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Synthesis of Solubility-Enhanced 6,8-Diarylated Dibromodibenzo[*a,j*]Phenazines via Pd-Catalyzed C—H Arylation and Skeletal Rearrangement

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Dedicated to the memory of Professor Masahiko Iyoda

We report the synthesis of a new class of dibromodibenzo[*a,j*]phenazine (DBPHZ) derivatives bearing diaryl substituents at the 6,8–positions. These compounds were obtained through a combination of regioselective Pd-catalyzed C—H direct arylation and oxidative skeletal rearrangement of appropriately functionalized binaphthalenediamines. The compatibility of bromine substituents with the C—H arylation conditions was confirmed, enabling the incorporation of various aryl groups including diphenyl, *tert*-butylphenyl, and 3,5-dimethylphenyl moieties. Crystallographic analysis of a representative compound revealed that the diaryl units adopt a twisted geometry relative to the DBPHZ core. Solubility tests demonstrated that the introduction of diaryl substituents having alkyl groups significantly enhances solubility in common organic solvents such as toluene and chloroform, compared to unsubstituted DBPHZ. Owing to the retained dibromo functionality, the synthesized DBPHZs would serve as valuable synthetic building blocks for constructing π-extended functional organic materials.

1. Introduction

π-Conjugated organic molecules have attracted considerable attention in modern materials science owing to their electroactive and photoactive π-electron systems, which allow for a wide range of electric and optoelectronic functionalities.[1] These molecular systems are widely used as key components in organic field-effect transistors (OFETs),[2] organic light-emitting diodes (OLEDs),[3] and organic photovoltaics (OPVs),[4] and have also been extended to applications in sensing, imaging, and biological devices.[5] Their tunable electronic structures, synthetic modularity, and compatibility with solution-based fabrication techniques make them particularly attractive for next-generation organic materials. As such, the synthesis of structurally novel π-conjugated organic molecules and the investigation of their fundamental physicochemical properties remain central challenges in the field. In parallel with the discovery of new π—conjugated frameworks, the development of synthetic building blocks that enable modular construction of π-extended systems is equally vital. These building blocks serve not only as synthetic intermediates but also as design elements that dictate the optical, electronic, and solubility properties of the resulting materials. Molecular-level engineering of these fragments is essential for advancing both fundamental understanding and practical utility in organic electronics.

As part of our long-standing interest in the development of organic π-conjugated functional materials, we have previously established a synthetic strategy for electron-deficient azaaromatic frameworks featuring a unique U-shaped geometry, specifically dibenzo[*a,j*]phenazine (DBPHZ).[6] Owing to its extended π-conjugation, rigidity, and strong electron-accepting character, the DBPHZ core has been successfully utilized as a variety of high-performance organic photofunctional materials.[7,8] In particular, DBPHZ-based donor–acceptor type compounds have been explored as emitters exhibiting thermally-activated delayed fluorescence (TADF)[9,10] and room-temperature phosphorescence (RTP),[11] both of which are key to achieving high-efficiency OLEDs. Additionally, the structural diversity of the DBPHZ derivatives has enabled their use in stimuli-responsive luminochromic materials applicable to sensing technology.[12] In these studies, 3,11- and 2,12-dibromo-substituted DBPHZs (compounds **1** and **2**, Figure 1) have played a pivotal role as functionalizable intermediates.[6,11] Their twisted donor–acceptor–donor (D–A–D) architectures often suppress π–π stacking, thereby enhancing solubility in organic solvents—a desirable feature for solution-processable devices. To further explore the potential of the DBPHZ framework, π-extension via Pd-catalyzed C—C bond forming cross-coupling reactions (e.g., Suzuki–Miyaura and Sonogashira reactions) represents a promising approach. However, such π–extended DBPHZ derivatives tend to become more planar, which intensifies intermolecular π–π stacking and leads to reduced solubility. Since processibility is a crucial requirement for device fabrication, enhancing the solubility of DBPHZ-based molecules is an important research objective.

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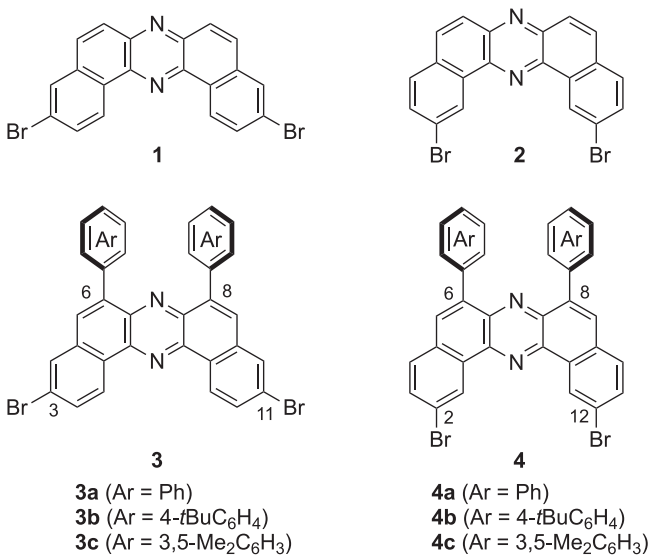


3a (Ar = Ph)
3b (Ar = 4-*t*BuC$_6$H$_4$)
3c (Ar = 3,5-Me$_2$C$_6$H$_3$)

4a (Ar = Ph)
4b (Ar = 4-*t*BuC$_6$H$_4$)
4c (Ar = 3,5-Me$_2$C$_6$H$_3$)

Figure 1. Chemical structures of non-substituted dibromo DBPHZs **1** and **2**, and 6,8-diarylated dibromo DBPHZs **3** and **4**.

In this study, we disclose the synthesis of 6,8-diarylated -DBPHZs derivatives (compounds **3** and **4**, Figure 1) as novel π–conjugated building blocks with improved solubility. Their solubility profiles were systematically evaluated in various organic solvents and compared to those of the unsubstituted analogues (**1** and **2**). The results provide valuable insights into how peripheral aryl substitutions influence molecular solubility, offering a rational design approach for future development of solution-processable π–conjugated materials.

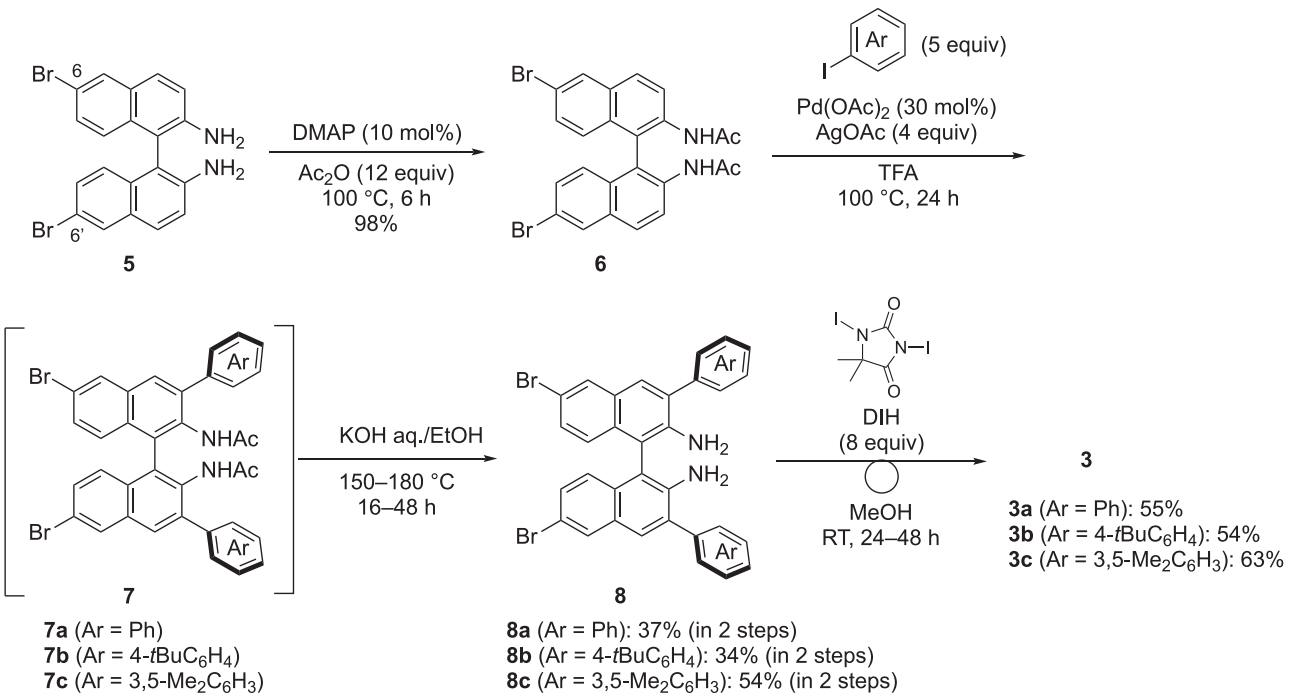
2. Results and Discussion

Previously, we reported the synthesis of a DBPHZ derivative bearing diphenyl substituents at the 6,8-positions.[6] This compound was obtained via an oxidative skeletal rearrangement of a 1,1′-binaphthalene-2,2′-diamine (BINAM) precursor, in which the diphenyl units were introduced adjacent to the diamino groups through a Pd-catalyzed C—H arylation of *N*,*N*′-diacetylated biaryldiamines, as originally developed by Stahl and co-workers.[13] Although there have been a report utilizing a similar C—H arylation strategy on BINAM frameworks to construct axially chiral bibenzo[*b*]carbazole derivatives,[14] no examples had been described for the C—H arylation of BINAM substrates bearing halogen substituents. Thus, it remained uncertain whether such halogen functionalities would be compatible with the Pd-catalyzed reaction conditions. Considering that the C—H arylation proceeds via a Pd(II)/Pd(IV) catalytic cycle, we hypothesized that the C—Br bonds might remain intact throughout the transformation.

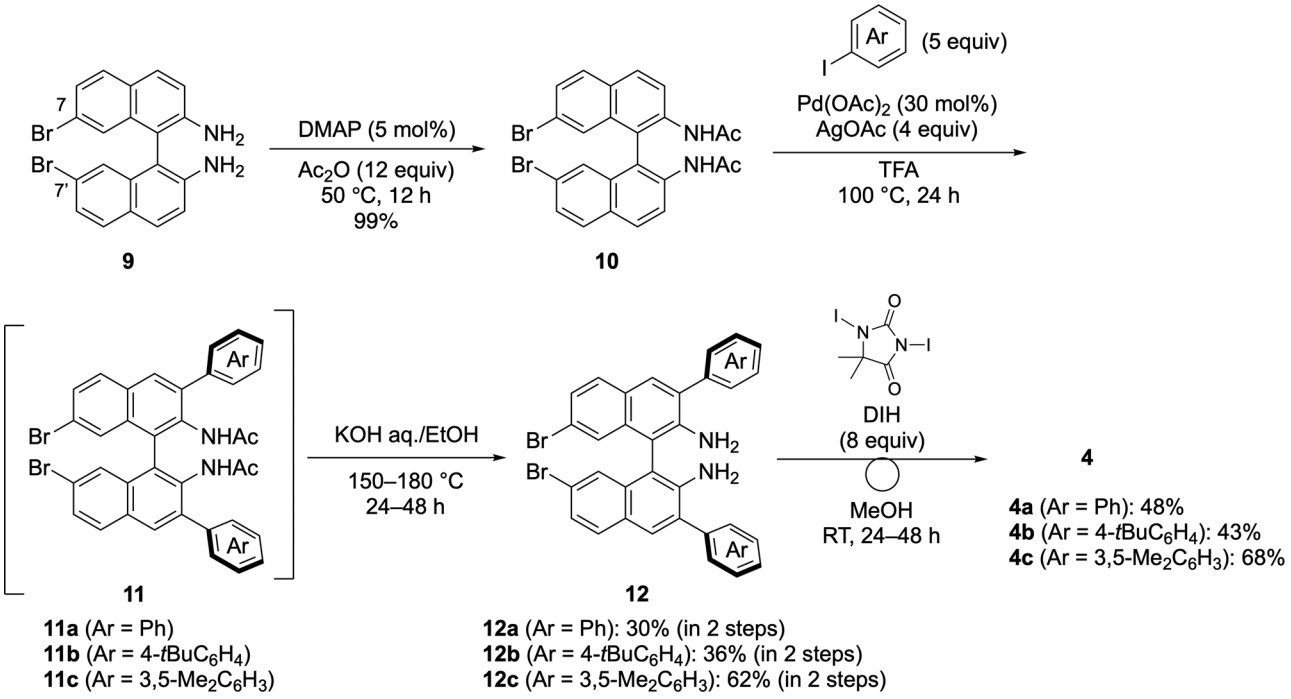
To examine this hypothesis and further explore the synthetic feasibility, we commenced our study by preparing 6,6′-dibromo-BINAM (compound **5**), which we had previously synthesized.[15] This compound was subjected to *N*,*N*′-diacetylation using acetic anhydride as both acylating reagent and solvent, in the presence of *N*,*N*-dimethyl-4-aminopyridine (DMAP) as a nucleophilic catalyst. The reaction proceeded cleanly to afford the desired acetylated derivative **6** in 98% yield (Scheme 1; for the detailed experimental procedures, see the Supporting Information). With compound **6** in hand, we then carried out the *N*-acetyl-directed C—H arylation using iodobenzene (5 equiv) as the arylating reagent, Pd(OAc)$_2$ (30 mol%) as the catalyst, and silver acetate (AgOAc) as the base (4 equiv) in trifluoroacetic acid (TFA) at 100 °C under reflux conditions (Scheme 1).[13] Gratifyingly, the arylation proceeded regioselectively to furnish the diphenylated dianilide **7a**. ^{1}H NMR analysis of the crude product revealed the disappearance of the two sets of doublet signals at 8.34 and 7.96 ppm corresponding to hydrogens at the 3 and 4 positions in **6** and emergence of singlet signal at 8.04 ppm, indicating successful substitution. Moreover, MALDI-TOF mass spectrometry confirmed the presence of two bromine atoms in the product (M^+:[M + 2]$^+$:[M + 4]$^+$= 1:2:1), providing strong evidence that the C—Br bonds remained intact during the transformation. These results suggest that the dibromo functionality is indeed compatible with the Pd(II)/Pd(IV) catalytic cycle employed in the arylation. Despite the successful introduction of aryl groups, the crude product mixture contained inseparable byproducts, possibly due to multiple-arylative side reactions, making purification challenging. Therefore, without isolating the intermediate **7a**, we directly subjected the roughly purified product to alkaline hydrolysis at elevated temperature, which cleanly removed the *N*-acetyl groups to afford the corresponding diamine **8a**. Delightedly, compound **8a** was isolated in 37% yield over the two steps. Subsequently, we carried out an oxidative skeletal rearrangement of **8a** using 1,3-diiodo-5,5-dimethylhydantoin (DIH) in methanol at room temperature. This transformation proceeded smoothly to yield the desired 6,8-diphenylated 3,11-dibromo-DBPHZ derivative **3a** in good isolated yield (Scheme 1).

Encouraged by this result, we further explored the synthesis of structurally modified analogues to investigate the synthetic protocol generality. Using 4-*tert*-butyl-iodobenzene as the arylating reagent under analogous reaction conditions, the C—H arylation furnished the corresponding diarylated intermediate **7b**, as estimated by ^{1}H NMR spectroscopy. However, purification was again hampered by inseparable byproducts. Nevertheless, the roughly purified product was directly subjected to hydrolysis to afford diamine **8b**, which underwent oxidative skeletal rearrangement to provide the corresponding desired product **3b** in good yield. Similarly, C—H arylation using 3,5-dimethyl-substituted iodobenzene proceeded regioselectively to afford the desired diarylated intermediate **7c**. Subsequent hydrolysis and rearrangement gave the 3,5-dimethylphenyl-substitued DBPHZ compound **3c** in high yield. These results demonstrate the robustness and modularity of our synthetic strategy for producing diverse 6,8-diarylated DBPHZ derivatives.

Encouraged by successful synthesis of the 3,11-dibromo-substituted DBPHZ derivatives (compounds **3**), we next turned our attention to the preparation of their regioisomeric analogues, namely the 2,12-dibromo-substituted DBPHZ derivatives (compounds **4**). These compounds were expected to offer structural diversity as well as complementary properties for future structure–property relationship studies. We employed a



Scheme 1. Synthetic routes to 6,8-diaryl-3,11-dibromodibenzophenazines **3**.



Scheme 2. Synthetic routes to 6,8-diaryl-2,12-dibromodibenzophenazines **4**.

synthetic strategy analogous to that used for compounds **3**, as outlined in Scheme 2 (for the detailed experimental procedures, see the Supporting Information). The required starting material, 7,7′-dibromo-substituted BINAM **9**, was prepared according to a previously reported protocol.[16] This diamine was subjected to *N*,*N*′-diacetylation using acetic anhydride in the presence of DMAP catalyst to afford the corresponding dianilide **10** in quantitative yield. Subsequent Pd-catalyzed C—H arylation of **10** was conducted using the same set of iodoarene coupling partners as before. The reactions proceeded regioselectively to afford the desired diarylated intermediates **11**. However, consistent with our earlier observations, the isolation of analytically pure product was complicated by the formation of inseparable byproducts, likely due to overarylation. To overcome this limi-

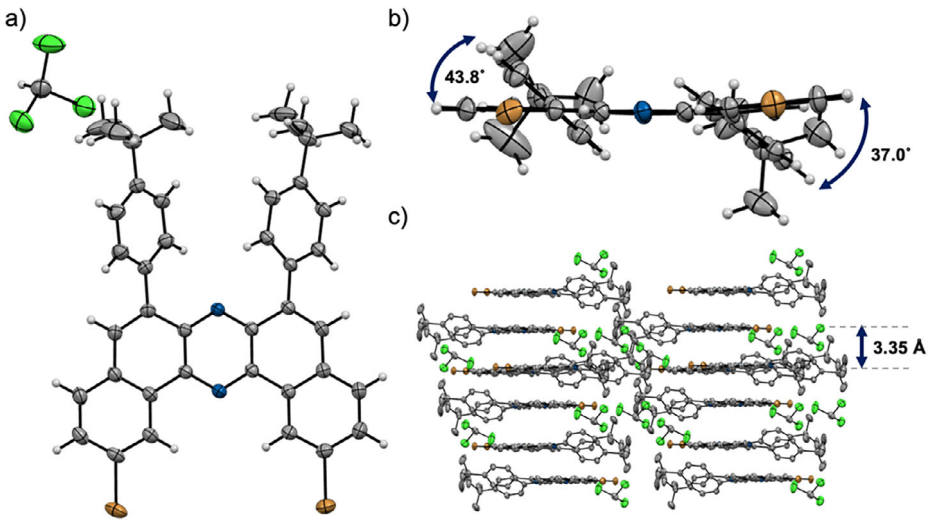


Figure 2. Crystallographic analysis of **4b**. a) top view; b) side view; c) packing structure.

tation, the roughly purified product was directly subjected to alkaline hydrolysis at elevated temperature, effectively removing the *N*-acetyl groups to furnish the corresponding diamines **12**. These intermediates were subsequently treated with DIH in methanol, smoothly affording the 6,8-diarylated 2,12-dibromo-DBPHZ regioisomers **4** in good yields.

To gain deeper insight into the molecular geometry and solid-state packing behavior of the newly synthesized diarylated DBPHZ derivatives, we attempted to grow single crystals of compounds **3** and **4**. Despite several crystallization trials, only compound **4b** yielded single crystals suitable for X-ray diffraction analysis. Crystals were successfully obtained by slow evaporation from a chloroform solution under ambient conditions.[17] The crystallographic analysis revealed that both *tert*-butylphenyl substituents are considerably twisted relative to the central DBPHZ plane (Figure 2a). The dihedral angles between the DBPHZ core and the *tert*-butylphenyl substituents were measured to be 43.8 ° and 37.0 °, respectively (Figure 2b). This significant torsion likely arises from steric repulsion between the closely positioned aryl rings and the planar π–conjugated DBPHZ core, resulting in a non–coplanar arrangement. In the crystal, compound **4b** adopts an anti-parallel dimeric packing motif, wherein two DBPHZ molecules align face-to-face with an interplanar distance of 3.35 Å between the aromatic cores (Figure 2c). This arrangement appears to minimize steric congestion between the adjacent aryl substituents while maintaining close π–π interactions.

Having successfully synthesized new families of diaryl-substituted dibromo DBPHZ derivatives, we next turned our attention to evaluating their solubility in organic solvents (for the detailed procedures, see the Supporting Information). Understanding solubility behavior is critical, as it directly influences solution processability, film formation, and ultimately, applicability in optoelectronic device fabrication. The solubility data for compounds **3** and **4** are visualized in Figure 3. Focusing on the 6,8-diarylated 3,11-dibromo-DBPHZs series (compounds **3**), although diethyl ether was not a good solvent for any of the compounds, we observed clear trends in solubility enhancement in toluene and chloroform compared to the unsubstituted parent compound **1** (Figure 3a). The diphenyl-substituted compound **3a** exhibited approximately 1.3-fold higher solubility in toluene and a modest 1.1-fold increase in chloroform relative to compound **1**. Further structural modification by introducing a bulky *tert*-butyl group on the phenyl ring, as in compound **3b**, led to a dramatic improvement in solubility—up to 6.2-fold in toluene and over 11-fold in chloroform. Compound **3c**, bearing two 3,5-dimethylphenyl substituents, also exhibited significantly improved solubility in both toluene and chloroform compared to **1**. Similarly, for compounds **4**, a significant enhancement in solubility was observed compared to the unsubstituted molecule **2** (Figure 3b). The introduction of two phenyl groups alone did not markedly change the solubility, but the presence of aryl groups bearing alkyl substituents (**4b** and **4c**) significantly increased solubility, up to fivefold in chloroform. Given that, in both series **3** and **4**, the incorporation of diphenyl substituents alone did not result in a substantial increase in solubility, and considering the anti-parallel stacking mode observed in the single crystals, we infer that alkyl groups enhance solubility through increased London dispersion interactions, which effectively outcompete the inherently strong π–π interactions.

3. Conclusion

In conclusion, we have successfully developed a synthetic strategy for accessing DBPHZs derivatives bearing diaryl substituents at the 6,8-positions. This was achieved through a combination of regioselective Pd-catalyzed C—H direct arylation and oxidative skeletal rearrangement of suitably functionalized binaphthalenediamines. The introduction of sterically demanding diaryl substituents bearing alkyl groups led to a substantial enhancement in solubility in common organic solvents such as toluene and chloroform. This improvement could be attributed to enhanced London dispersion interactions rather than to the twisted spatial orientation of the peripheral aryl groups. Importantly, the retention of dibromo functionalities in the

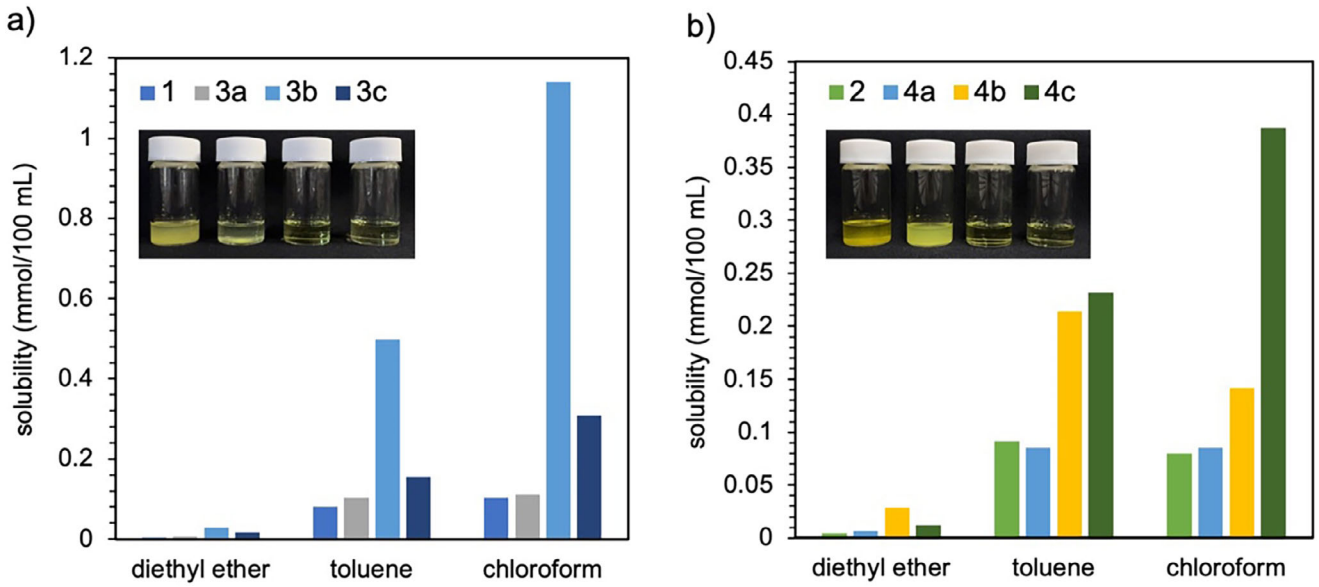


Figure 3. Solubility of a) **1** and **3**; b) **2** and **4** in various organic solvents (25 °C, mmol/100 mL). The inset photographs show the appearance of each compound (5 mg) in chloroform (5 mL) (from left to right, a) **1**, **3a**, **3b**, and **3c**; b) **2**, **4a**, **4b**, and **4c**).

final products offers synthetic versatility, positioning these compounds as valuable intermediates for further π–extension and functionalization. Ongoing efforts in our laboratory are focused on leveraging these building blocks to construct advanced π–conjugated materials.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

Keywords: Building blocks · Phenazines · Skeletal rearrangement · Solubility; π-conjugated molecules

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