonitrile (B) to the surface.[133] In this case, the silica gel carriers were modified with the terminal primary organic amines prior their coupling with 4-(3,4-dicyanophenoxy)benzoic acid chloride (Scheme 4B). Asymmetric A_3B phthalocyanine **10** was cleaved from the surface by the alkaline hydrolysis of the amide bond in phthalocyanine **9** in TFH/water mixture.

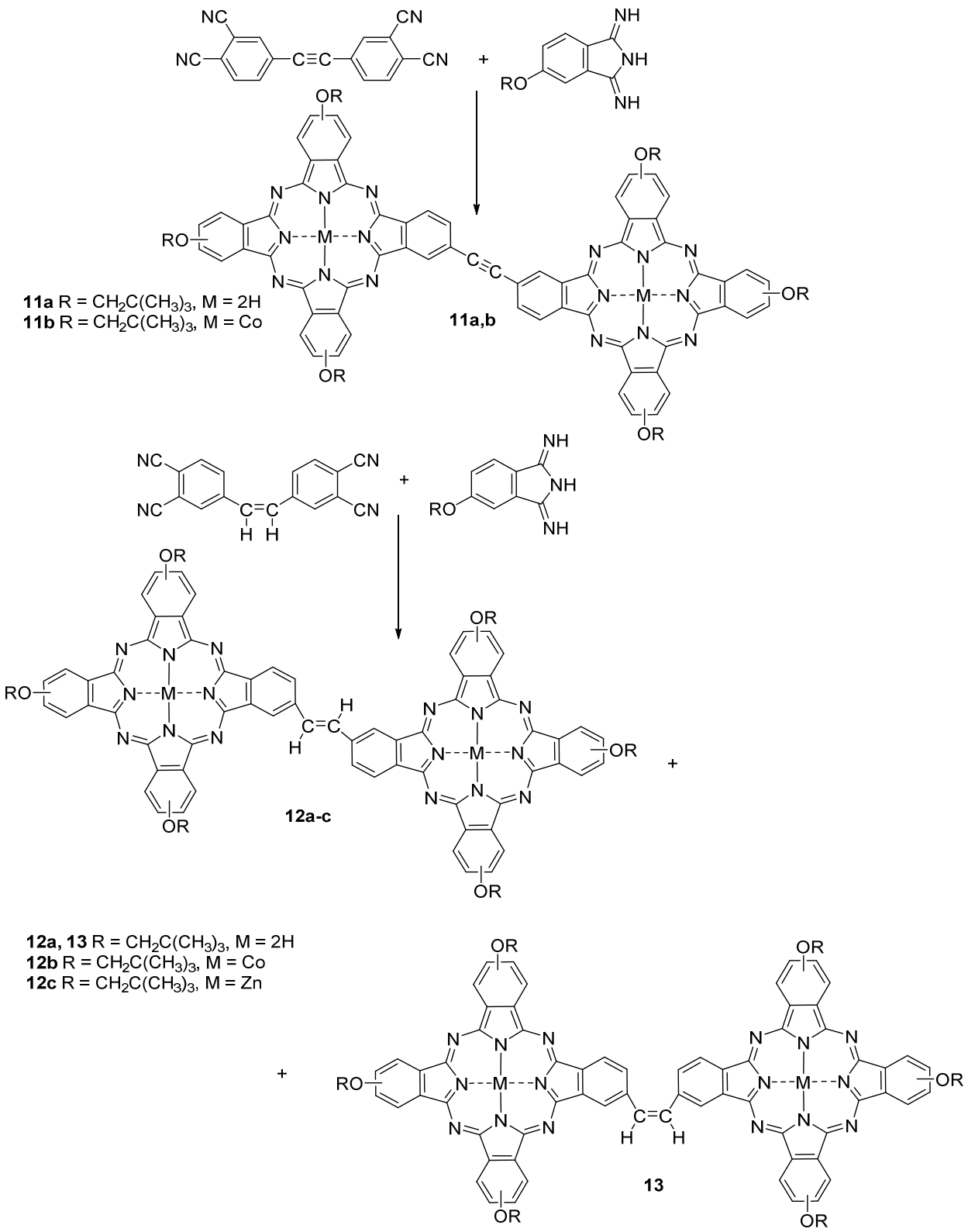
The key advantage of the polymer support-based method is elimination of the necessity of tedious chromatographic steps for the product purification. There are two major current drawbacks for such synthetic strategy, however, which should be overcome for the large-scale preparation of A_3B systems. First, despite the variety of commercially available polymeric supports and silica gels, choice of immobilized dinitriles or 1,3-diiminoisoindolines (B) is currently limited to those which can form either ether or amide bond with the support surface and later be easily cleaved by the acidic or alkaline hydrolysis. Such hydrolysis requires that the substituents (if present) in the second dinitrile or 1,3-diiminoisoindoline (A) should be stable for hydrolysis conditions. Second, an achievable target A_3B phthalocyanine load on polymer or silica gel surfaces is quite limited by the porosity, functionalization site availability, and topology of the carrier. For instance, only 0.6 – 6 mg (7.7×10^{-7} – 7.4×10^{-6} mol) of the A_3B phthalocyanine were obtained from 1g of modified silica gel with covalently bound phthalocyanine by Wöhrle and co-workers.[133]

2.4 Self and cross-condensation strategy involving bis(phthalonitriles)

In the simplest variation of this synthetic strategy, bridged 3,3′- or 4,4′-bis(phthalonitriles) or the corresponding bis(1,3-diiminoisoindolines) (B-B) used in the cross-condensation reaction with an excess of the second substituted or unsubstituted phthalonitrile or 1,3-diiminoisoindoline

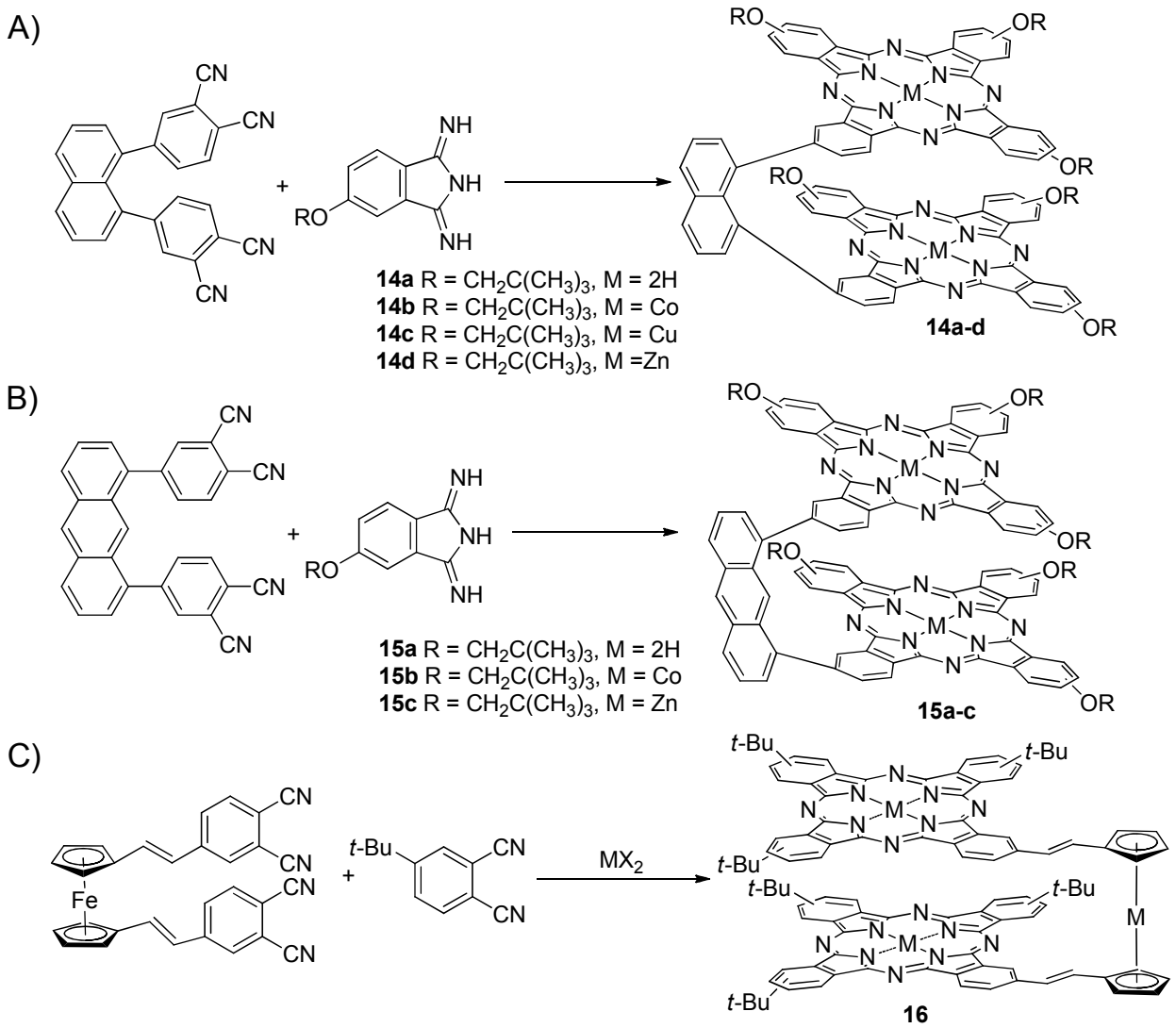


Scheme 4. General strategy for preparation of A_3B-type asymmetric phthalocyanines using polymer support-based approach.



Scheme 5. Synthetic pathways for the preparation of co-planar asymmetric A_3B-BA_3 type phthalocyanines.

precursor A to form, for instance, the asymmetric A_3B-BA_3 dimeric phthalocyanine products **11 - 13** (Scheme 5). Similar to the standard synthesis of asymmetric A_3B compounds described earlier, the main by-product in such synthesis is symmetric A_4 phthalocyanine, which could be eliminated by the conventional chromatographic methods. Depending on rigidity of the linking group in starting B-B phthalonitrile, planar or co-facial dimeric phthalocyanines could be prepared in extreme cases (Scheme 5).[96] For instance, Lever, Leznoff and co-workers reported variety of A_3B-BA_3 type asymmetric dimeric phthalocyanines connected via alkynyl-, alkenyl-, and saturated hydrocarbon bridges.[96] Unsaturated bridging groups in these compounds force coplanar geometry of phthalocyanines and though to facilitate electronic coupling between two macrocycles although no strong coupling was observed in alkynyl- and alkenyl-derivatives of dimeric phthalocyanines **12** and **13** (Scheme 5).[96]



Scheme 6. Synthetic strategies for the preparation of cofacial A_3B-BA_3 type asymmetric phthalocyanines.

The other extreme of this strategy is the formation of a co-facial dimeric phthalocyanine compound as reported, for instance, by Leznoff, Lever and co-workers[134] as well as by Torres and co-workers[135] (Scheme 6). In the first example, naphthalene or anthracene-containing bis(phthalonitriles) were statistically condensed with the substituted phthalonitrile to form co-facial naphthalene or anthracene-bridged A_3B-BA_3 systems **14, 15** (Scheme 6A,B).[134] In the second, a ferrocene-containing bis(phthalonitrile) was used as starting material for a cross condensation reaction with 4-*tert*-butylphthalonitrile (Scheme 6C).[135] In all cases, UV-vis spectroscopy of the final asymmetric A_3B-BA_3 compounds **14-16** were suggestive of a co-facial arrangement of two phthalocyanine macrocycles, which varied depending on the type of linking group and which facilitates potential electronic coupling in these systems. A similar co-facial orientation in asymmetric A_3B-BA_3 phthalocyanines **17** and **18** could be achieved using *o*-xylylene or BINOL–based bis(phthalonitriles), which provide the desired conformational rigidity (Figure 3).[136,137]

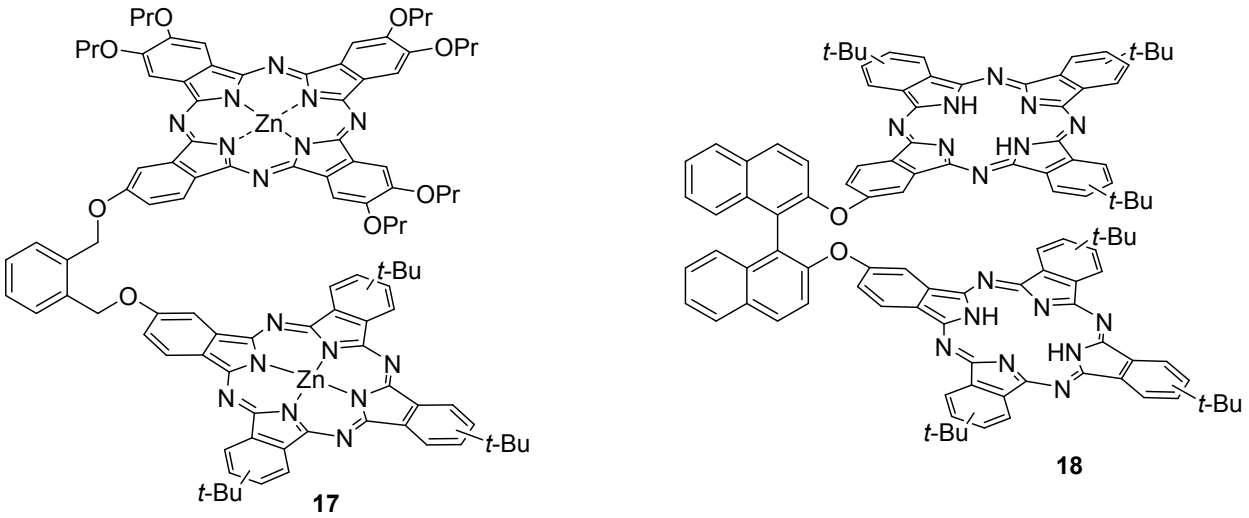
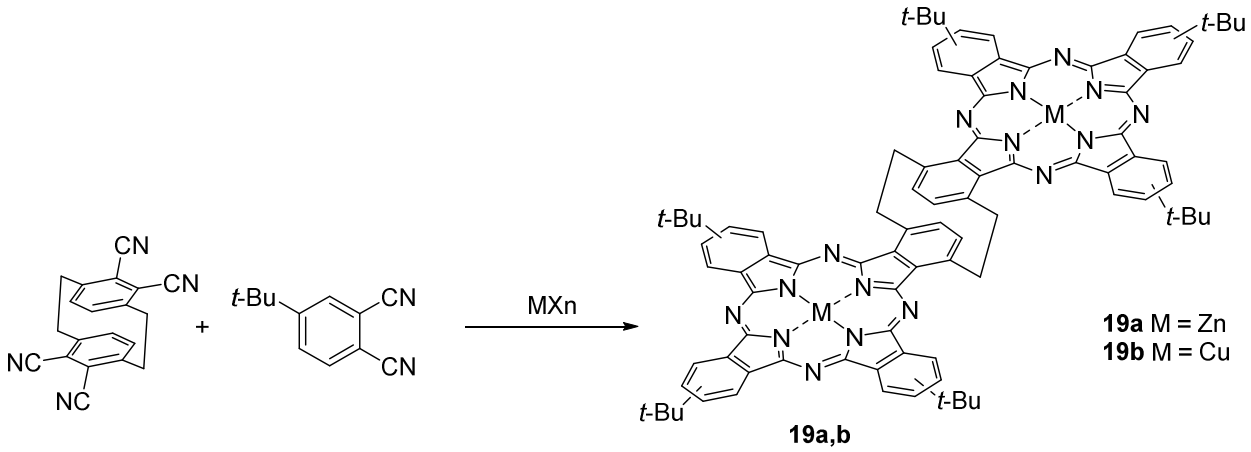


Figure 3. Representative examples of cofacial asymmetric A_3B-BA_3 type phthalocyanines

Finally, when saturated conformationally flexible linking groups used for the preparation of A_3B-BA_3 systems, the conformation of the resulting dimeric phthalocyanine compounds could easily adopt any configuration between co-planar and co-facial.[96] An interesting case of an A_3B-BA_3 system was reported by Kobayashi and co-workers (Scheme 7).[138] Prepared by cross-condensation between tetracyanoparacyclophane and a substituted phthalonitrile, the dimeric phthalocyanines **19a,b** have two co-planar phthalocyanine macrocycles connected through a paracyclophane fragment, which provides π–π conjugation for the system and shifts the Q-band into the near IR region.

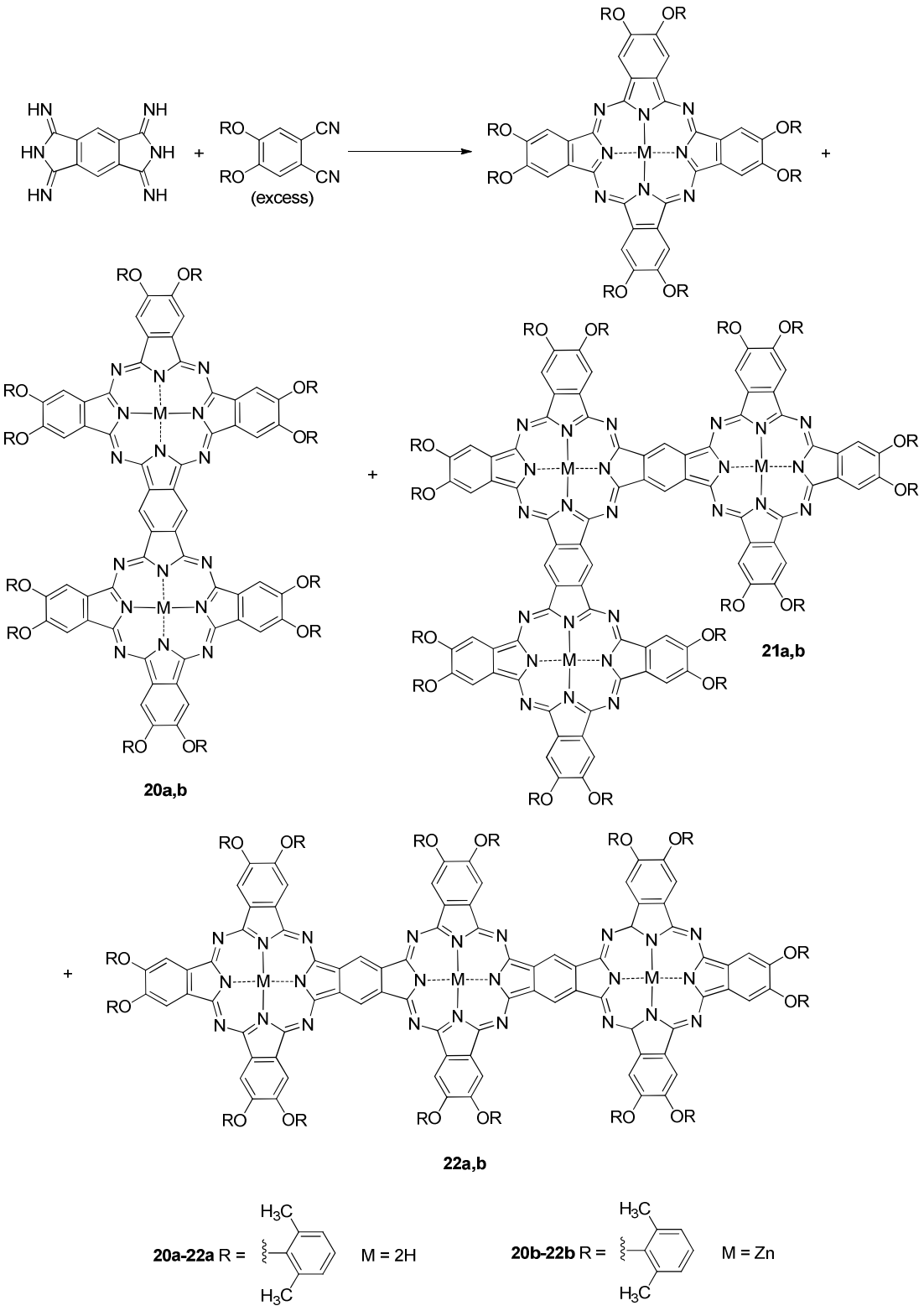


Scheme 7. Synthesis of paracyclophane-conjugated A_3B-BA_3 phthalocyanines.

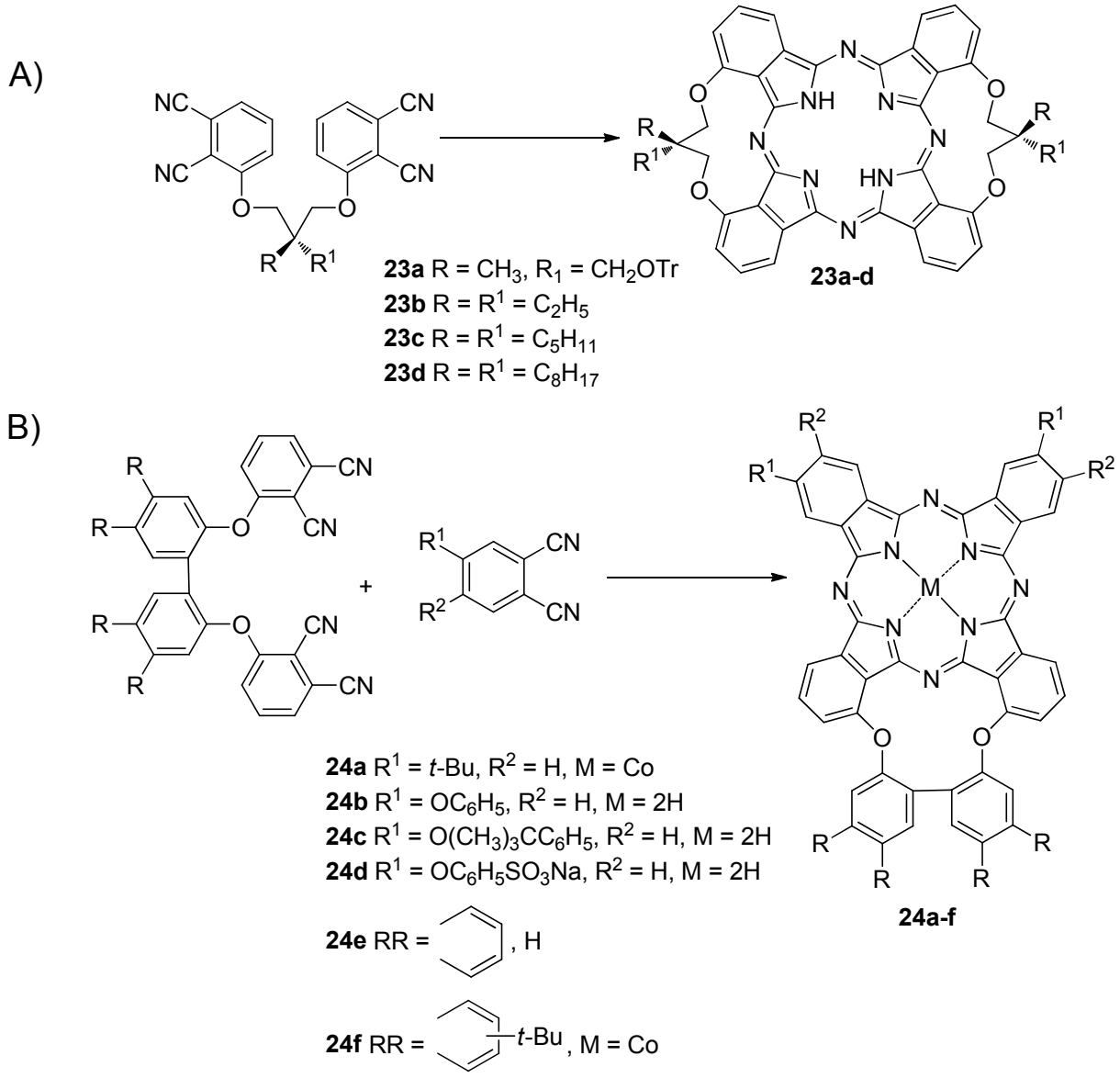
Other interesting asymmetric systems which rely on the bis(phthalonitrile) cross condensation approach are the fully conjugated planar extended phthalocyanine analogues of Scheme 8.[139] In these cases, tetracyano-benzene, -naphthalene or -anthracene precursors undergo cross-condensation with substituted phthalonitriles to form fused bis-, tris-, and higher rank asymmetric phthalocyanine derivatives. Simon,[140-142] Kobayashi,[142-146] Tomilova,[147-154] and their respective co-workers reported several such systems, while Wöhrle and co-workers prepared an interesting set of linear dimer **20** and linear and angular fully conjugated phthalocyanine trimers **21** and **22**.[139]

The synthetic strategy for the synthesis of monophthalocyanines using bis(phthalonitrile) precursors was first developed by Leznoff and co-workers for a single-isomer preparation of a tetrasubstituted symmetric phthalocyanine (Scheme 9A).[155] Self-condensation of the 3,3′-bisphthalonitrile leads to the formation of pure 1,11,15,25-tetrasubstituted phthalocyanines **23a-d** in 7-21% yields along with polymeric and oligomeric by-products.

Kobayashi and co-workers have extended this synthetic strategy to the preparation of asymmetric *adjacent* AABB phthalocyanines.[156] In their modification, a chiral or non-chiral 3,3′-bis(phthalonitrile) undergoes cross-condensation with an appropriate phthalo- or naphthalonitrile to form symmetric A_4 and asymmetric *adjacent* AABB phthalocyanines **24a-f** in 1.5–3.3% yields (Scheme 9B). Although formation of the other asymmetric and symmetric by-products in this reaction is unavoidable and thus purification of the target *adjacent* AABB phthalocyanines requires extensive chromatography steps, this method allows formation of rare AABB type compounds in a reasonably selective way.[156-161] Moreover, the key advantage of the use of the bis(phthalonitriles) with short rigid bridging groups similar to, for instance, 2,2′-dihydroxy-1.1′-binaphthyl, is suppressed formation of oligomeric phthalocyanines by the self-condensation reaction of such building blocks.



Scheme 8. Synthetic approach to the preparation of fully conjugated asymmetric phthalocyanines.



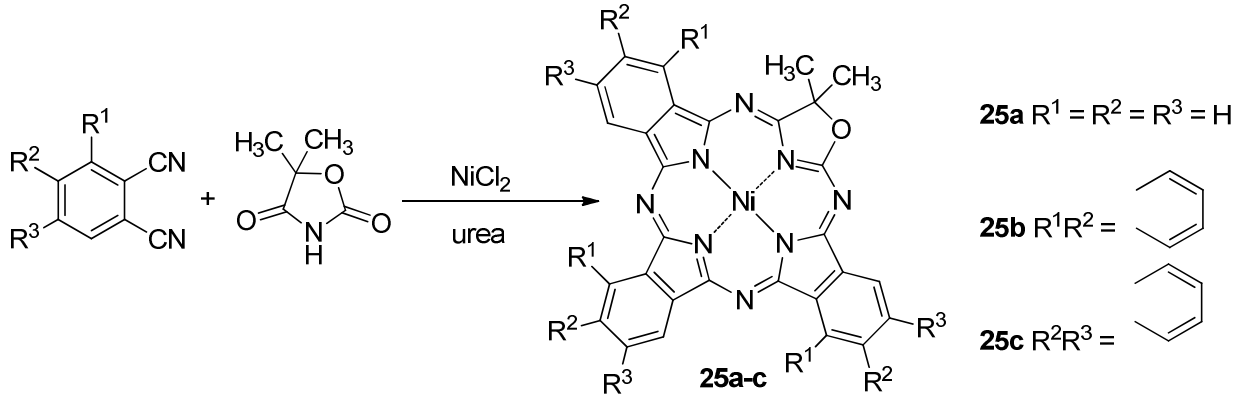
Scheme 9. Directed synthesis of AABB-type asymmetric phthalocyanines.

3. Cross Condensation Between Phthalonitrile or 1,3-Diiminoisoindoline and Non-nitrile Components

3.1 Cross condensation between phthalonitrile and anhydride/imide components

Because of the large difference in reactivity between the phthalonitrile or 1,3-diiminoisoindoline component (A) and anhydride or amide component (B), cross-condensation using such reactants is rarely used in the preparation of asymmetric phthalocyanines and their analogues. One example which uses this strategy is the cross-condensation between phthalo- or 1,2-naphthalonitrile as A and 5,5-dimethyl-1,3-oxazolidine-2,4-dione as B, using a nickel template. In this

case, symmetric A_4 phthalocyanine and asymmetric A_3B β-oxatetraazachlorins **25a-c** (4 – 8% yield) were formed (Scheme 10).[162] Another example of such an approach is the cross condensation between 4-nitrophthalimide and 3,6-dialkoxyphthalonitrile in the presence of copper acetate, urea, and ammonium molybdate, to form mono-nitro- A_3B type copper phthalocyanine.[163]

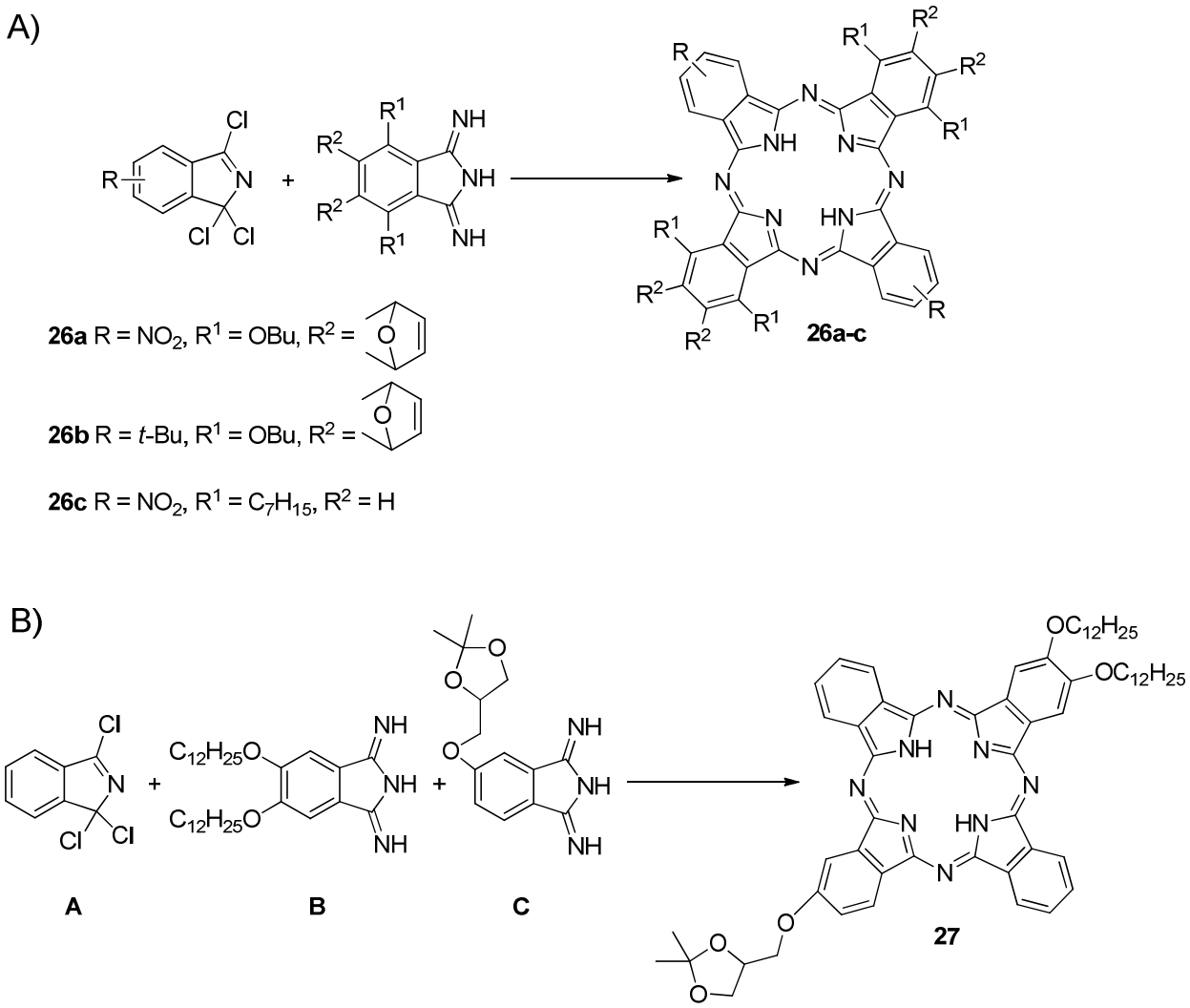


Scheme 10. General strategy for the preparation of tribenzotetraazachlorins using dinitrile and imide components.

3.2 Cross condensation between nitrile and 1,1,3-trichloro-1*H*-isoindole or isoindoline-1,3-dithione components

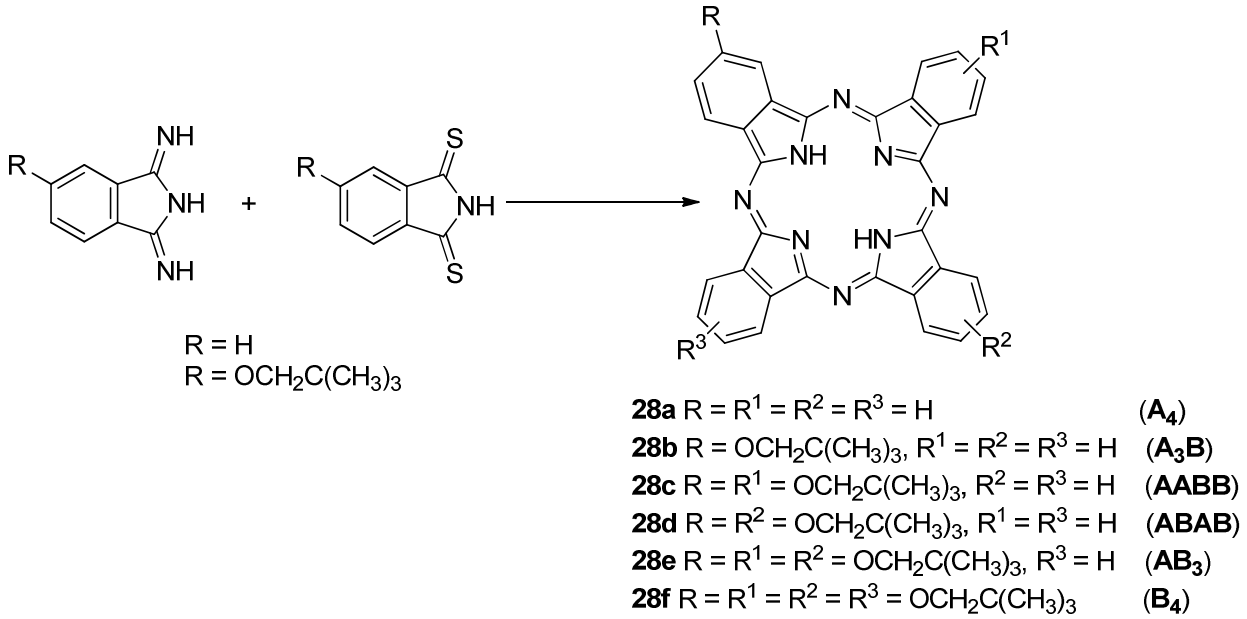
In theory, the 1 : 1 cross condensation reaction between 1,3-diiminoisoindoline (A) derivatives and 1,1,3-trichloro-1*H*-isoindole (B) derivatives should result in selective formation of the *opposite* type ABAB asymmetric phthalocyanines. Indeed, in the first two reports on this reaction, dating back to 1977[164] and 1990,[97] the authors claimed that the effective D_{2h} symmetry ABAB phthalocyanine forms exclusively in up to 50% yield when a 1 : 1 ratio of A and B were used in the presence of organic base and a reducing agent. Later, however, other research groups which applied this method for the selective preparation of ABAB systems reported significant contamination of the product mixture by the A_3B asymmetric phthalocyanine derivative. As a result, observed yields of ABAB products **26a-c** were significantly lower (15 – 25%), and conventional purification methods should be used to obtain a target ABAB compound in pure form.[165-174] It seems that this synthetic approach has low sensitivity to the substituents present in the 1,1,3- trichloro-1*H*-isoindole as well as the 1,3-diiminoisoindoline derivative (Scheme 11A).

In a recent report, 1,1,3-trichloro-1*H*-isoindole (A) was used for cross condensation with two different 4,5- (B) and 4-substituted (C) 1,3-diiminoisoindolines. The authors reported that formation of the first ever ABAC asymmetric phthalocyanine **27** could be achieved in 9% yield when precursors A, B, and C interact at 6 : 1 : 2 ratio.[175] It is interesting to note that only the ABAC and ACAC compounds were observed in the product mixture in significant amounts and the target ABAC phthalocyanine **27** could easily be separated by chromatography (Scheme 11B).



Scheme 11. Preparation of ABAB and ABAC phthalocyanines using a 1,1,3-trichloro-1*H*-isoindole.

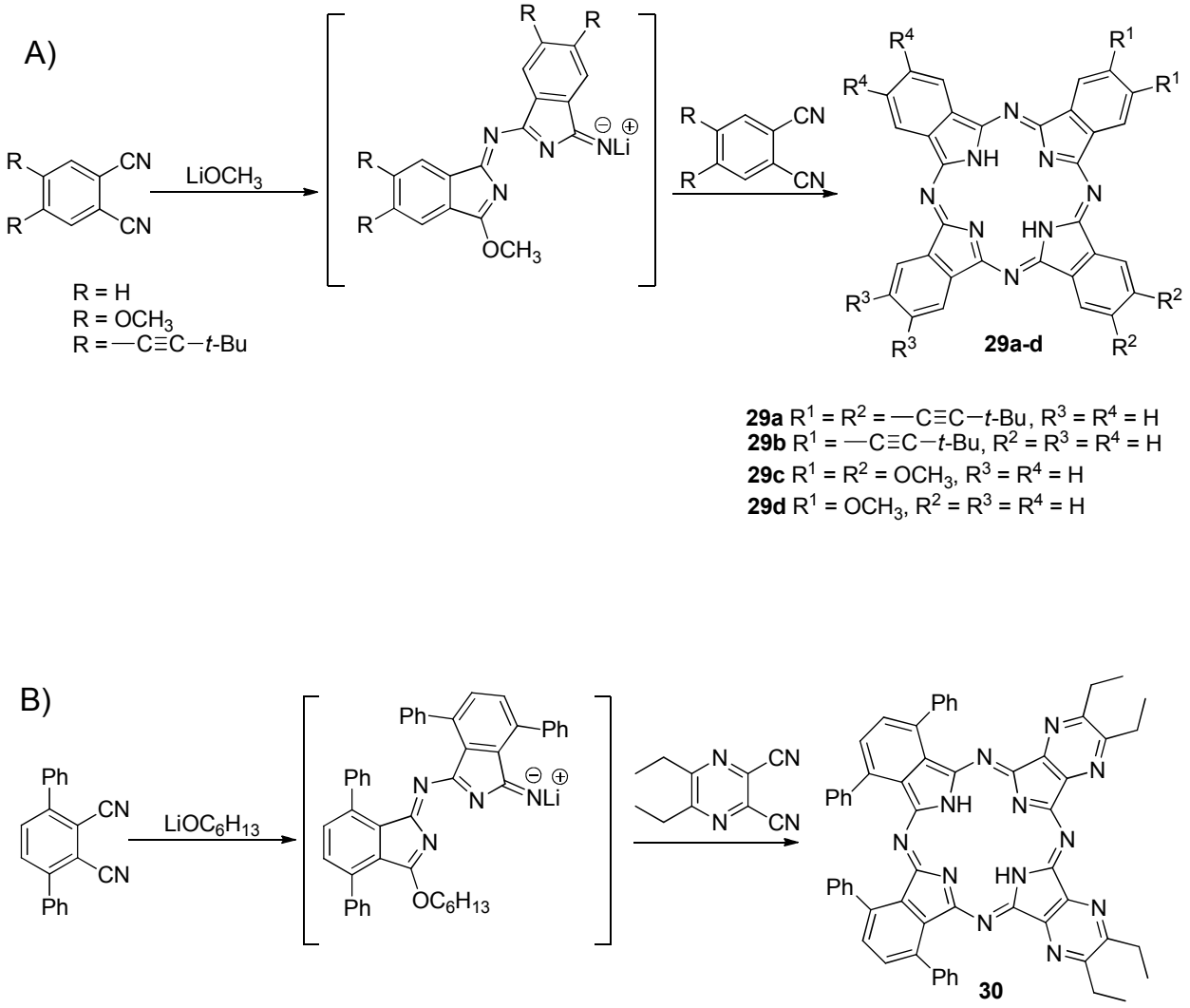
In similar strategy, Leznoff and co-workers used cross condensation between a 1,3-diimino-isoindoline derivative and an isoindoline-1,3-dithione to form as target an *opposite* ABAB phthalocyanine **28d** (Scheme 12).[98] In this case, however, the authors observed formation of all six possible (A_4, A_3B, ABAB, AABB, AB_3, and B_4) products **28a-e**, which is indicative of a scrambling reaction similar to that observed in the preparation of asymmetric porphyrin derivatives[176-179] as well as the reaction of subphthalocyanine with 1,3-diiminoisoindoles described later in this review. Because of such scrambling, the 1,3-diiminoisoindoline and isoindoline-1,3-dithione cross condensation route has no advantage over the more simple statistical condensation or 1,1,3-trichloro-1*H*-isoindole strategies and is currently not in use by research groups.



Scheme 12. Use of isoindoline-1,3-dithione in the preparation of asymmetric phthalocyanines.

4. Targeted Synthesis of AABB-type Asymmetric Phthalocyanines from a Pre-formed AA-type Intermediate

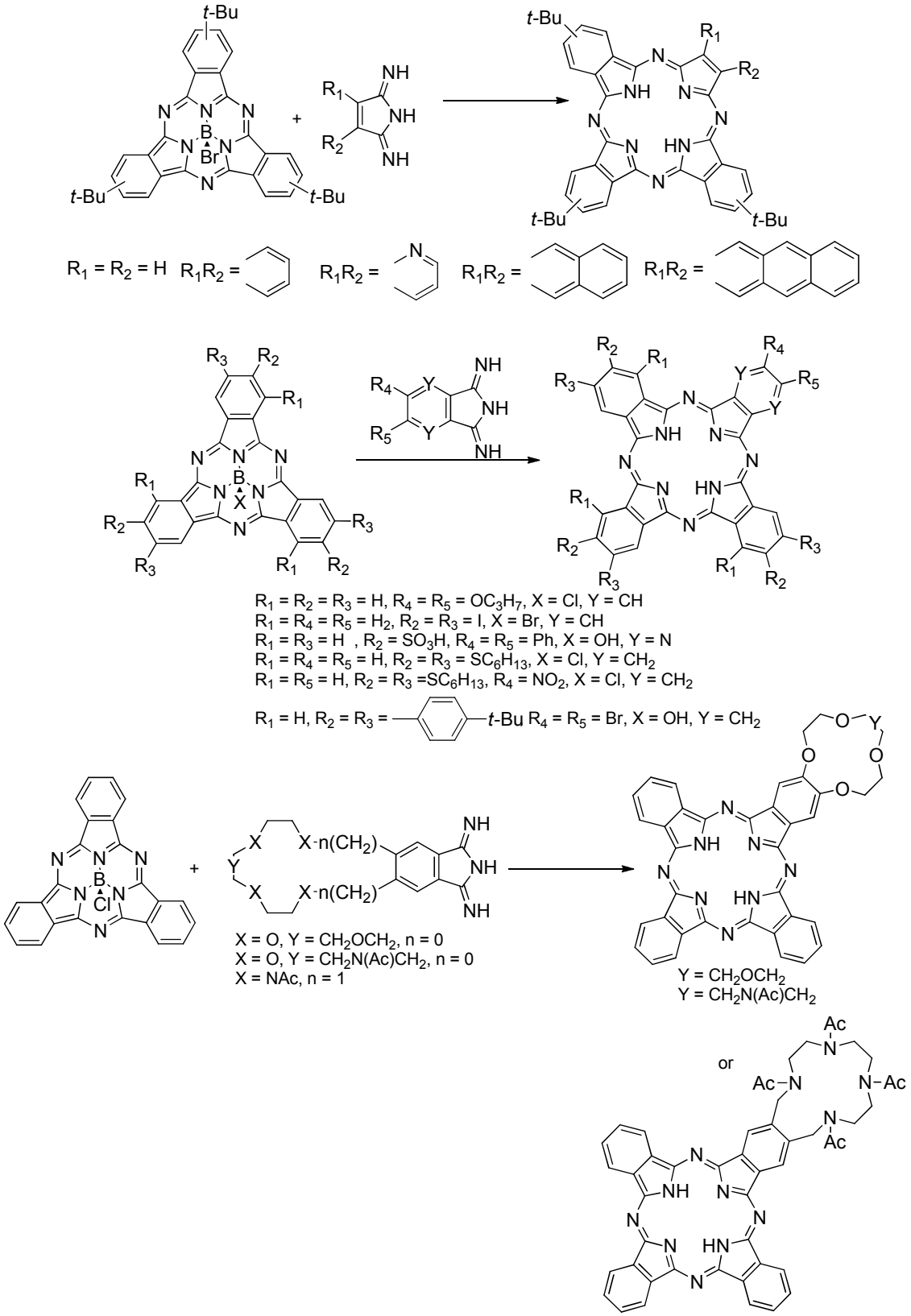
The "half-Pc" intermediate of AA type is another useful precursor for the preparation of asymmetric *adjacent* AABB phthalocyanines, which are difficult to prepare by the other synthetic methodologies and are promising candidates for non-linear optical applications. Formation of such intermediates was pioneered by Oliver and Smith at the end of the 1980s.[180] Although these authors initially suggested that AA intermediates can only be formed from phthalonitriles with electron-withdrawing groups, several years later Leznoff and co-workers proved that the reaction between 4,5-bis-(3,3-dimethyl-1-butynyl)phthalonitrile with lithium methoxide in boiling methanol could also result in the formation of the desired AA compounds **29a**-**d** (Scheme 13A).[181] Moreover, Kobayashi and co-workers have shown that even the sterically demanding 3,6-diphenylphthalonitrile can form "half-Pc" intermediates under mild reaction conditions (Scheme 13B).[182] In all cases, once formed, the "half-Pc" intermediate could be further reacted with a second phthalonitrile or its analogue to form the target AABB phthalocyanine as the major macrocyclic product. Although yields of AABB phthalocyanines can be quite high (around 20%), some quantities of the other possible asymmetric and symmetric phthalocyanines were also observed in the reaction mixture and thus standard separation methods should be used for purification of the target material.



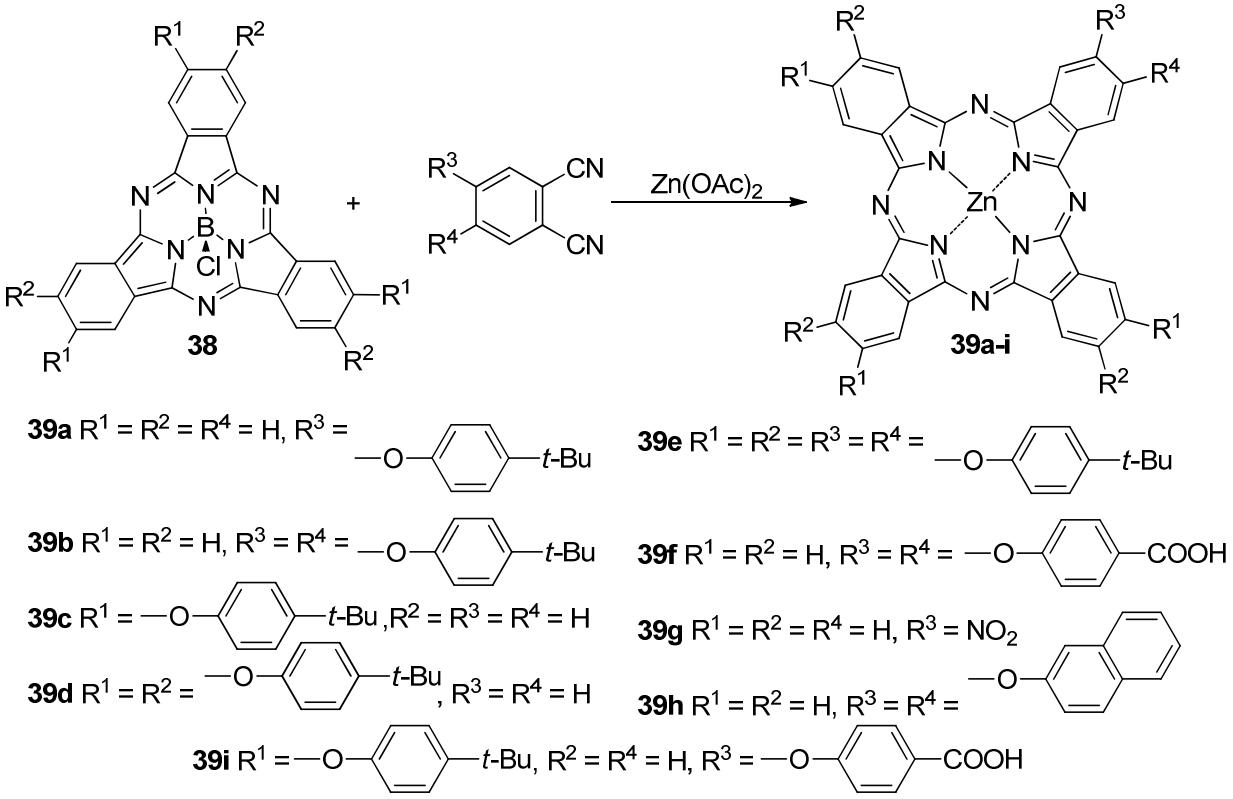
Scheme 13. Synthetic strategy for the selective preparation of AABB type asymmetric phthalocyanines using the "half-Pc" method.

5. Subphthalocyanine Ring Expansion Strategy

The smallest phthalocyanine analogues are subphthalocyanines (SubPcs), which have only three isoindole fragments with the tetrahedral boron as a central atom.[183] These bowl-shaped aromatic macrocycles have effective C_{3v} symmetry and could be easily prepared by the reaction between substituted or unsubstituted phthalonitrile and BX_3 (X = F, Cl, Br). In 1988 and then in 1990, Ando and Mori[99,184] as well as Kobayashi and co-workers in 1990[100] found that SubPcs undergo ring expansion reaction when treated with 1,3-diaminoisoindoline or its analogues, resulting in the metal-free asymmetric A_3B phthalocyanines (Schemes 14-15).[99,100,184-203]



Scheme 14. Subphthalocyanine ring expansion strategy for the preparation of the metal-free A_3B type asymmetric phthalocyanines.



Scheme 15. Subphthalocyanine ring expansion strategy for the preparation of zinc A_3B type asymmetric phthalocyanines

Based on chemical kinetic data gained by UV-vis spectroscopy, the SubPc ring expansion reaction is a first-order reaction with respect to SubPc.[188,195] The proposed reaction mechanism requires the cleavage of the SubPc ring, extrusion of the central boron atom, and further cyclization of the resulting open phthalonitrile trimer with the available 1,3-diiminiisoindoline. One of the initial reports[100] claimed that such a ring expansion reaction is highly selective and the asymmetric A_3B phthalocyanine is the only major product. It was soon realized, however, that the reaction selectivity is highly dependent on the reaction conditions, the nature of the solvent(s), the structure of the SubPc, and the electronic properties of the 1,3-diiminoisoindolines. Indeed, in some cases it was found that the ring expansion reaction is highly selective and the yield of pure A_3B phthalocyanine could be as high as 90%,[100] while other research groups found by HPLC and other spectroscopic methods that this synthetic strategy leads to the formation of all possible reaction products (A_4, A_3B, AABB, ABAB, AB_3, and B_4).[204] On this basis, it was suggested that once the SubPc ring is cleaved, the resulting open-chain AAA trimer undergoes a scrambling reaction followed by statistical condensation between available subunits, which results in the formation of all the observed products. Several research groups have found that the ring expansion reaction selectivity towards the formation of an A_3B phthalocyanine could be improved by the following factors.[67] Firstly, the best yields of a desired A_3B compound

could be achieved when the SubPc macrocycle has electron-withdrawing substituents or no substituents, and the 1,3-diiminoisoindoline reactant has electron-donating groups. Secondly, when SubPcs reacted with the lower-activity phthalonitrile (instead of a 1,3-diiminoisoindoline) and a strong base (DBU), the yields and selectivity of formation of A_3B phthalocyanines are quite good.[204] Finally, when zinc A_3B phthalocyanines are the target, they could be prepared in reasonable yield and selectivity when SubPcs are treated with the corresponding phthalonitriles in the presence of a zinc salt (Scheme 15).[204]

In general, when the target asymmetric phthalocyanine is of A_3B type, the SubPc ring expansion reaction is as popular these days as the statistical condensation method. Yields of A_3B phthalocyanines in both methods are similar, and several SubPc precursors are currently commercially available, which obviates an additional synthetic step in ring expansion synthetic strategy. Another advantage of the SubPc method is obvious when one needs to prepare A_3B phthalocyanine with A fragments of low solubility (*i.e.* when only C-H or C-halogen bonds are present). In this case the statistical condensation reaction tends to give A_4 and A_3B mixtures, which, because of strong intermolecular aggregation, is very difficult to separate by conventional purification methods.[67] On the other hand, both unsubstituted and dodecahalo SubPcs are quite soluble precursors, and if the ring expansion reaction conditions are optimized to give the A_3B phthalocyanine as the main or only reaction product, purification of the target compound is not a problem.

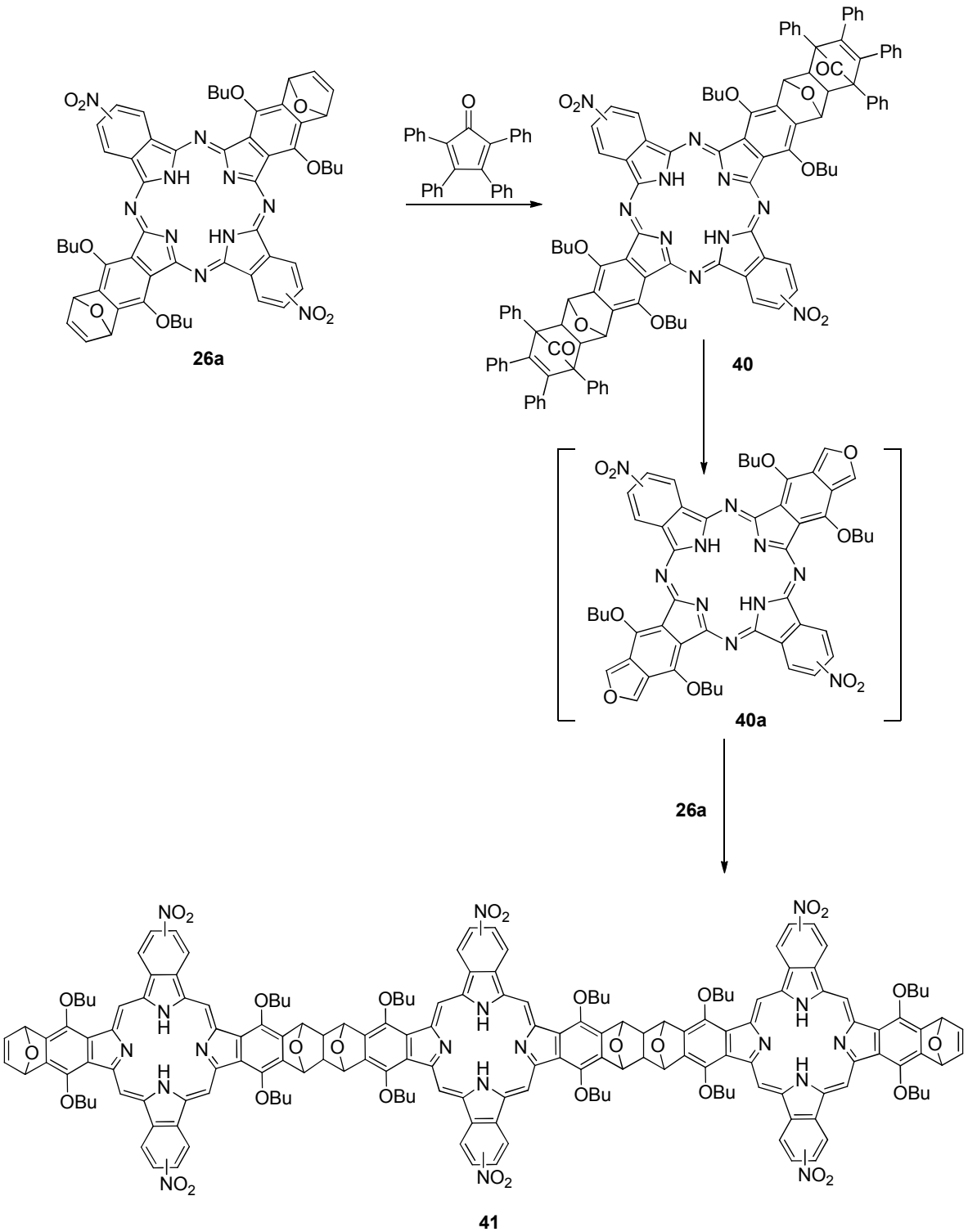
6. Post-modification of Pre-formed Macrocycles

Asymmetric phthalocyanines and their analogues can also be prepared using symmetric or asymmetric phthalocyanines using a variety of synthetic strategies. Such transformations are discussed in this part of the review.

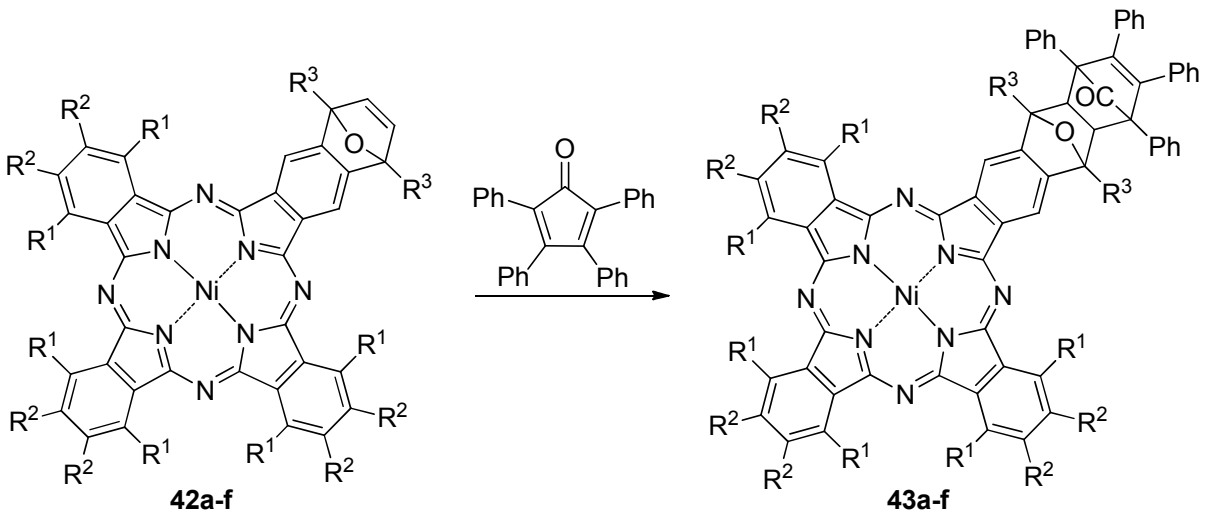
6.1 Cycloaddition reactions

Hanack and co-workers have pioneered the use of the oxygen-bridged bicyclic asymmetric phthalocyanines **26** and **42** in cycloaddition reactions (Schemes 16, 17).[167,168,205-208] Such phthalocyanines easily form Diels-Alder reaction products when reacted as dienophiles under mild conditions with different dienes. When tetraphenylcyclodienone is used in reaction with asymmetric phthalocyanine **26a**, thermal decomposition of the reaction product **40** *in situ* generates the furan-substituted phthalocyanine intermediates **40a**, which could be used as dienes in further Diels-Alder reactions with bicyclic dienophiles to form ladder-type oligomers **41** incorporating phthalocyanine units (Scheme 16). The asymmetric bicyclic diene-containing phthalocyanine **45** could be further reacted with fullerene to form cycloaddition fullerene-containing phthalocyanine analogue **46** (Scheme 18).[209] Similarly, Kobayashi and co-workers used Diels-Alder reaction between C_{60} and diene prepared *in situ* from phthalocyanine-4,5-diazine to form covalent phthalocyanine : C_{60} adduct.[210] In another interesting reaction, Hanack

and team found that the oxygen-bridged phthalocyanine **42e** could undergo cycloaddition reactions with substituted pyridine oxides to form the heterocyclic adducts **47a-c** (Scheme 19).[211]

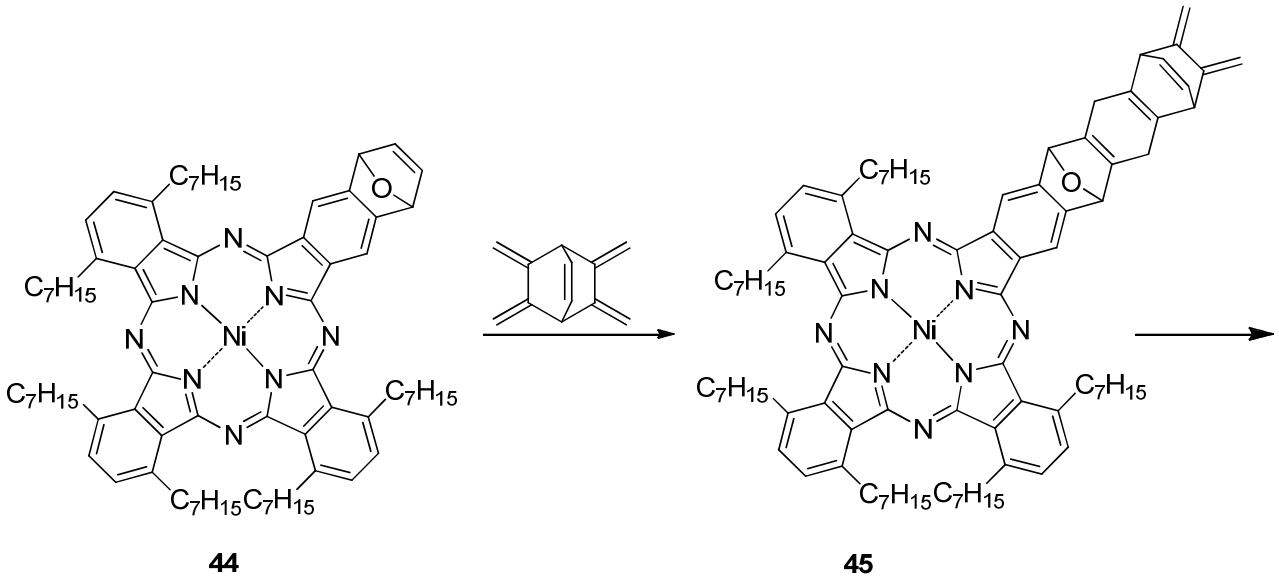


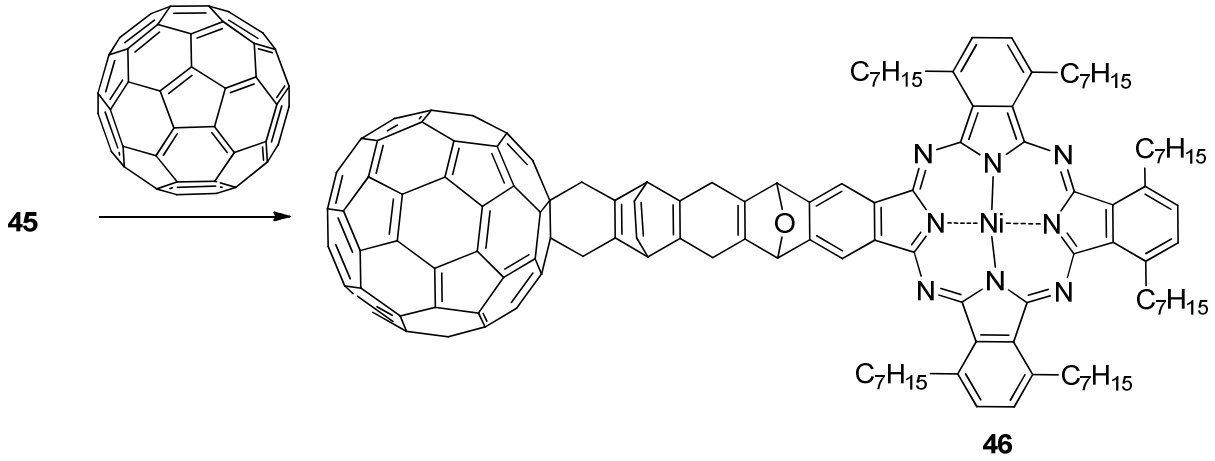
Scheme 16. Use of the Diels-Alder reaction in the preparation of "ladder" type asymmetric phthalocyanines.



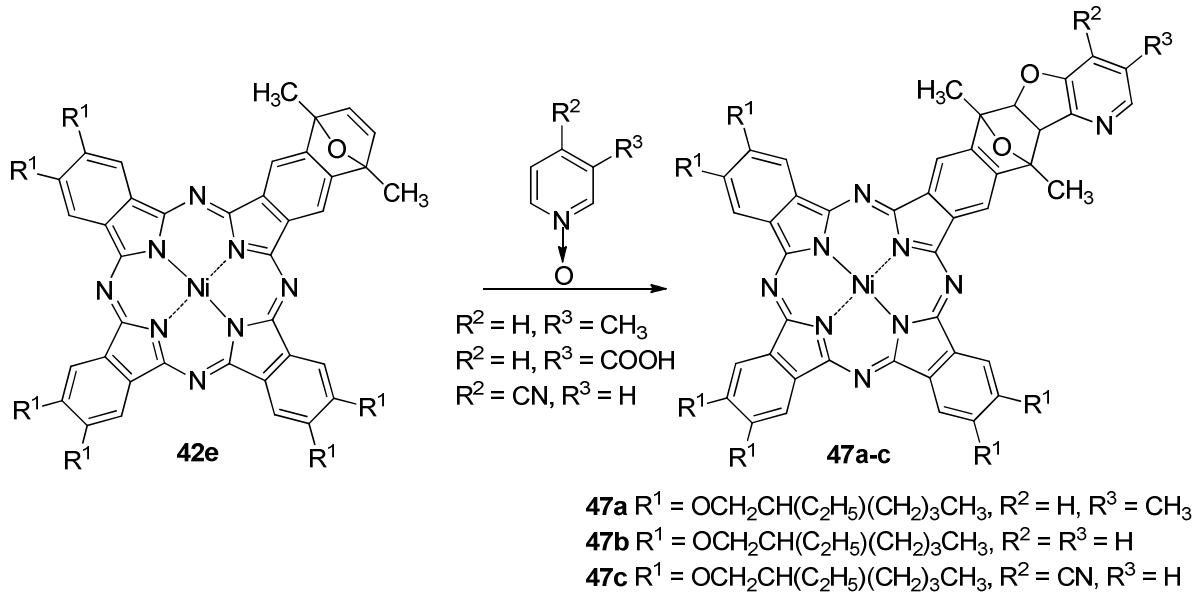
42a, 43a $R^1 = OC_4H_9$, $R^2 = H$, $R^3 = H$
42b, 43b $R^1 = H$, $R^2 = OC_8H_{17}$, $R^3 = H$
42c, 43c $R^1 = H$, $R^2 = OC_{10}H_{21}$, $R^3 = H$
42d, 43d $R^1 = H$, $R^2 = CH_3CH(C_2H_5)(CH_2)_3CH_3$, $R^3 = H$
42e, 43e $R^1 = H$, $R^2 = OCH_2CH(C_2H_5)(CH_2)_3CH_3$, $R^3 = CH_3$
42f, 43f $R^1 = R^2 = OCH_2CH(C_2H_5)(CH_2)_3CH_3$, $R^3 = CH_3$

Scheme 17. Diels-Alder reactions in the preparation of A_3B type asymmetric phthalocyanines.



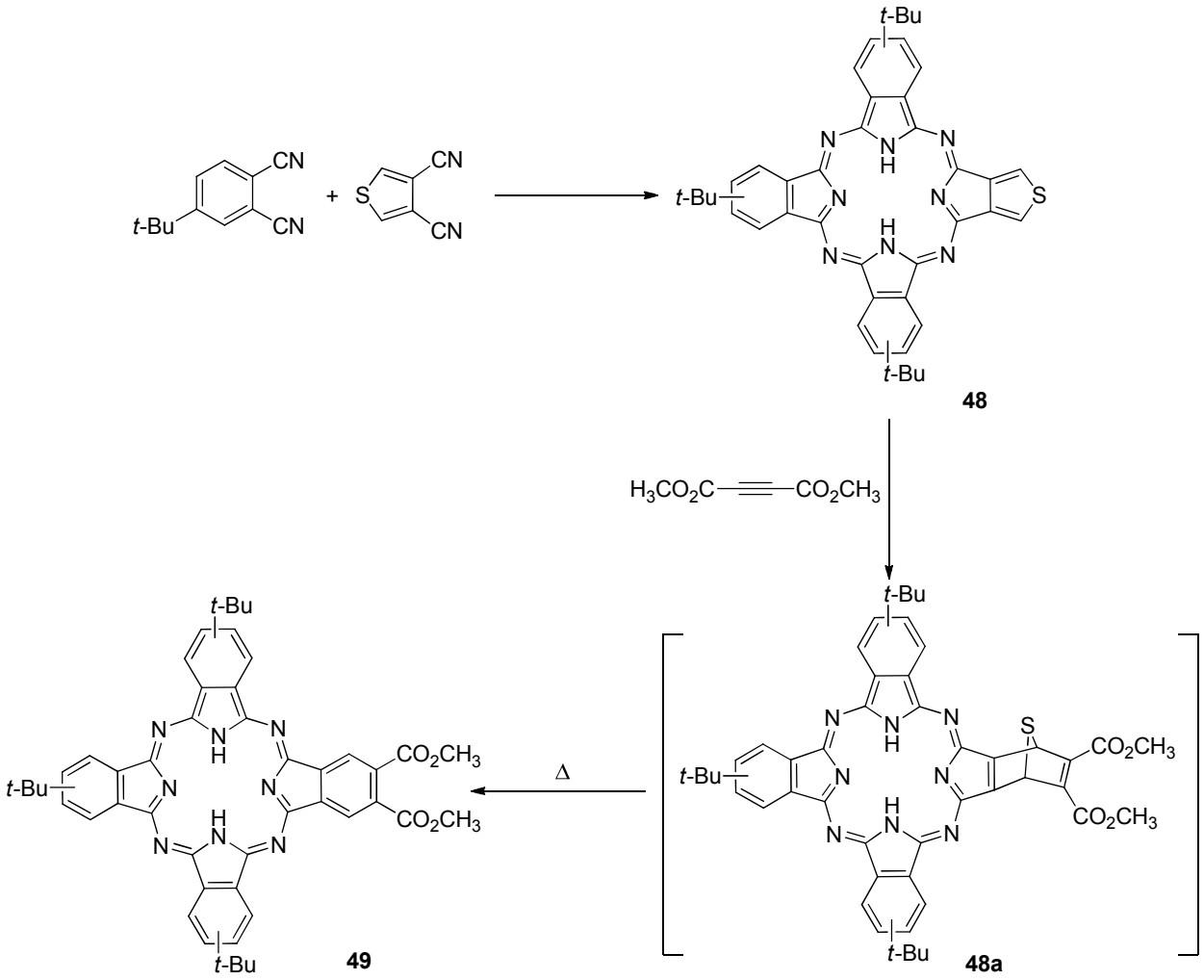


Scheme 18. Formation of the A_3B type phthalocyanine: C_{60} adduct using the Diels-Alder reaction.



Scheme 19. Use of pyridine *N*-oxides in cycloaddition reactions for the preparation of A_3B type asymmetric phthalocyanines.

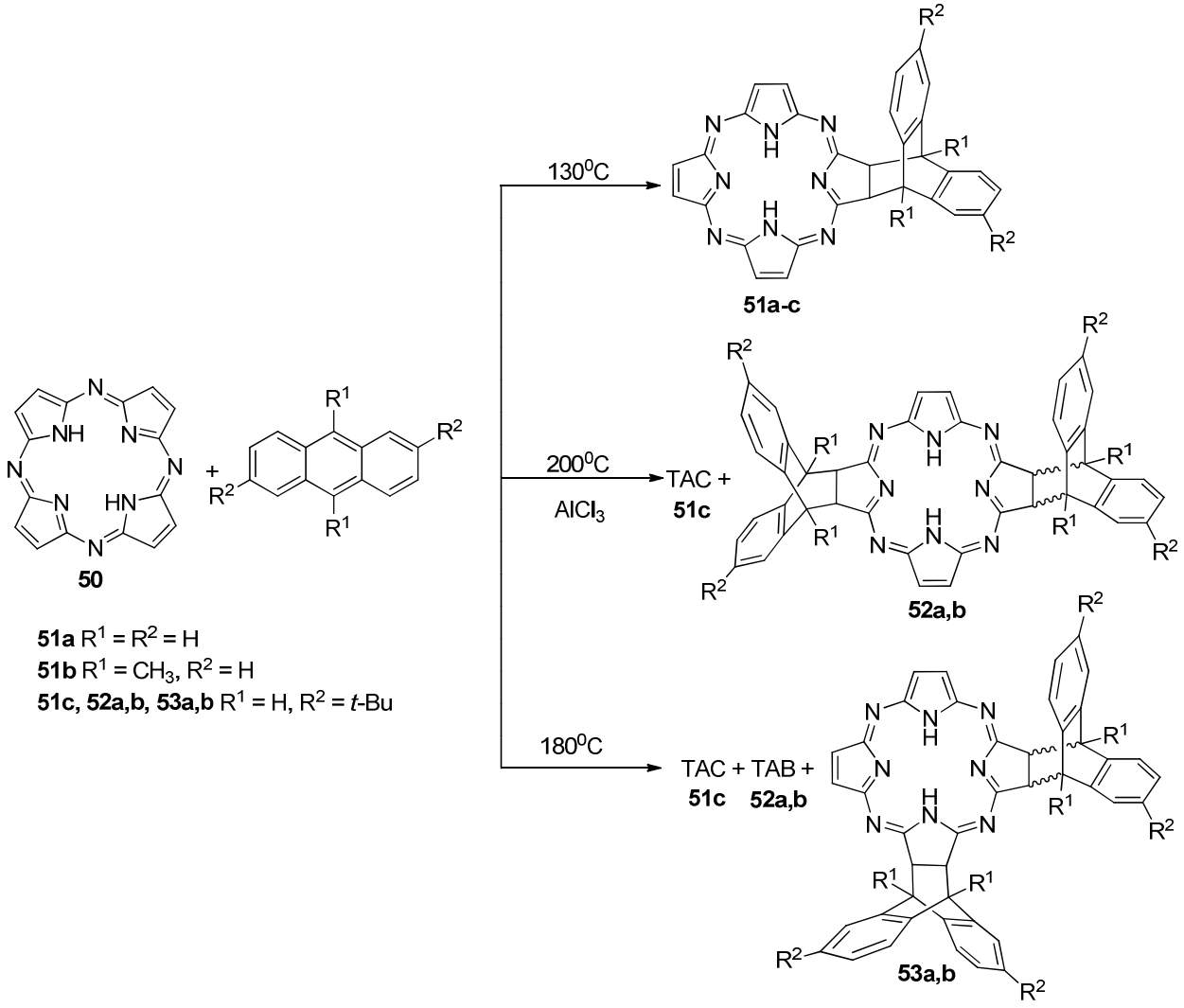
Thiophene-containing phthalocyanine analogues are less explored in cycloaddition reactions compared to the above discussed asymmetric furan systems studied by Hanack and co-workers. Indeed, only one report is available on the Diels-Alder reaction between an A_3B type thiophene-containing system **48** with dimethyl acetylenedicarboxylate (DMAD). An initial tribenzotetraazachlorin-type DMAD adduct **48a** could be transformed into an A_3B phthalocyanine ester **49** by simple heating of the reaction mixture (Scheme 20).[212]



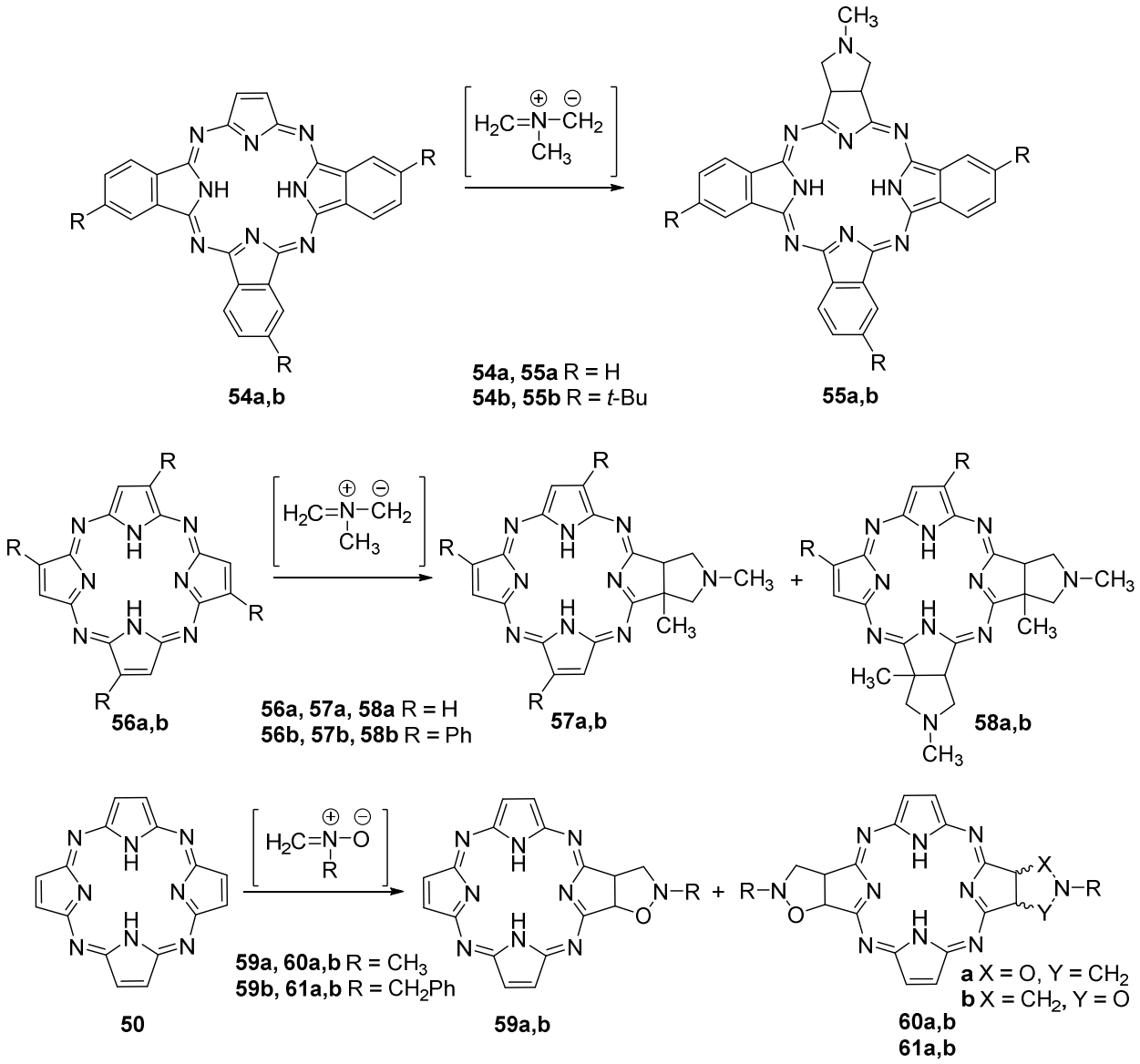
Scheme 20. Use of the thiophene-containing phthalocyanine analogue for the preparation of an A_3B type asymmetric phthalocyanine.

Luk'yanets and co-workers have shown that the unsubstituted porphyrazines (TAPs) could be used as dienophiles in Diels-Alder or [3+2] cycloaddition reactions with a variety of reactants.[213-216] Depending on the reaction temperature and the nature of the diene, tetraazachlorins (TACs), tetraazabacteriochlorins (TABs), and tetraazaisobacteriochlorins (TAiBs) could be isolated from the reaction mixture (Schemes 21, 22).[213-215] For instance, the Diels-Alder reaction between unsubstituted porphyrazine **50** and anthracene derivatives at 130°C results in the selective formation of tetraazachlorins **51**, while raising the reaction temperature leads to the formation of tetraazabacteriochlorins **52** and tetraazaisobacteriochlorins **53** as the major products (Scheme 21);[213] similar results were obtained in the cyclopentadiene series.[216] Similarly, [3+2] cycloaddition reaction between tetraazaporphyrins **50**, **54** or **56** and generated *in situ* dipolar reactants results in formation of respective tetraazachlorins **55**, **57**, or **59** along with tetraazabacteriochlorins **60** and **61** or tetraazaisobacteriochlorin **58** (Scheme 22). Of course, in

the case of tribenzotetraazaporphyrin **54**, the [3+2] cycloaddition reaction selectively leads to the formation of the tetraazachlorin derivative **55**.



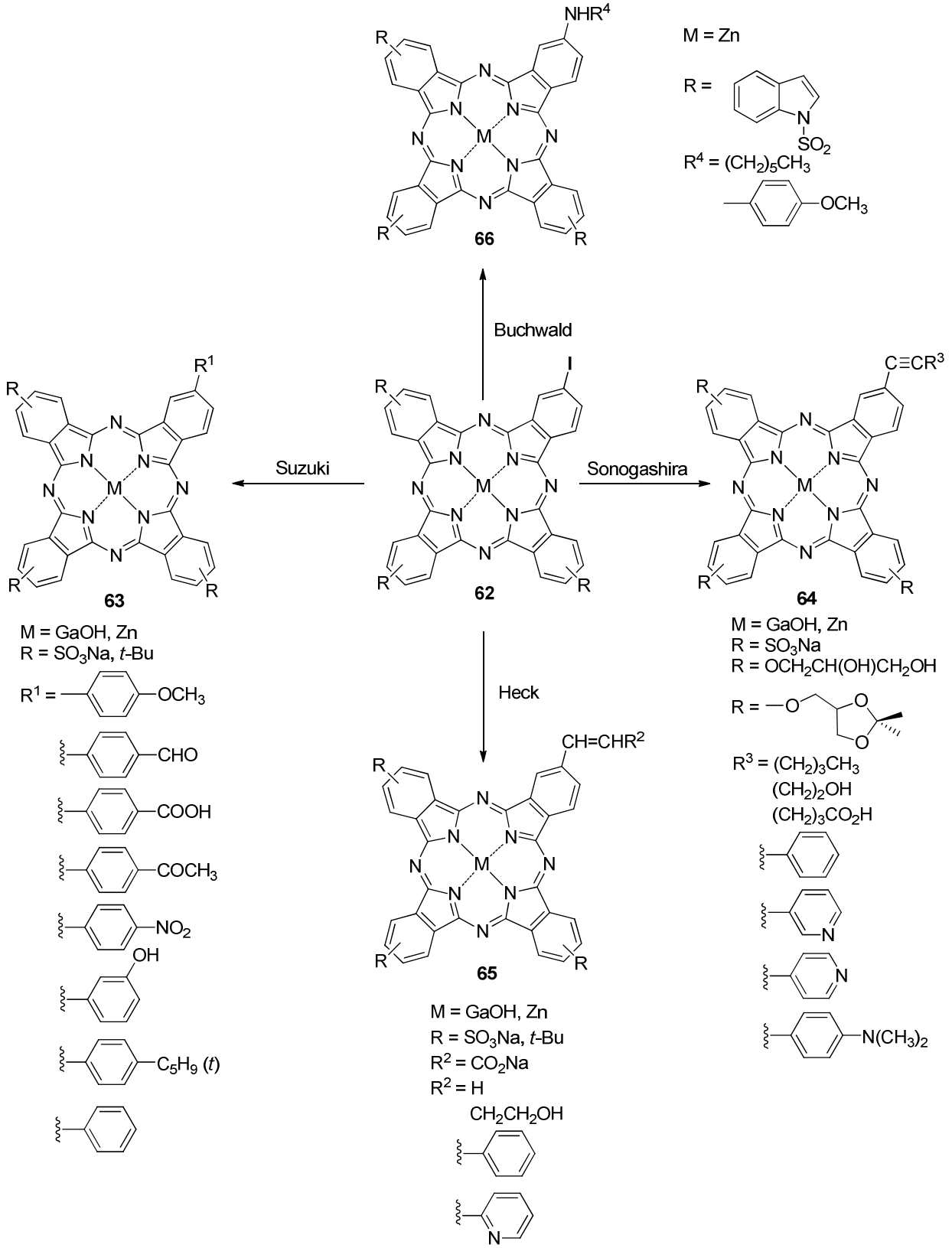
Scheme 21. Preparation of tetraazachlorins, tetraazabacteriochlorins, and tetraazaisobacteriochlorins using the Diels-Alder reaction.



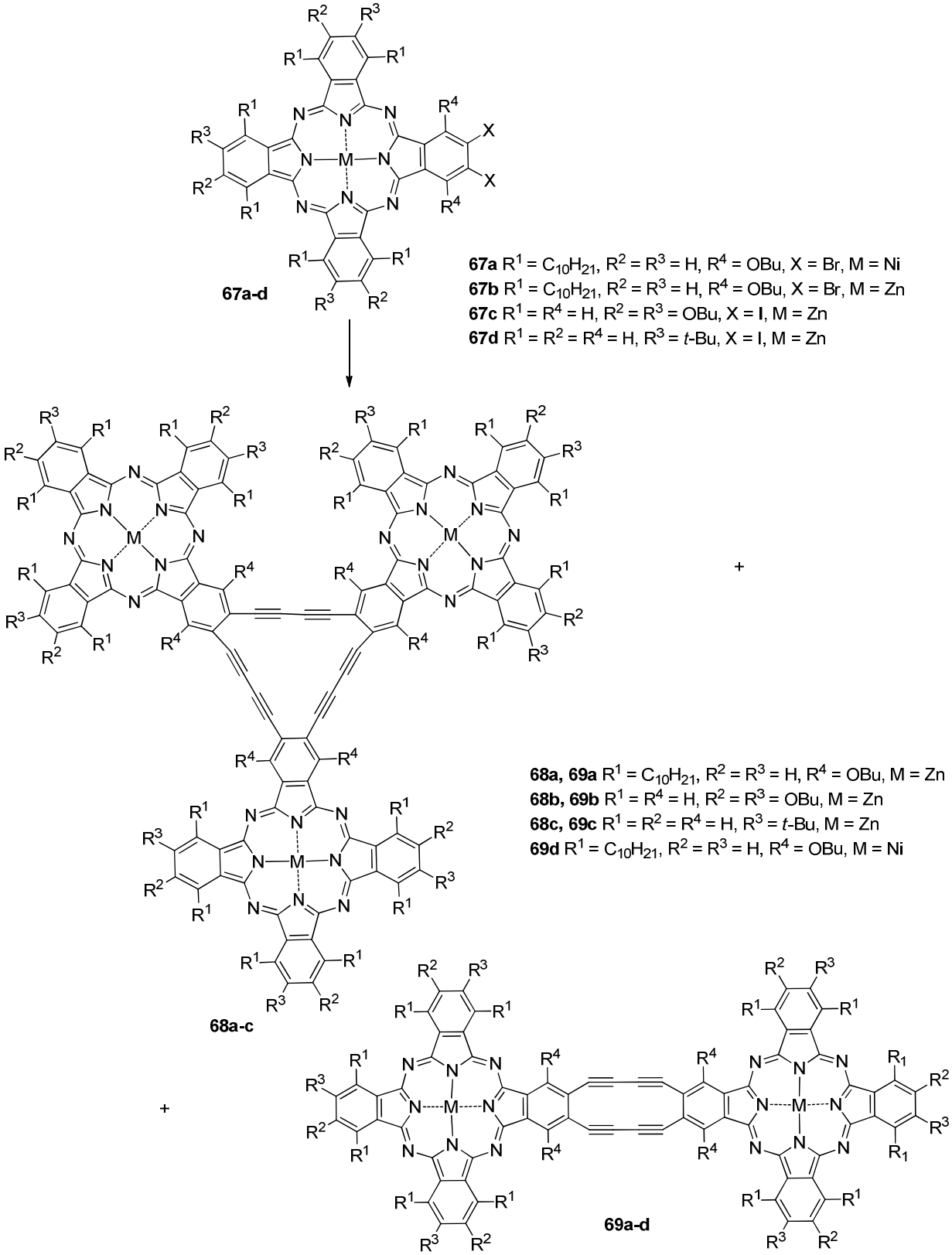
Scheme 22. Using of the [3+2] cycloaddition reaction for preparation of tetraazachlorins, tetraazabacteriochlorins, and tetraazaisobacteriochlorins.

6.2 Cross-coupling approach

The Suzuki, Sonogashira, Heck, Buchwald, and related coupling reactions have become very popular as a universal synthetic approach for the selective transformation of asymmetric phthalocyanines over the past few decades (Schemes 23, 24 and Figures 4, 5).[217-243] In particular, as shown in the laboratories of Torres, van Lier, and many others, the mono-iodo A_3B phthalocyanines **62** can easily be made to undergo a variety of coupling reactions (Scheme 23).[218,220,221,223,227,228,236-242] This precursor can be used for the introduction of direct carbon-carbon bonds as aryl, alkenyl, and alkynyl substituents.[217,219,220,226,234,235] In addition, the Buchwald reaction can be used for carbon-nitrogen bond formation.[218,220,223]



Scheme 23. General strategy for the peripheral modification of asymmetric phthalocyanines using coupling reactions.



Scheme 24. General strategy for the formation of cyclic phthalocyanine dimers and trimers using Glaser and Eglinton reactions.

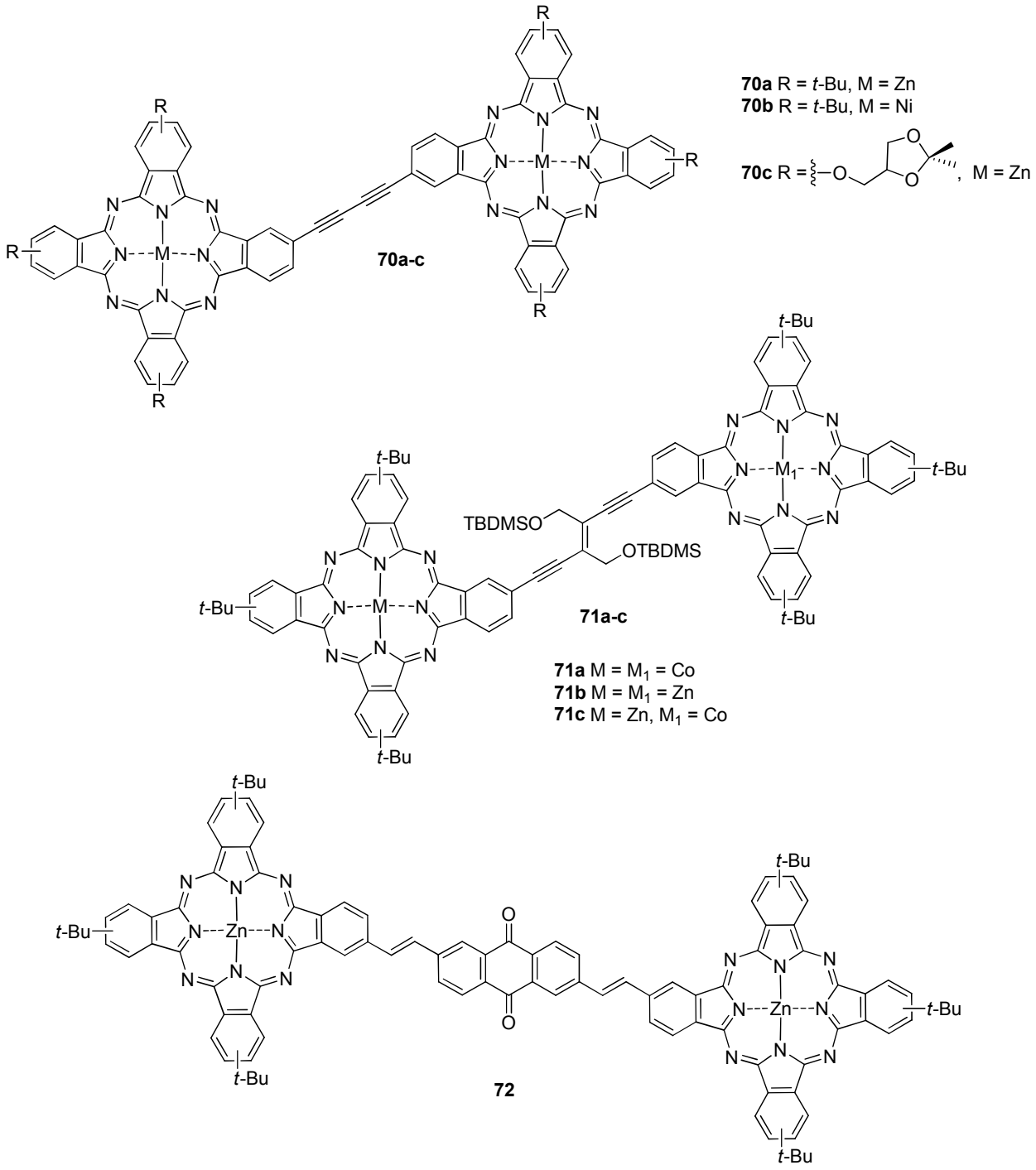
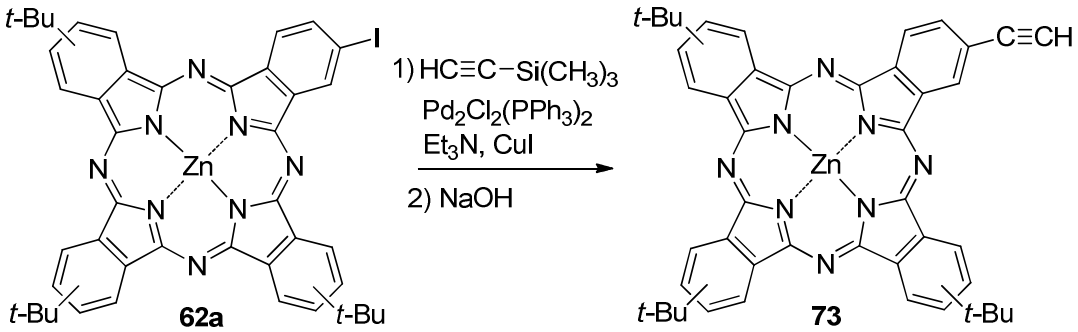


Figure 4. Representative examples of dimeric phthalocyanines prepared using coupling reactions with the incorporation or formation of carbon-carbon triple and double bonds.

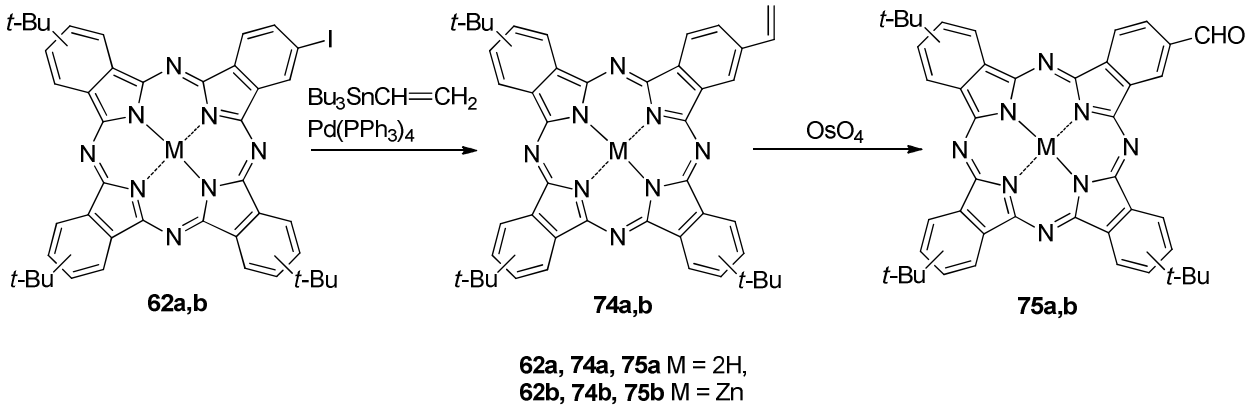
Palladium-catalyzed coupling of the mono-iodo A_3B phthalocyanine **62** with trimethylsilyl-acetylene forms an ethynyl-containing phthalocyanine, which can be deprotected under basic conditions to give the phthalocyanine **73** (Scheme 25) containing a highly reactive terminal C-H

bond.[218,223] A similar result could be achieved by direct introduction of the alkynyl fragment using Stille coupling between the halogen-containing A_3B phthalocyanine **62** and tributylstannyl-acetylene.[218] Asymmetric A_3B phthalocyanines with one or two terminal acetylene substituents are excellent precursors to binuclear ethyne-bridged phthalocyanines **70-72** (Figure 4).[217,219,226,230] In the simplest case, a monoacetylene-substituted phthalocyanine was coupled with the mono iodo-substituted phthalocyanine, giving the ethyne-bridged binuclear compound **70** (Figure 5).[217,219] Another interesting example, which follows a similar synthetic strategy, couples an A_3B type monoiodo-containing phthalocyanine with a monoprotected DEE-containing A_3B phthalocyanine to form (*E*)-1,2-diethynylethene-bridged binuclear phthalocyanine **71** in which each phthalocyanine fragment could have different central metal and different peripheral substituents (Figure 4).[226] Torres' and Cook's research groups utilized Glaser and Eglinton reactions for the preparation of cyclic binuclear and trinuclear diyne-bridged phthalocyanines **68** and **69** (Scheme 24).[224,225,229] In this case, dihalo A_3B type phthalocyanines **67** with neighboring halogen atoms were coupled with the alkyne fragments using a palladium-catalyzed reaction. Once transformed into acetylene-containing compounds with terminal C-H bonds, they undergo self-condensation to form cyclic binuclear or trinuclear compounds.



Scheme 25. Standard approach for the preparation of asymmetric phthalocyanine with a terminal alkyne substituent.

Alkene substituents could be introduced in the phthalocyanine core using a Heck reaction (Scheme 23). Alkene, alkyl, aryl, carboxyl, steroid and the other biologically related functional groups could be introduced by this reaction.[218,220] Similarly, palladium-catalyzed Stille reaction between monoiodo-substituted A_3B phthalocyanines **62** and tributylstannylethylene leads to formation of the vinyl-containing phthalocyanine **74** (Scheme 26).[221] In another synthetic strategy, carboxaldehyde-containing asymmetric phthalocyanine could be used for preparation of alkene-substituted phthalocyanines. The aldehydic A_3B phthalocyanines can be prepared in two steps. First, aldehyde-protected phthalocyanine should be prepared by statistical condensation with aldehyde-protected phthalonitrile because of the low stability of aldehyde group under



Scheme 26. Synthetic strategies for preparation of the asymmetric vinyl-substituted phthalocyanines.

phthalocyanine condensation conditions. The protected A_3B phthalocyanine can then be deprotected to generate the peripheral aldehyde substituent.[221] Another synthetic pathway to prepare aldehyde-containing phthalocyanine **75** is by oxidative cleavage of vinylphthalocyanine (Scheme 26).[221] Prepared by any of the above-mentioned methods, an aldehyde-containing phthalocyanine can then form a desired conjugated alkene-bridged binuclear phthalocyanine in a Wittig reaction.[222] The Heck reaction can also be used to prepare binuclear alkenyl-bridged A_3B phthalocyanines. One such example, phthalocyanine **72**, formed by coupling between a vinyl-containing phthalocyanine and dihaloanthraquinone, is shown in Figure 4.[230]

Direct phthalocyanine to sp^3 carbon bond formation could easily be achieved by the Suzuki coupling reaction. This synthetic approach can be used for preparation of mono- (Scheme 23) as well as di- and tri-nuclear (Figure 5) asymmetric phthalocyanines **76-78**.[218,220,223,237,239]

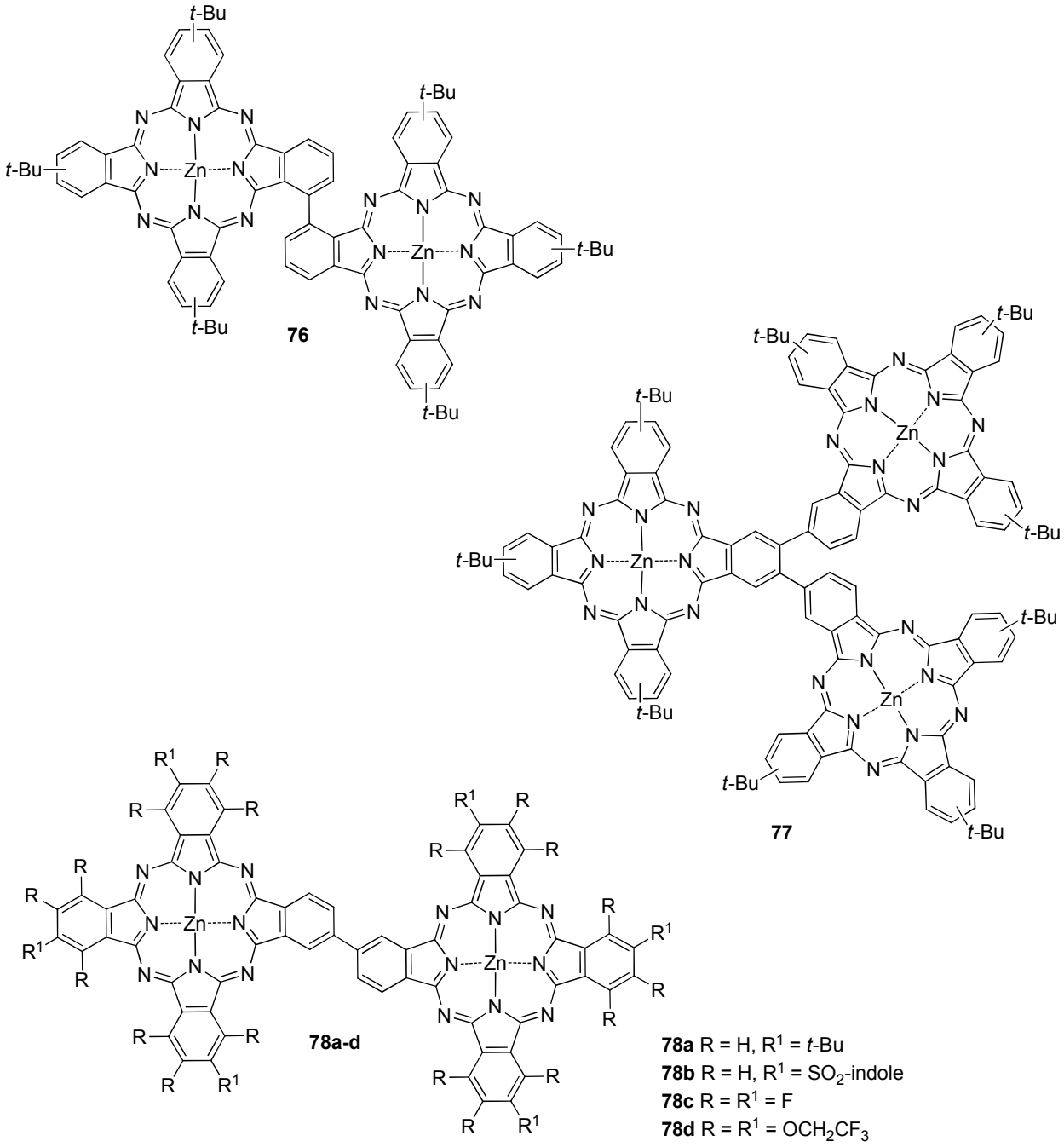


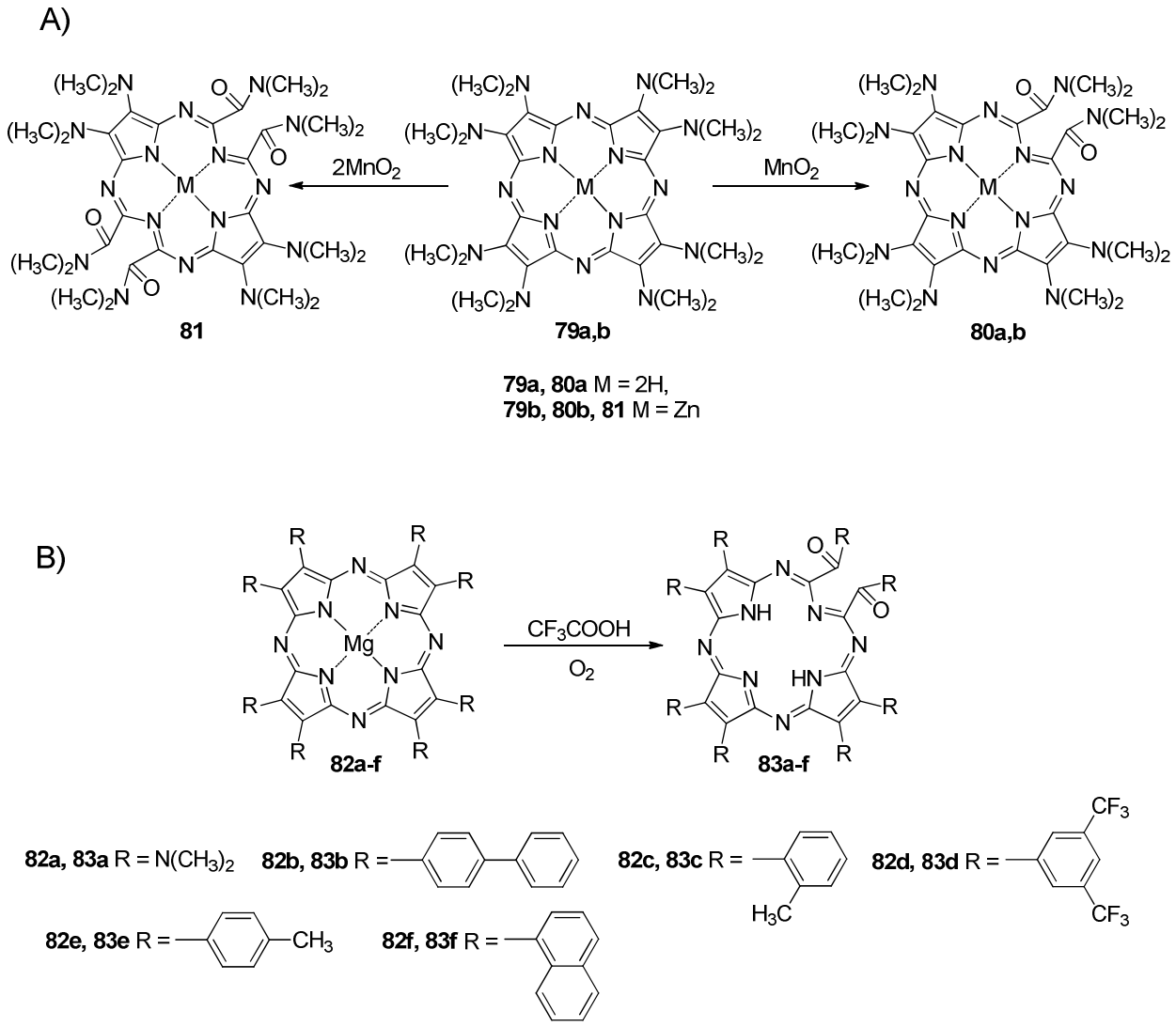
Figure 5. Representative examples of dimeric and trimeric phthalocyanines prepared using coupling reactions with formation of a direct carbon-carbon bond.

6.3 Oxidative transformation strategy

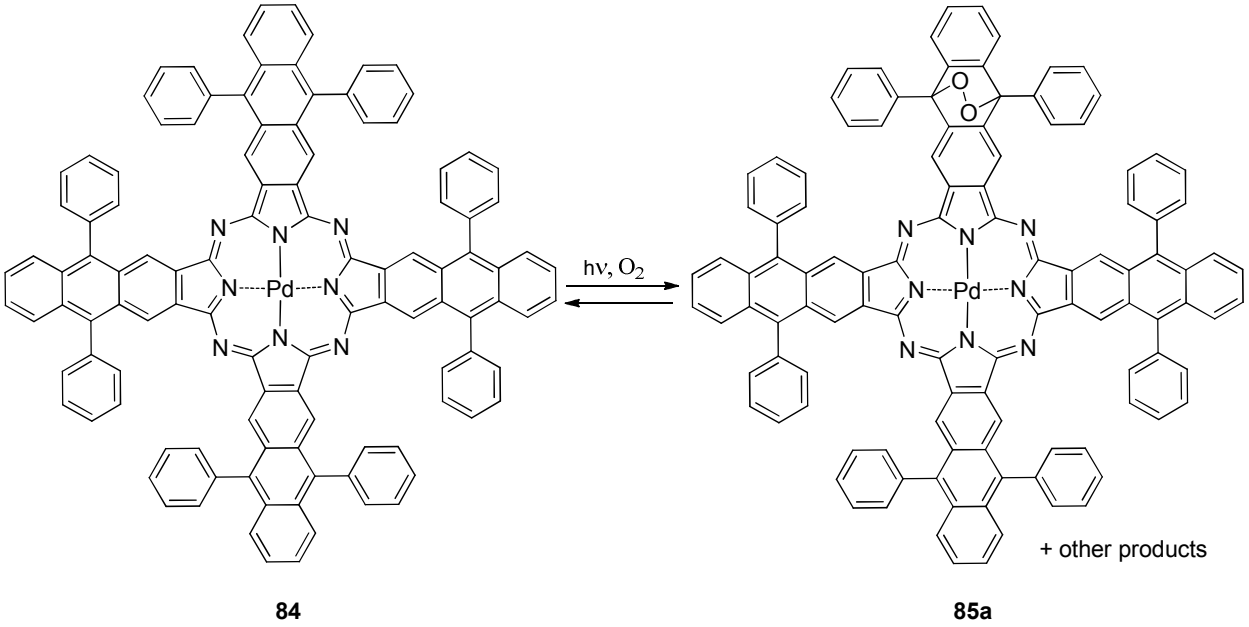
Peripheral oxidation transformation is a very popular approach for preparation of asymmetric functionalized porphyrins,[244-255] but so far has only limited application in phthalocyanine chemistry. Thus, octa(dimethylamino)-substituted tetraazaporphyrins **79** can be oxidized by manganese(IV) oxide to form two different *seco*-porphyrazines **80** and **81** (Scheme 27A).[256-258]

Similarly, trifluoroacetic acid-catalyzed cleavage of different octasubstituted porphyrazines **82** results in aryl- or amino-substituted *seco*-porphyrazines **83** (Scheme 27B).[259-261]

Another interesting oxidation reaction is shown in Scheme 28. In this case, oxygen can form an adduct with anthracyanines **84** to form a variety of symmetric and asymmetric compounds, *e.g.* **85**, which could be reversibly transformed into the starting material.[262]



Scheme 27. Formation of asymmetric *seco*-porphyrazines using oxidation reactions.

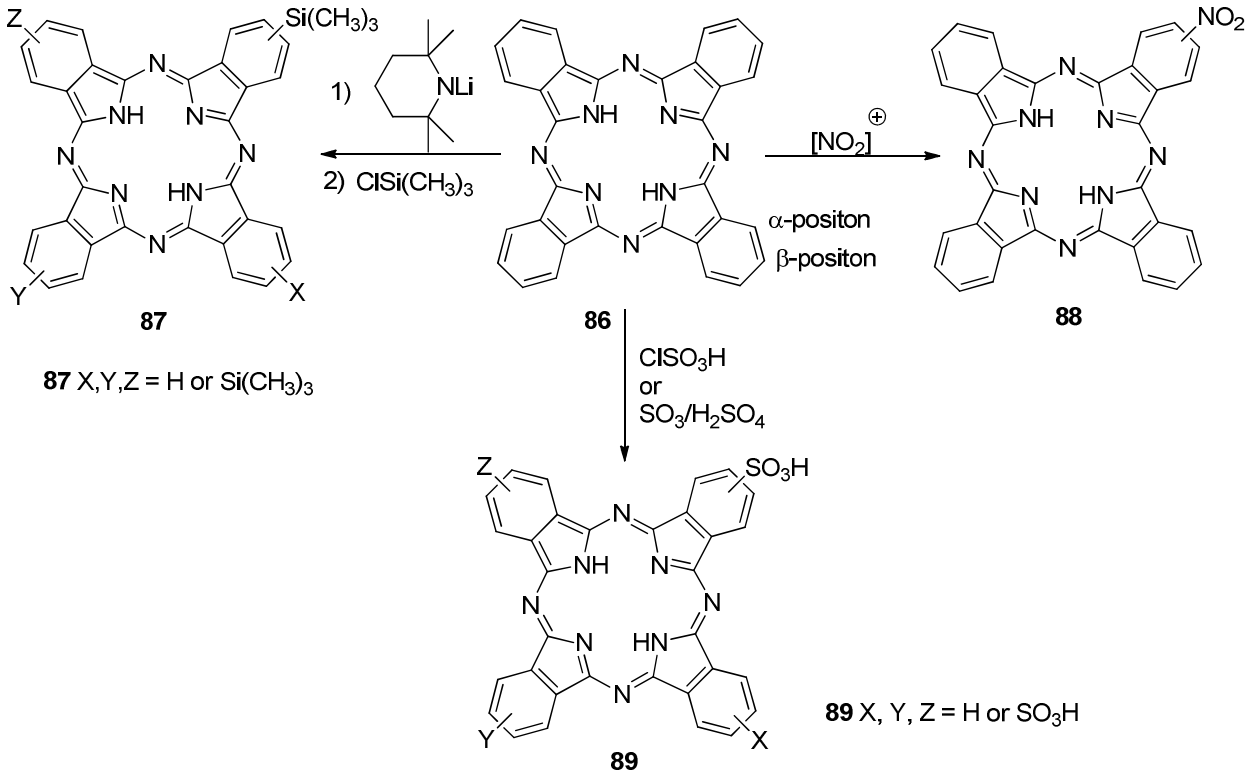


Scheme 28. Reversible partial oxidation of an anthracyanine using molecular oxygen.

6.4 Simple aromatic electrophilic or nucleophilic reactions

In general, aromatic substitution reactions could be used for preparation of asymmetric phthalocyanines. For instance, it was suggested that the nitration of the unsubstituted symmetric phthalocyanine **86** with $[NO_2]^+$ electrophile results in formation of the mononitro A_3B type derivative **88** (Scheme 29).[263] Similarly, depending on the reaction conditions (solvent and the temperature) and reactants used (sulfuric acid, oleum, or chlorosulfonic acid), unsubstituted phthalocyanines **86** can be modified with one up to four sulfogroups located at so-called "peripheral" (β) or so-called "non-peripheral" (α) positions. It has been shown that the asymmetric di- and trisulfo-substituted phthalocyanines **89** prepared in this way are the most active in photodynamic cancer therapy (PDT) (Scheme 29).[23]

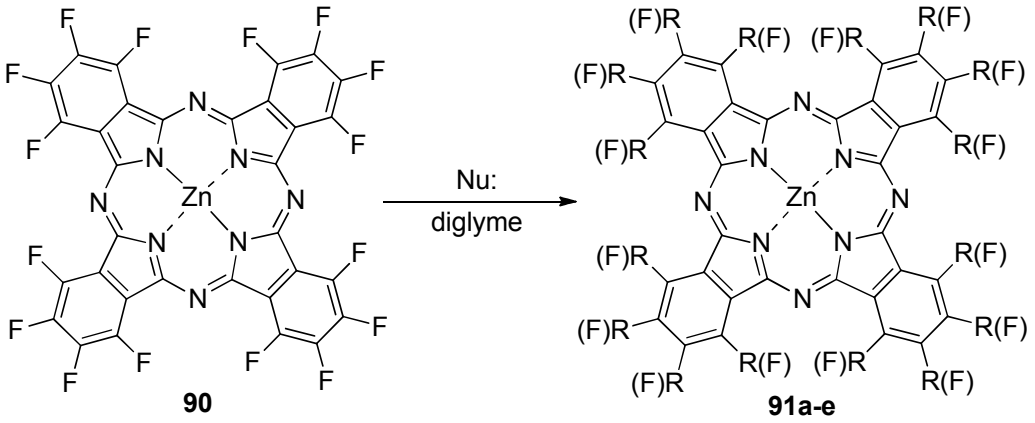
Chen and co-workers have shown that direct lithiation of the unsubstituted phthalocyanines takes place predominantly at non-peripheral (α) positions of the phthalocyanine core.[264] The lithium salts from this reaction can be quenched with a variety of reactants. For instance, when unsubstituted metal-free phthalocyanine **86** was treated with lithium 2,2,6,6-tetramethyl-piperidine and the resulting salt was quenched with chlorotrimethylsilane, a mixture of trimethylsilyl-substituted phthalocyanines, $(Me_3Si)_nPcH_2$ (n = 2-4) **87** was formed. This mixture was further separated using column chromatography to yield asymmetric (n = 2-3) phthalocyanines (Scheme 29).[264]

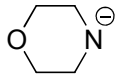
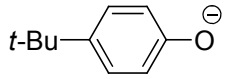


Scheme 29. Formation of asymmetric phthalocyanine derivatives using simple aromatic nucleophilic or electrophilic substitution reactions.

Another synthetic strategy, using nucleophilic aromatic substitution in symmetric phthalocyanines to form asymmetric derivatives, was developed by Leznoff and co-workers.[265-267] This research group showed that the C-F bonds in zinc hexadecafluorophthalocyanine **90** could be replaced by a variety of carbon-, oxygen-, sulfur-, and nitrogen-centered nucleophillic reagents to form mixtures of asymmetric phthalocyanines **91** with various degrees of substitution. The reaction product distribution was studied by mass spectrometry. It was found that such aromatic nucleophilic substitution reaction results in formation of several products rather than individual compounds, although in several cases authors have seen narrowly distributed mixtures of polysubstituted products. The average number of oxygen-, nitrogen-, sulfur-, and carbon-centered nucleophiles present in the reaction product correlates well with their relative nucleophilicity and increases in the order: HNRR′ < RO^- < CN^- < RS^- (Scheme 30).[265,266] The reactivity of **90** was further investigated in aromatic nucleophilic substitution reactions with primary and secondary amines as well as tertiary butyl esters of aminoacids as nucleophiles, using various reaction conditions.[265-267] It was found that asymmetric mono- and di-substituted fluorophthalocyanines are formed under mild reaction conditions, while higher degrees of substitution can be achieved with the amines as the reaction solvents. If diamines were used as the nucleophiles, the reaction products are mixtures of cyclic substituted phthalocyanines,

binuclear and trinuclear (amine bridged) compounds, or mixtures of both of these types depending on the structures of the diamines used.[265-267]



	Nucleophile (R^-)	Average number of replaced fluorine atoms
91a		8
91b		12
91c	$(CH_3)_3CCH_2O^-$	12
91d	CN^-	14
91e	$CH_3(CH_2)_7S^-$	16

Scheme 30. Formation of asymmetric phthalocyanines using partial substitution of the peripheral C-F bonds in hexadecafluorophthalocyanine.

6.5 Peripheral substituent coordination approach

Peripheral substituents in symmetric and asymmetric phthalocyanines can be used for further coordination of transition-metal ions or formation of supramolecular assemblies.[268-275] For instance, asymmetric A_3B type phthalocyanine analogues can easily form mono- or dinuclear phthalocyanine analogues **92-95** when reacted with the main-group or transition-metal ions (Figure 6). Similarly, Ercolani and co-workers have shown that six out of eight available pyridine-type nitrogen atoms in symmetric phthalocyanine could be methylated using standard methylation agents.[274] The remaining two pyridine substituents could be coordinated to transition-metal ions to form asymmetric phthalocyanines **96**. Such platinum-containing compounds are potentially useful for combinational (PDT and chemical cytotoxicity) therapy of cancer (Figure 6). In addition, they easily form DNA intercalates which leads to DNA damage.

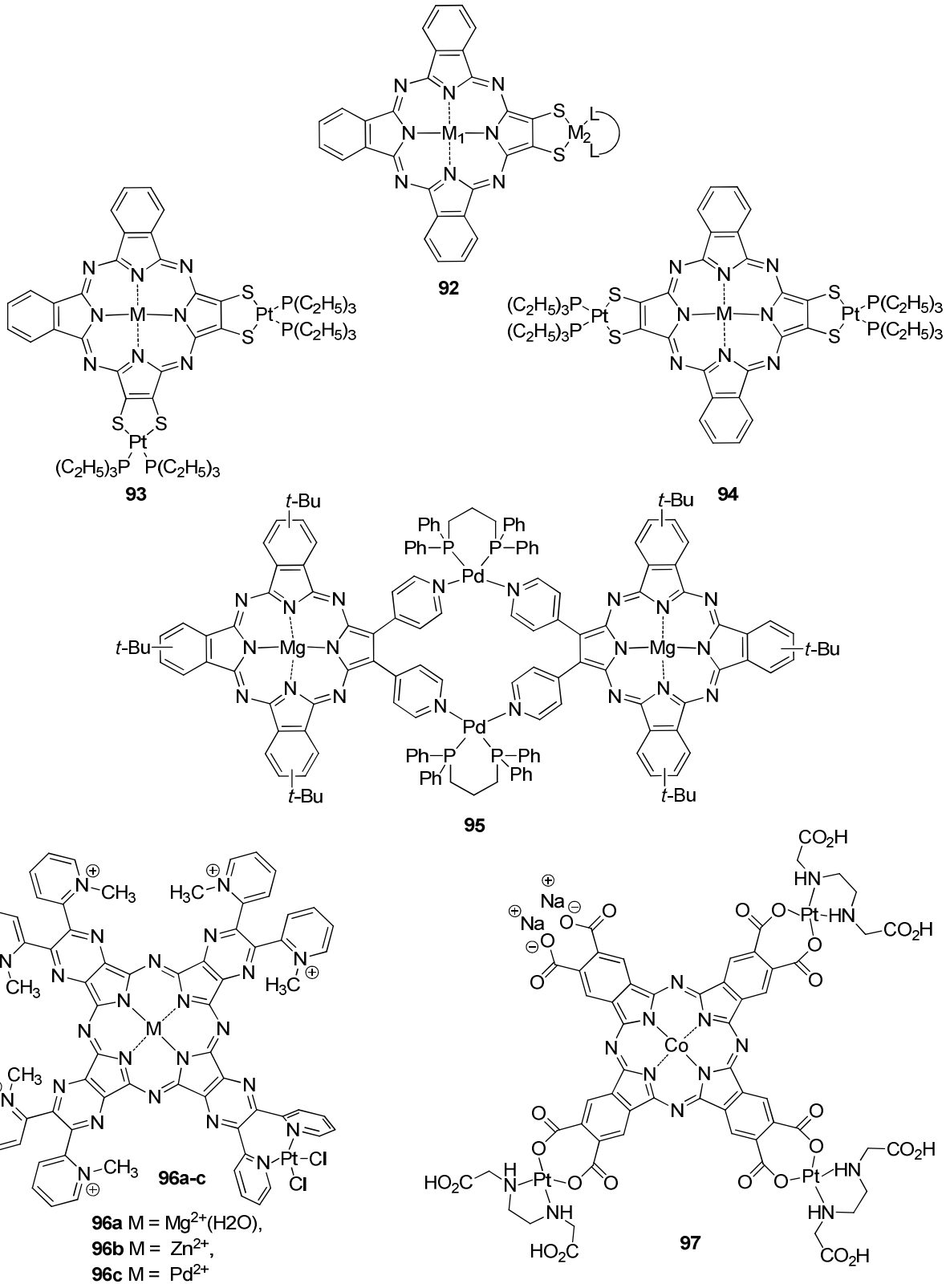
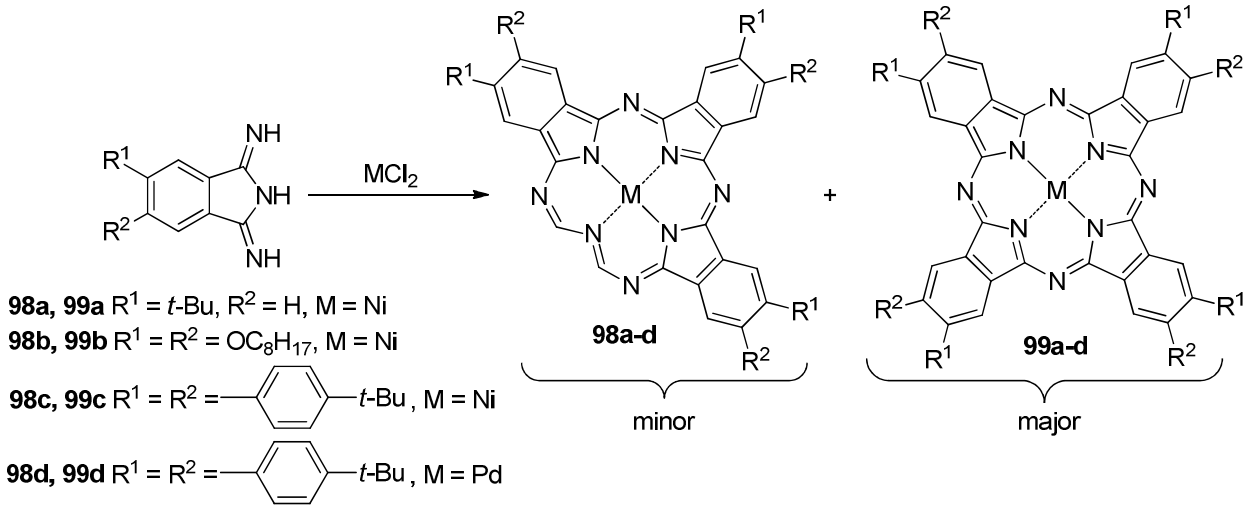


Figure 6. Representative examples of asymmetric phthalocyanines and their analogues formed using the coordination approach.

Kalya and co-workers have shown that analogues with partial platinum ions coordination to octacarboxyphthalocyanines lead to formation of asymmetric platinum-containing derivatives **97** potentially useful in combinational cancer therapy (Figure 6).[276]

7. Miscellaneous Strategies

An interesting set of *seco*-tribenzoporphyrazines was reported in 2012 and later in 2013 (Scheme 31).[277,278] In the initial report, it was found that statistical condensation between 1,3-diiminoisoindolines and 2,5-diamino-3,4-dicyanothiophene in the presence of the nickel salt results in the formation of nickel *seco*-tribenzoporphyrazines **98a,b**.[277] Later on, it was shown that the same nickel and palladium *seco*-tribenzoporphyrazines **98c,d** could be formed even when 1,3-diiminoisoindolines were reacted with the transition-metal salts.[278] The reaction mechanism and the scope of such *seco*-tribenzoporphyrazine core formation is still unclear.

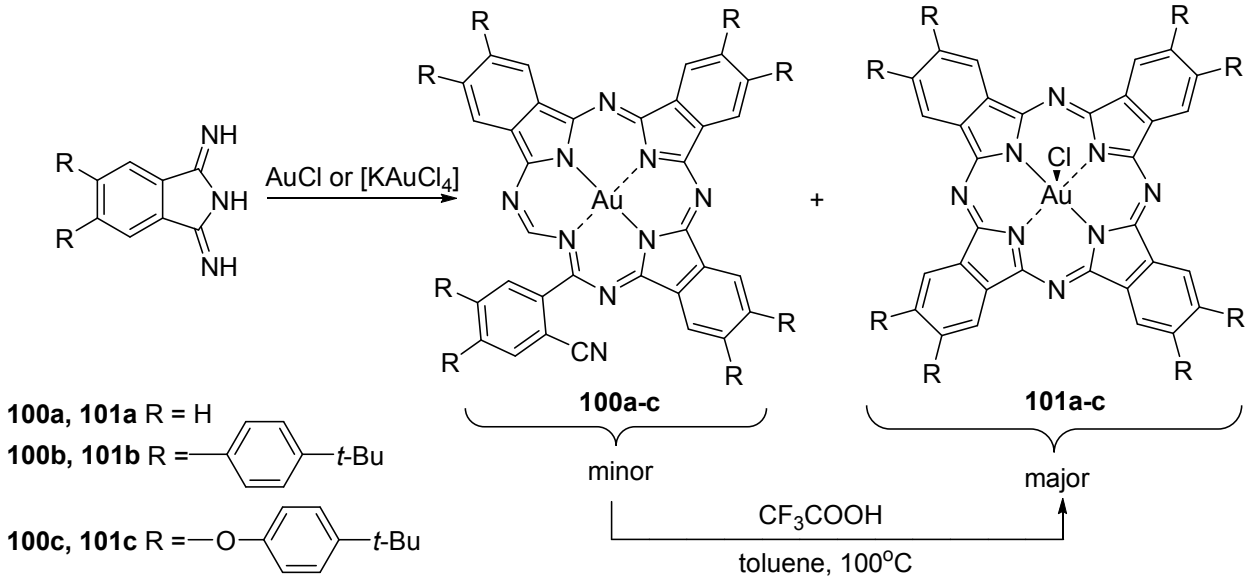


Scheme 31. Formation of *seco*-tribenzoporphyrazines using direct condensation of 1,3-diimino-isoindoline.

Leznoff, Kobayashi, and co-workers shown that the long-time assumed formation of the square-planar Au(II) phthalocyanine **101** does not correctly reflect the reaction products.[279] Indeed, these authors observed formation of the expected PcAuCl complex along with an unusual macrocycle **100**, which can be converted into PcAuCl under specific conditions (Scheme 32).[279]

An interesting conjugated polymer was prepared from the asymmetric thiophene-containing ABAB phthalocyanine. Polymerization was conducted on the thiophene-substituted phthalocyanine at electrochemical oxidation conditions.[280] Finally, two asymmetrically substituted phthalocyanines (**102** and **103**) of A_3B type were prepared by statistical condensation

and used to form double-decker terbium complexes.[281-283] The synthetic routes are tedious, but they provide an access to the derivatives represented in Figure 7.



Scheme 32. Formation of *seco*-tribenzoporphyrazines by direct condensation of 1,3-diiminoisoindoline in the presence of Au^{+} or Au^{3+} salts.

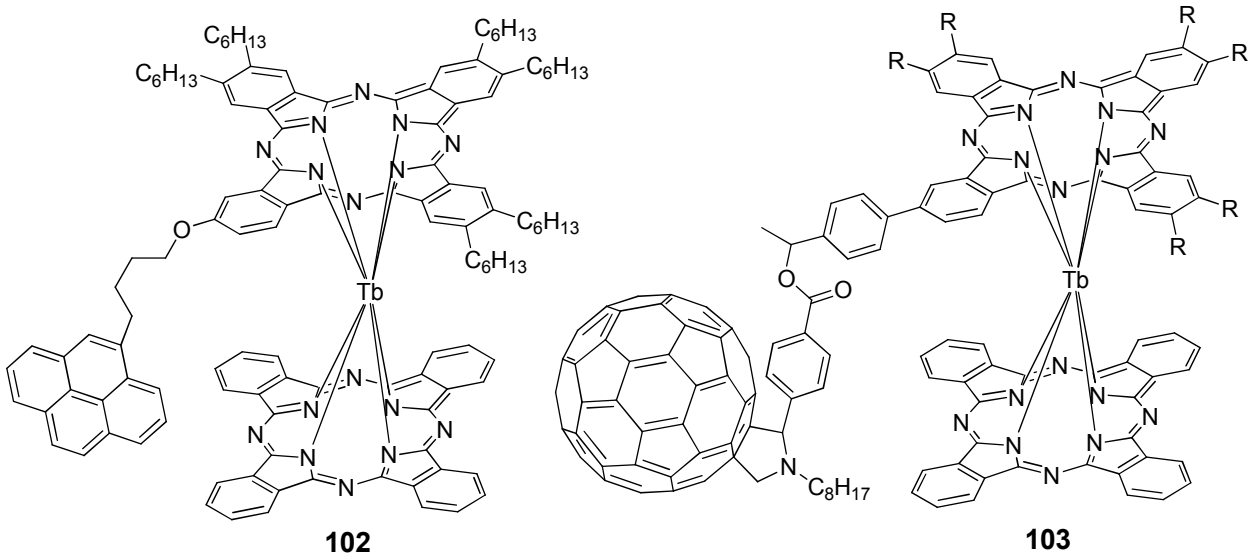


Figure 7. Examples of double-decker complexes which include asymmetric A_3B type phthalocyanine fragments.

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