

Diversity-Oriented Synthesis of [2.2]Paracyclophane-derived Fused Imidazo[1,2-*a*]heterocycles by Groebke-Blackburn-Bienaymé Reaction: Accessing Cyclophanyl Imidazole Ligands Library

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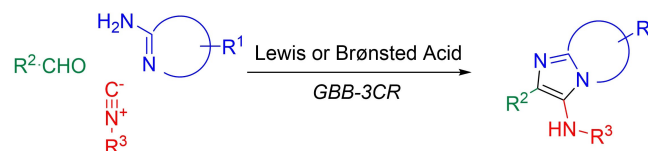
Abstract: This report describes the synthesis of a [2.2]paracyclophane-derived annulated 3-amino-imidazole ligand library through a Groebke-Blackburn-Bienaymé three-component reaction (GBB-3CR) approach employing formyl-cyclophanes in combination with diverse aliphatic and aromatic isocyanides and heteroaromatic amidines. The GBB-3CR process gives access to skeletally-diverse cyclophanyl imidazole ligands, namely 3-amino-imidazo[1,2-*a*]pyridines and imidazo[1,2-*a*]pyrazines. Additionally, a one-pot protocol

for the GBB-3CR by an in situ generation of cyclophanyl isocyanide is demonstrated. The products were analyzed by detailed spectroscopic techniques, and the cyclophanyl imidazo[1,2-*a*]pyridine was confirmed unambiguously by single-crystal X-Ray crystallography. The cyclophanyl imidazole ligands can be readily transformed to showcase their useful utility in preparing N,C-palladacycles through regioselective *ortho*-palladation.

The co-facially stacked, π -conjugated, and prochiral [2.2]paracyclophane (cyclophanyl; PCP) has been the focus of extensive research due to unique structural features and inherent planar chirality upon selective substitution.^[1] Its rigid, distorted geometry and the resulting proximity of the stacked benzene rings lead to transannular communication between the π -systems.^[2] The selective introduction of substituents on the benzene decks provides various derivatives for applications in catalysis, asymmetric synthesis, material science, and polymer

chemistry. Our research group and others have a long-standing interest in enlarging the chemical space around the PCP scaffold. A series of novel PCP-based molecular systems and their applications as a practically useful class of ligands and catalysts to facilitate selective asymmetric transformations has been demonstrated.^[3] However, due to its unusual chemical reactivity caused by transannular effects, the PCP scaffold poses hurdles and synthetic challenges. Especially the incorporation of heteroaromatic residues is quite challenging using conventional synthesis strategies.^[4] Employing a multicomponent reaction (MCR) approach can give access to a broad spectrum of structurally diverse unprecedented fused heteroaromatic PCP-derivatives.

The Groebke-Blackburn-Bienaymé three-component reaction (GBB-3CR),^[5] one of the representative MCR-transformations based on isocyanide chemistry,^[6] has enormously contributed to the progress of organic synthesis, medicinal chemistry, and materials science.^[7] The GBB-approach combines three components; an aldehyde, an α -aminoazine, and an isocyanide, in the presence of a Lewis or Brønsted acid to constitute the privileged scaffolds of *N*-bridgehead imidazoheterobicycles in a single step (Scheme 1). Predictive reactivity, selectivity control,



Scheme 1. Synthesis of fused imidazoles by one-pot Groebke-Blackburn-Bienaymé three-component reaction: heteroaromatic amidines (Blue), formyl PCP-component (Green), and diverse aliphatic/aromatic isocyanides (Red).

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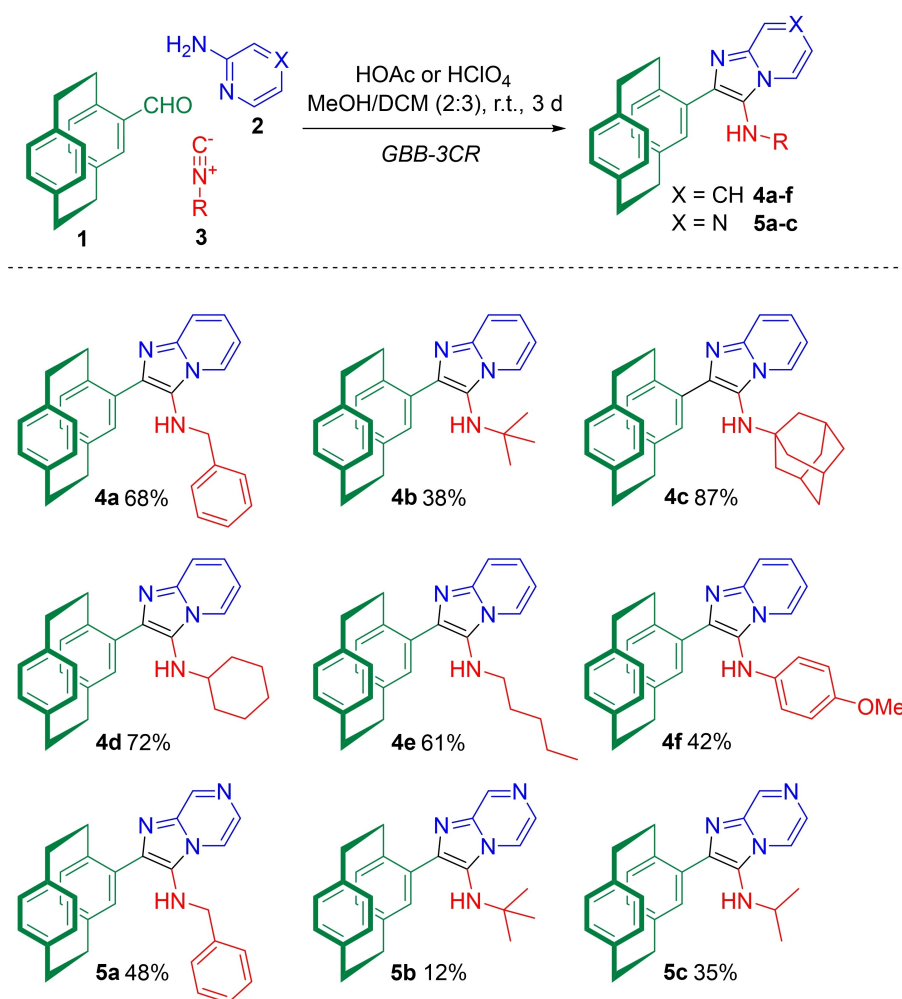
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and the choice of largely available precursors used in GBB-3CR are the particularly attractive aspects that bring synthetic diversity and functional versatility to the fused-imidazo[1,2-*a*]-heterocyclic scaffolds,^[8] which are largely employed as key intermediates in the synthesis of diverse biological targets.^[9] Advancing the GBB-approach, various protocols and method developments have been reported in recent years that offer a diverse library of molecules by combining multiple molecular fragments within the imidazo[1,2-*a*]pyridines aiming for diverse application perspectives in bio-,^[10] and emerging materials.^[11] This work sought to develop a GBB-3CR approach for the diversity-oriented synthesis of PCP-based imidazo[1,2-*a*]pyridyl-substituted ligands by modular variation of the three participating components. This allows the facile introduction of a sophisticated residue to the PCP-core and a chiral element into the non-chiral imidazo[1,2-*a*]pyridine-based fluorophores, particularly interesting for chiroptical application possibilities.^[12]

Initially, the optimal reaction conditions were evaluated for the GBB-3CR using 4-formyl-PCP (**1**), 2-aminopyridine (**2**), and *tert*-butyl isocyanide (**3a**). Due to the low solubility of **1**, a mixture of MeOH/DCM was used. As a catalyst, glacial acetic

acid and perchloric acid were tested. For this model system, both performed similarly. After successful optimization of the reaction conditions, we investigated the generality, compatibility, synthetic scope, and limitations of this protocol by employing 4-formyl-cyclophane and 2-aminopyridine or 2-aminopyrazine, and various isocyanides (**3a–g**), affording PCP-derived 3-amino-imidazo[1,2-*a*]pyridines (**4a–f**) or -pyrazines (**5a–c**) in 42%–87% yield (Scheme 2).

Aromatic and aliphatic isocyanides were compatible in the GBB-3CR, with overall good yields. The imidazo[1,2-*a*]pyrazines (**5a–c**) yields were lower, ranging between 12% and 48%. Since pyrazine is more electron-withdrawing than pyridine, its amino group is less nucleophilic, thus, inhibiting the first step of the GBB-3CR, the formation of an imine from aldehyde and amidine. The structures of the corresponding products were elucidated by spectral analysis, including NMR spectroscopy, mass spectrometry (see Supporting Information). Well-defined crystals of **4b** were obtained by layering techniques and analyzed by single-crystal X-ray crystallography (Figure 1). The corresponding enantiomerically pure cyclophanyl imidazo[1,2-*a*]heterocycles, in principle, can also be obtained starting from



Scheme 2. Synthesis of PCP-derived imidazo[1,2-*a*]pyridines **4a–f** and imidazo[1,2-*a*]pyrazines **5a–c** by GBB-3CR through varying isocyanide and amidine components.

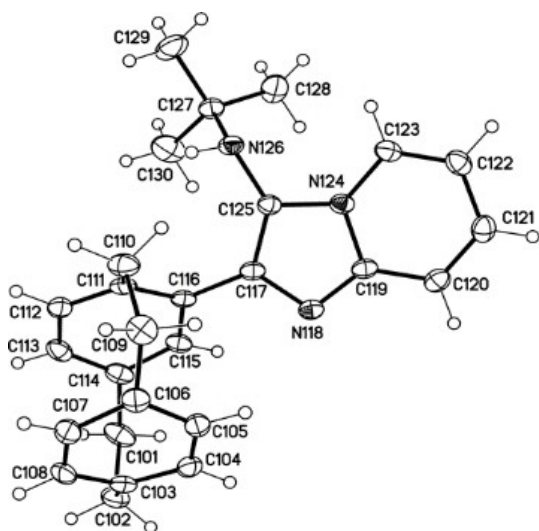
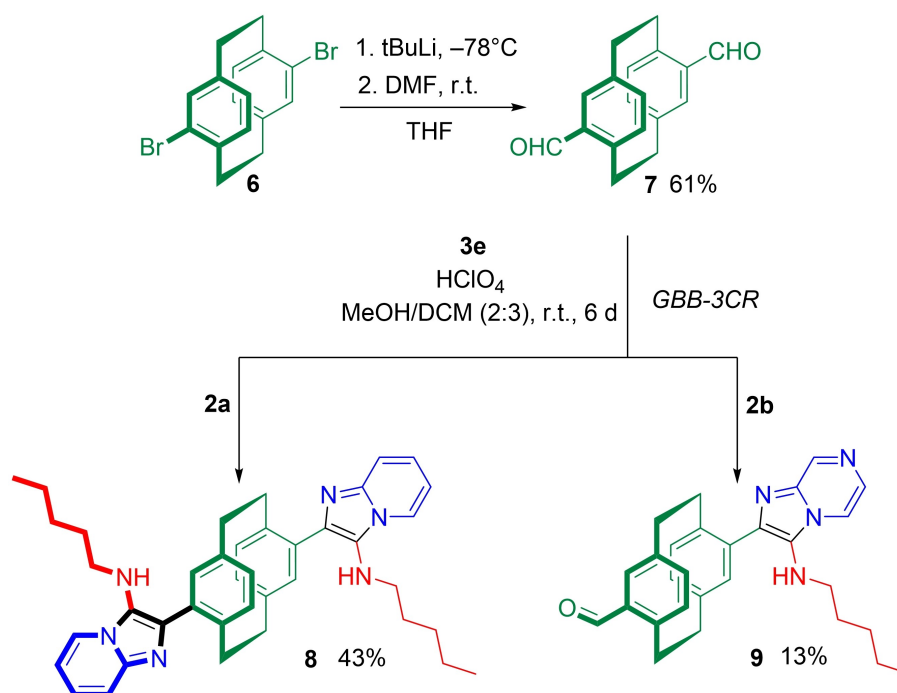


Figure 1. Single-crystal X-Ray structure of the cyclophanyl 3-aminoimidazo[1,2-*a*]pyridine **4b** (one of the crystallographic independent molecules is shown, displacement parameters are drawn at 50% probability level).

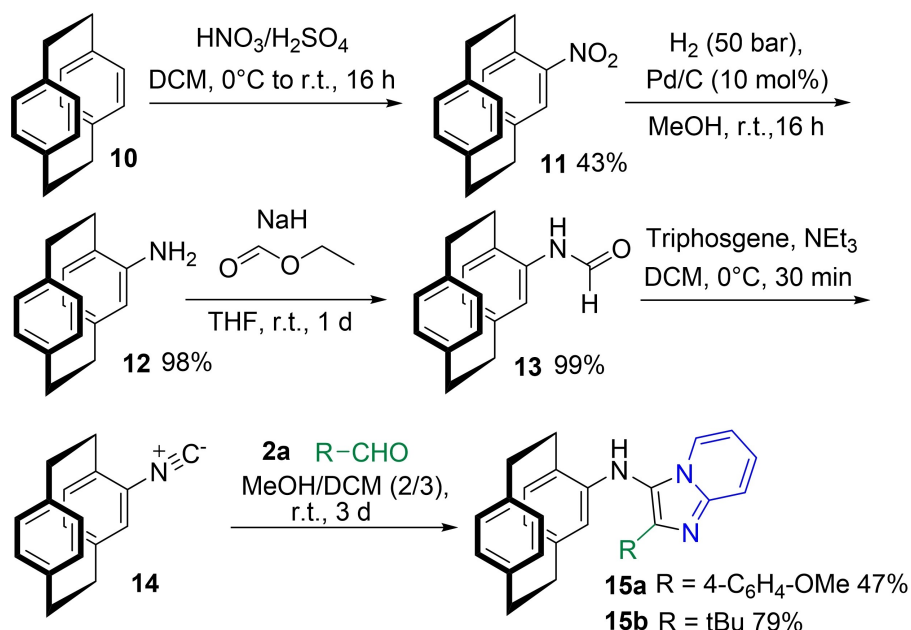
enantiomerically pure PCP-derivatives. For the formation of enantiomerically pure derivatives, chiral resolution of formyl-PCP (**1**) has been crucial to access enantiomerically pure planar chiral precursors.^[13] In this current work, a comprehensive study to prepare and investigate both enantiomers of the formyl-PCP for comparative studies in the GBB reaction was not further investigated.

PCP-scaffolds bearing tunable multiple functional sites can be applied as modular building blocks,^[14] while controlling regio-, and chemoselectivity is among the crucial factors when employing multiple functionalities. The di-functionalized PCP **7** bearing an additional formyl moiety in the pseudo-*para* position was investigated to prepare bis-imidazo[1,2-*a*]pyridine scaffold **8** (Scheme 3). After a prolonged reaction time of 6 days accounting for the additional reactive site, compound **8** was obtained in a 43% yield. To study a controlled transformation employing GBB reaction, experiments were performed to selectively synthesize a mono-adduct formation from the pseudo-*para*-substituted bis-aldehyde PCP **7** using 1.0 equivalent of the isocyanide and amidine components. Employing 2-aminopyrazine, the respective mono-adduct **9** was obtained in a low yield of 13%. The employed bis-formyl-PCP was mostly re-collected due to incomplete transformation. To obtain an unsymmetrical bis-adduct from the mono-adduct **9**, a second GBB-reaction was subsequently performed employing different isocyanide and heteroaromatic amidine components. This turned out into a sluggish mixture, even after a prolonged reaction time of 6 days.

To further expand the structural diversity of the GBB-3CR involving PCP-derivatives, we synthesized 4-formamido[2.2]paracyclophane (**13**), the precursor of the corresponding [2.2]paracyclophane-4-isocyanide (**14**), following the procedure reported earlier by de Meijere et al.^[15] [2.2]Paracyclophane-4-isocyanide (**14**) was previously applied as a ligand in transition metal complexes.^[16] To avoid isolating the unstable isocyanide intermediate, we performed an isocyanide-free variant of the GBB-3CR as reported by Dömling et al.,^[17] in which the isocyanide is generated in situ by dehydration of the



Scheme 3. Synthesis of the PCP-derived mono-adduct and bis-imidazo[1,2-*a*]pyridine through GBB-3CR process.



Scheme 4. Preparation of 4-formamido[2.2]paracyclophane and its utilization in an isocyanide-free GBB-3CR process.

formamide using triphosgene (Scheme 4). The formamide **13** is obtained in a three-step synthesis, starting with the nitration of PCP (**10**), followed by reduction to amine **12** and formylation using ethyl formate. Compound **13** was obtained in a 42% yield over three steps. For the one-pot GBB-3CR in which the isocyanide is generated in situ, the formamide **13** is first dehydrated by using triphosgene in dichloromethane. The corresponding aldehyde and 2-aminopyridine (**2a**) in methanol are then added. The respective imidazo[1,2-*a*]pyridines **15a** and **15b** were obtained in 47% and 79% yields.

Fluorescence properties

PCP-derivatives have been demonstrated as a promising scaffold in the design of spatially-oriented through-space conjugated TADF-emitters.^[18] Having access to a variety of novel heteroaromatic cyclophanyl-based scaffolds, we first investigated their fluorescence properties. The tested substrates were observed as being strongly blue fluorescent in solution and solid-state; the fluorescence emission wavelengths could be tuned by variation of the individual precursor components. Changing the amidine component did not substantially differ in emission wavelength, whereas the Stokes shift was reduced slightly. Comparing **4f** and **4d** reveals how strongly electron-donating isocyanide residues like 4-methoxyphenyl also decrease emission wavelength and Stokes shift. Bis-imidazo[1,2-*a*]pyridine **8** shows a similar absorption and emission profile, with slightly increased emission wavelength and Stokes shift and broadening of the emission peak. The PCP-isocyanide-derived imidazo[1,2-*a*]pyridines **15a,b** exhibit a lower emission wavelength (Table 1 and Figure 2). By employing different π -extended or substituted components, the fluorescence proper-

Nr.	λ_{Abs} [nm]	λ_{Em} [nm]	Stokes Shift [nm]	Nr.	λ_{Abs} [nm]	λ_{Em} [nm]	Stokes shift [nm]
4a	343	471	128	5a	350	469	119
4b	335	464	129	5b	340	464	124
4d	334	473	139	5c	350	471	121
4e	343	476	133	15a	319	449	130
4f	356	456	100	15b	328	447	119
8	351	483	132	–	–	–	–

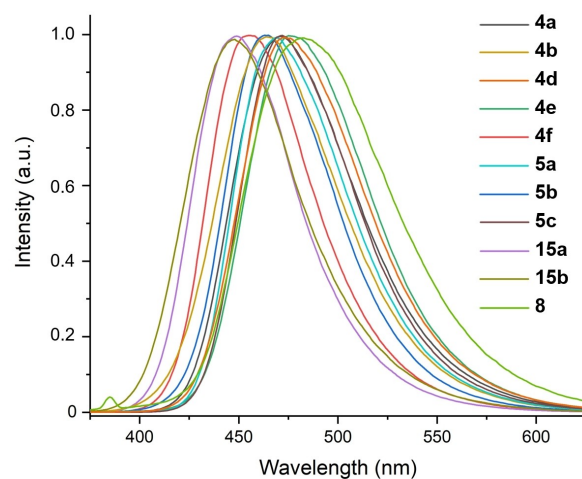


Figure 2. Normalized emission spectra of selected compounds in ethyl acetate (80 μM). $\lambda_{\text{ex}} = 345$ nm.

ties of the GBB-products could be varied even more. Functionalization of the other deck could lead to interesting effects due

to the transannular communication. Thus, this would offer a synthetic platform for preparing donor-acceptor chromophores.

Moreover, we investigated the pH-dependency of the fluorescence exemplary for the PCP-derived imidazo[1,2-*a*]pyridine **4f** (Figure 3). Since the spectra have been recorded using aqueous solutions, a bathochromic shift of 16 nm is observed when comparing the fluorescence in ethyl acetate and neutral water. This solvatochromic effect suggests a larger charge separation in the excited state which is stabilized in more polar solvents. In acidic solutions, however, the fluorescence intensity is significantly decreased. Presumably, the protonation of the nitrogen atom of the imidazole ring leads to fluorescence quenching. In contrast, the fluorescence intensity increases in basic solutions, which is also accompanied by a hypsochromic shift. One possible explanation for this could be the decreased stabilization of the excited state in basic media.

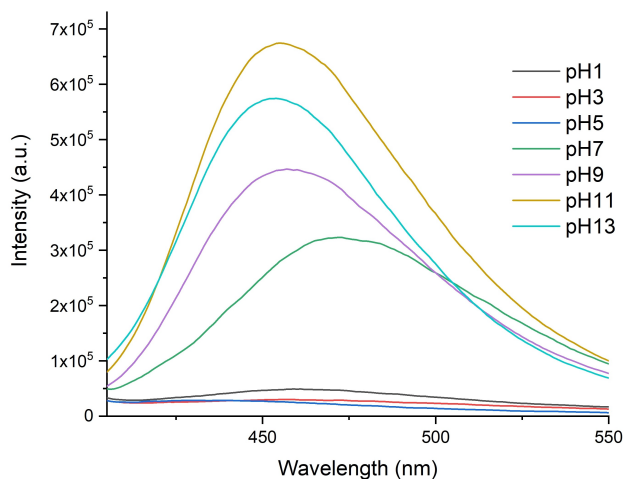


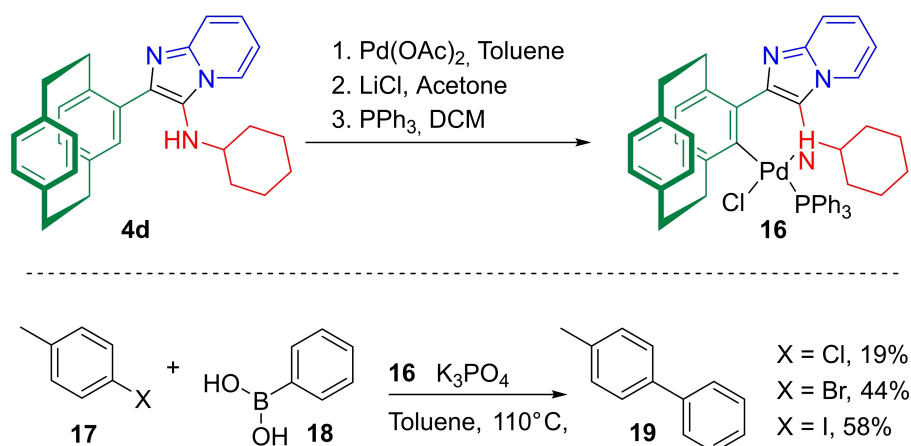
Figure 3. Quantitative emission spectra of **4f** in aqueous solutions of different pH values (8 μ M). $\lambda_{\text{ex}} = 345$ nm.

Cyclophanyl imidazole ligands for N,C-palladacycles

Cyclophanyl-derived ligands bearing coordination-capable moieties enable the installation of various metal centers.^[19] We have reported PCP-based planar and central chiral N,C-palladacycles by regioselective *ortho*-palladation of amine- and imine-functionalized PCPs.^[20] To showcase the utilization of the obtained cyclophanyl imidazole ligands, we applied this *ortho*-palladation method, employing stepwise Pd(OAc)₂ and LiCl followed by subsequent treatment with PPh₃ (Scheme 5). N,C-palladacycle **16** was obtained in 37% yield in a highly selective manner. The complex was purified by flash column chromatography and remained air-stable. The regioselectivity of the *ortho*-palladation was examined by NMR spectroscopic techniques, confirming the coordination of the secondary amine to the palladium rather than nitrogen of the imidazole ring.

Palladacycle-directed various synthetic transformations to control regioselectivity are well documented,^[21] and could overcome certain synthetic hurdles and drawbacks associated with conventional approaches for regioselective transformations.^[22] We tested the catalytic reactivity of PCP-derived palladacycle **16** in a Suzuki-Miyaura cross-coupling reaction using 4-halotoluenes (**17**) and phenylboronic acid (**18**) as reaction components under the standard reaction conditions. The biaryl coupling product **19** was obtained from 19% to 58% (I > Br > Cl). The preliminary results obtained for the biaryl coupling product suggest potential applications of PCP-palladacycle **16** as a catalyst. To identify the specific role of the substituents grafted onto the imidazo[1,2-*a*]heterocycles for chelating ability or enabling higher stability and exploring their catalytic utility in other synthetic transformations, some further studies are certainly needed.

In summary, we report a one-step Groebke-Blackburn-Bienaymé three-component reaction to realize the synthesis of structurally diverse cyclophanyl-derived imidazole ligands of 3-amino-imidazo[1,2-*a*]pyridines and imidazo[1,2-*a*]pyrazines. Furthermore, a modified protocol for the in situ preparation of



Scheme 5. Synthesis of PCP-derived N,C-palladacycle **16** and its synthetic application in a Suzuki-Miyaura cross-coupling reaction.

[2.2]paracyclophane-4-isocyanide and its synthetic application in the GBB reaction is described. The products obtained through Groebke-Blackburn-Bienaymé reactions can be readily transformed to showcase their useful utility in preparing N,C-palladacycles as a potential candidate for carbon-carbon bond-forming reactions. In future investigations, we are interested in a comprehensive study to prepare and investigate cyclophanyl-derived constitutional isomers of formyl-PCPs as well as their specific stereochemical features (element of planar chirality) for comparative studies in the Groebke-Blackburn-Bienaymé reaction.

Supporting Information

Experimental procedures and spectral data for all these new compounds are available in Supporting Information.

Deposition Number 2109623 (for **4b**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

General procedure of Groebke-Blackburn-Bienaymé cyclization process

2-Aminopyridine (1.00 equiv.) was dissolved in methanol and o-bromobenzaldehyde (1.00 equiv.), and glacial acetic acid (2.00 equiv.) or a 1 M solution of perchloric acid in methanol (0.10 equiv.) were added. The respective isocyanide (1.00 equiv.) was added, and the solution was stirred at room temperature. After 3 days, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography (SiO₂, CH/EtOAc/NET₃).

Synthesis of cyclopalladated-PCPs (**16**)

2-(1,4(1,4)-Dibenzenacyclohexaphane-12-yl)-N-cyclohexylimidazo[1,2-a]pyridin-3-amine (84.0 mg, 199 μmol, 1.00 equiv.) and palladium(II) acetate (47.0 mg, 209 μmol, 1.05 equiv.) were dissolved in 1.6 mL of dry toluene and heated to 90 °C for 20 min. The solvent was removed under reduced pressure, and the residue was suspended in 2.1 mL of dry acetone. Lithium chloride (25.3 mg, 598 μmol, 3.00 equiv.) was added. After stirring at r.t. for 16 h, triphenylphosphine (52.3 mg, 199 μmol, 1.00 equiv.) was added. After another 16 h, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (SiO₂, n-pentane/EtOAc 2:1). Compound **16** was isolated as a yellow solid (60 mg, 72.8 μmol, 37%). Details on Suzuki-Miyaura reaction is provided in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Fused-imidazoles · Groebke-Blackburn-Bienaymé (GBB) reaction · Isocyanide Chemistry · Multicomponent reactions · [2.2]Paracyclophane

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