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Pd-Catalyzed Dehydrogenative Arylation of Aryl Hydrazines to Access Non-Symmetric Azobenzenes, Including Tetra-*Ortho* Derivatives

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Abstract

Azobenzenes are photoresponsive compounds widely used in molecular switches, light-controlled materials, and sensors, but despite extensive studies on symmetric derivatives, efficient methods for synthesizing non-symmetric analogues remain scarce due to regioselectivity issues, multi-step procedures, and limited applicability to tetra-ortho-substituted structures. Herein, we describe a direct, one-pot Pd-catalyzed dehydrogenative C–N coupling between aryl bromides and aryl hydrazines to access non-symmetric azobenzenes. The use of bulky phosphine ligands and sterically tuned

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substrates promotes selective N-arylation at the terminal nitrogen. The protocol tolerates a wide range of functional groups and enables the synthesis of well-decorated azobenzenes, including tetra-ortho-substituted derivatives. Notably, the reaction proceeds under an O2 atmosphere and in the presence of water, highlighting its robustness.

Keywords

Azo Compounds; Palladium; Cross-Coupling; Phosphine ligands; Domino catalysis.

Introduction

Azobenzenes are a widely studied class of compounds known for their distinctive photoresponsive properties, rendering them valuable in a variety of applications, including molecular switches, sensors, and light-controlled materials [1]. The photo-switching behavior arises from the reversible photoisomerization between the *E*- and *Z*-forms of the azobenzene chromophore, driven by the isomerization of the N=N double bond. This photo-switching event involves a molecular size reduction between the *E* and *Z* isomers, thereby driving structural changes that enable applications in molecular machines, biological allosteric modulators, and advanced functional materials (Figure 1A) [2]. Despite the widespread interest in azobenzenes, most synthetic methods have focused on the preparation of symmetric derivatives[3]. Traditional approaches, such as oxidative coupling of anilines [4], or reductive coupling of nitroarenes [5], or cross-coupling between anilines and nitroarenes have proven efficacious but face significant challenges when applied to non-symmetric systems [6], particularly in achieving regioselectivity. These methods frequently require a particular reagent pair or an excess of one reactant, which limits their efficiency and versatility.

In contrast, Baeyer-Mills reactions, which rely on nitroso-aniline couplings, provide a route for the synthesis of non-symmetric azobenzenes, but their substrate specificity and use of hazardous precursors limit their practical applicability [7]. An alternative approach involves the SeAr reaction, which utilizes potentially hazardous diazonium salts and electron-rich arenes (mainly limited to phenols) [8], including metalated arenes [9].

The growing demand for structurally complex compounds across diverse applications has rendered the synthesis of non-symmetrical azoarenes with differently substituted azo bonds intricate and inefficient using these standard synthetic protocols. Transition metal-catalyzed C–N bond formation has emerged as a viable route to access non-symmetric azobenzenes, owing to the broad functional group tolerance of Buchwald–Hartwig amination reactions [10]. Li and co-workers developed a Chan-Evans-Lam-type oxidative cross-coupling reaction between *N*-aryl phthalic hydrazides and aryl boronic acids using copper catalysis [11]. Similarly, in 2003, Lee and co-workers introduced a desymmetrization approach employing simpler N=N precursors, specifically *N*-protected hydrazines. Their method involved a three-step process comprising Cu- and Pd-catalyzed C–N bond formations followed by a dehydrogenative deprotection step (Figure 1B, top) [12]. This desymmetric approach was further employed by Oestreich and co-workers in 2022, who introduced silicon-masked diazenyl anions in a Pd-catalyzed three-step sequence to access a wide range of non-symmetric azobenzenes (Figure 1B, bottom) [13].

Inspired by these approaches and building on recent advances in the dehydrogenation of 1,2-diarylhydrazines to azobenzenes [14], we developed a one-pot strategy for synthesizing non-symmetric azobenzenes *via* a Pd-catalyzed cascade involving C–N coupling of aryl hydrazines with aryl bromides, followed by oxidative dehydrogenation (Figure 1C). As our study was nearing completion, Váňa and co-workers disclosed a

related Buchwald–Hartwig approach employing the Pd(OAc)$_2$/BINAP catalytic system [15], which enabled selective C–N coupling at the terminal nitrogen and suppressed denitrogenative byproducts [16]. Although the general strategy is similar, our method uses the [PdCl(C$_3$H$_5$)]$_2$/*t*BuXPhos catalytic system, which provided higher yields and broader substrate scope (functional group tolerances), including challenging *tetra*-ortho-substituted azobenzenes.
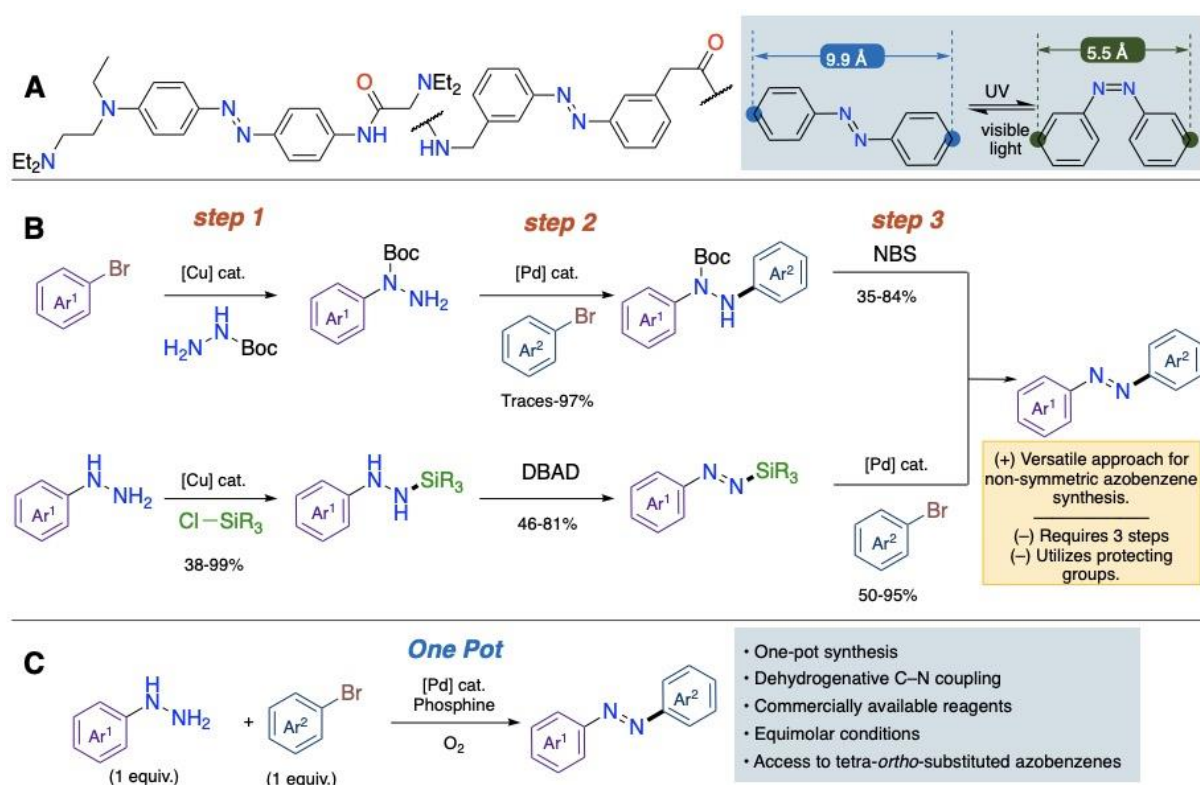
Figure 1: General Overview of Azobenzene Chemistry. (**A**) Selected examples and photoisomerization of azobenzenes; (**B**) Previous Pd-catalyzed methods for the synthesis of non-symmetric azobenzenes; (**C**) This work: Pd-catalyzed dehydrogenative C–N coupling of aryl hydrazine.

Results and Discussion

We started our investigation by using 2-bromotoluene (**1a**) and phenylhydrazine (**2a**) as model substrates. In the beginning, standard Buchwald amination conditions were

tested ([PdCl(allyl)]$_2$, XPhos, *t*BuONa in 1,2-dimethoxyethane (DME)) [17]. The reaction outcomes were analyzed with both GC/MS and GC/FID analysis. Under these conditions, we were pleased to find that 1-phenyl-2-(o-tolyl)diazene (**3a**) was obtained with GC yield of 50% (Table 1, entry 1). While all starting materials were consumed, various impurities, including biphenyls, diarylamines, aniline, and toluidine, were formed in varying amounts. Since a final dehydrogenation step is required to complete the reaction, the experiment was repeated with various oxidants tested as additives. The use of di-*tert*-butyl peroxide as an oxidant, combined with NaH as the base, increased the formation of **3a**, achieving GC yields of up to 65% (Table 1, entry 3). Control experiments demonstrated that palladium, phosphine, and base were all essential for this reaction (Table S4). However, under identical conditions with other aryl bromides like 4-bromotoluene, the reaction failed to form azobenzene **3b**, instead yielding 1-phenyl-1-(*p*-tolyl)hydrazine, resulting from arylation of the central nitrogen (Table 1, entry 4 & SI). This unexpected result prompted us to further optimize the reaction conditions, with particular focus on the choice of ligand, especially for non-ortho-substituted aryl bromide as substrates. Notably, the use of bulkier phosphines, such as P(tBu)$_3$ and tBuXPhos, was found to promote the reaction regardless of the substitution pattern of the bromotoluene (Table 1, entries 5-8). For subsequent optimizations, we selected tBuXPhos for practical reasons, as it is less sensitive to oxidative conditions. Further optimization revealed that Cs$_2$CO$_3$ is more efficient than NaH for this reaction (Table 1, entry 9). However, reactions conducted with a new batch of Cs$_2$CO$_3$ showed a dramatic reduction in product yield (Table 1, entry 9). Control experiments with varying amounts of water (0–10 equiv.) demonstrated that a small amount of water is crucial for the reaction (Table S7 and Table 1, entry 11). This effect, previously reported in Buchwald-Hartwig reactions, enhances yield by facilitating the reduction of Pd(II) to Pd(0) and improving the solubility of the base [18]. To ensure the

generality of the conditions, 1-bromo-2-(trifluoromethoxy)benzene was also tested, yielding the desired azobenzene **3c** in 69% yield with the addition of 2 equivalents of water (Table 1, entries 12 and 13). Finally, the oxidant tBu-OO-tBu could be replaced by O_2, yielding compound **3a** with GC yields of up to 79% (Table 1, entry 13, 75% isolated yield). Notably, this work led to the development of a reaction protocol that operates without the need for inert conditions and tolerates small amounts of water, simplifying practical implementation.

Table 1: Selected Optimization of Conditions for the Synthesis of Azobenzene from Phenylhydrazine and Aryl Bromides. The Gray Box Provides a Detailed List of All Identified Side Products.
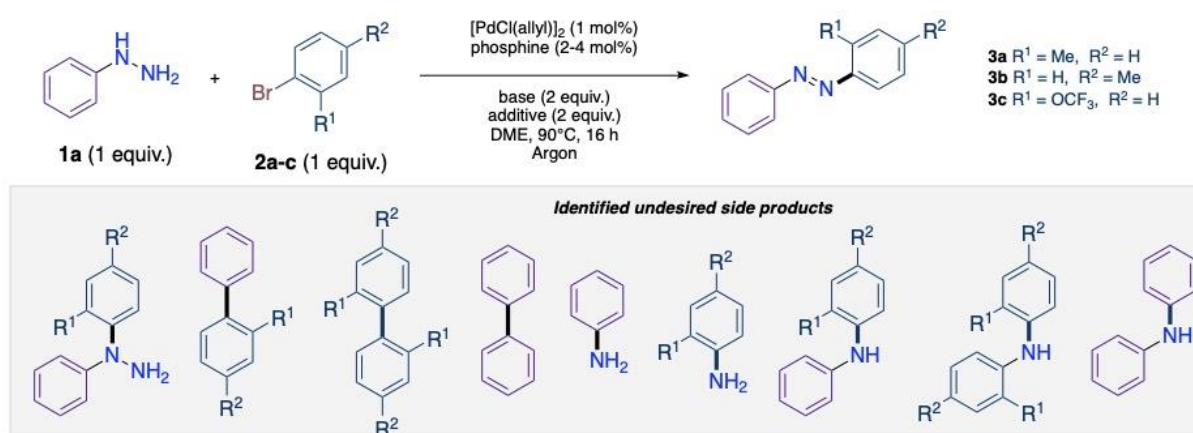

Entry	**2a, 2b** or **2c**	Phosphine	Base	Additive	H_2O (eq.)	Yield [%] in **3**[f]
1[a]	**2a**	XPhos	tBuONa	No additive	0	50
2[a]	**2a**	XPhos	NaH 60%	No additive	0	62
3[a]	**2a**	XPhos	NaH 60%	tBu-O-O-tBu	0	65
4[a]	2b	XPhos	NaH 60%	tBu-O-O-tBu	0	0
5[a]	**2a**	P(tBu)$_3$	NaH 60%	tBu-O-O-tBu	0	51
6[a]	**2b**	P(tBu)$_3$	NaH 60%	tBu-O-O-tBu	0	19
7[a]	**2a**	tBuXPhos	NaH 60%	tBu-O-O-tBu	0	27
8[a]	**2b**	tBuXPhos	NaH 60%	tBu-O-O-tBu	0	26
9[a]	**2a**	tBuXPhos	Cs_2CO_3	tBu-O-O-tBu	0	62
10[b,c]	**2a**	tBuXPhos	Cs_2CO_3	tBu-O-O-tBu	0	64
11[b,c]	**2a**	tBuXPhos	Cs_2CO_3	tBu-O-O-tBu	2	71
12[b,c]	**2c**	tBuXPhos	Cs_2CO_3	tBu-O-O-tBu	0	4
13[b,c]	**2c**	tBuXPhos	Cs_2CO_3	tBu-O-O-tBu	2	69

| 14[b,c,d,e] | **2a** | *t*BuXPhos | Cs$_2$CO$_3$ | No additive | 2 | Up to 77 (75%) |

[a]Reactions performed on a 0.5 mmol scale in 1 mL of DME. [b]Reactions performed in 1 mL of DME (1 M). [c]New batch of Cs$_2$CO$_3$ dry. [d]Under O$_2$ atmosphere (100 ml, 0.84 mmol). [e]2 h. [f]Yields determined by GC/FID analysis using tetradecane as an internal standard, with isolated yields shown in parentheses.

With the most suitable reaction conditions, the substrate scope was examined. First, the reactivity of different aryl bromides with phenylhydrazine (**1a**) to form non-symmetric azobenzene was explored (Scheme 1). Most of the azobenzene were obtained in purified yield between 70 and 85%. Various functional groups at the *ortho-* or *para*-position were well tolerated in this reaction, including electron-withdrawing groups such as trifluoromethoxy (**3c**, 69%), nitrile (**3e**, 81%), methyl ester (**3h**, 74%), *N,N*-dimethylamide (**3i**, 73%) and nitro (**3j**, 35%), as well as electron-donating groups such as methoxy (**3d**, 77%), dimethylamino (**3k** 55%) , and thiomethoxy (**3l**, 71%). Moreover, the reaction tolerated C–F (**3f**, 86%) and C–Cl (**3g**, 66%) bonds, enabling orthogonal functionalization. *It should be noted that, as a general trend –and in contrast to classic Buchwald-Hartwig couplings– aryl bromides with substituents at the ortho-position (**3a** and **3c**–**g**) are more reactive than those with substituents at the para-position (**3b** and **3h**–**l**).* This difference might be explained by steric repulsion, which may favor C–N bond coupling with the terminal nitrogen over the internal nitrogen. From phenylhydrazine and phenyl bromide, azobenzene (**3m**) was isolated in 43% yield. Substituent place at the *meta*-position did not affect the reaction yield, as azobenzene **3n** and **3o** are isolated in 84% and 78% yield, respectively. Interestingly, 3-bromopyridine also proved to be a suitable coupling partner, enabling the preparation of azoarene **3p** in 70% yield. Moreover, starting from 1,4-dibromobenzene and 2

equivalents of **1a**, a double reaction occurred, enabling the one-step synthesis of 1,4-bis[(*E*)-2-phenylethenyl]benzene (**3q**) in high yield.
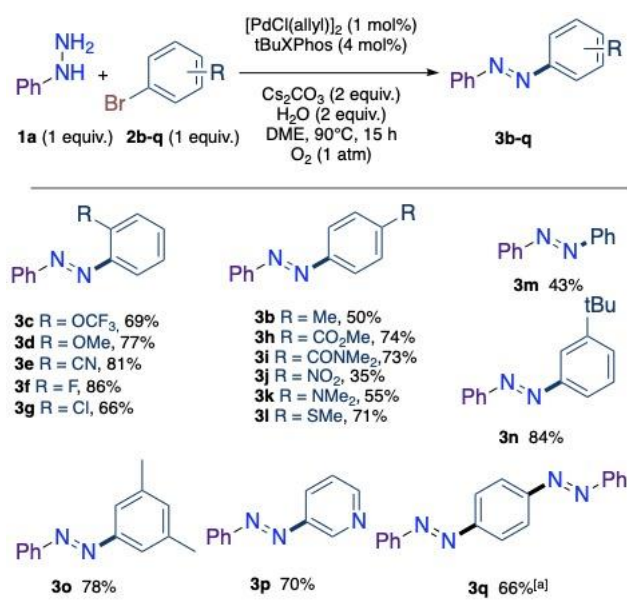

Scheme 1: Scope of Aryl Bromides in Palladium-Catalyzed Dehydrogenative C–N Coupling with Phenylhydrazine (**1a**).

We next investigated the scope of aryl hydrazines to assess their compatibility under the optimized reaction conditions (Scheme 2). While some aryl hydrazines are commercially available, it was observed that their hydrochloride salts were ineffective, even with the addition of excess base. Examining the substituent effects, *para*-substituted hydrazines such as *para*-trifluoromethylphenyl hydrazine (**1b**) and *para*-chlorophenyl hydrazine (**1c**) reacted efficiently with 2-bromotoluene to deliver the corresponding azobenezenes **4a** and **4d** in 78% and 37% yield, respectively. Notably, 2-tolylhydrazine (**1d**) exhibited good reactivity, yielding **4c** in 63%. Additionally, 2-fluorophenyl hydrazine provided the product in 55% yield, while 2-chloro-5-trifluoromethylphenyl hydrazine furnished the desired compound **4e** in a moderate yield of 32%. The lower yields observed with substrates containing a C–Cl bond may be attributed to the competitive Pd-catalyzed side-reaction.
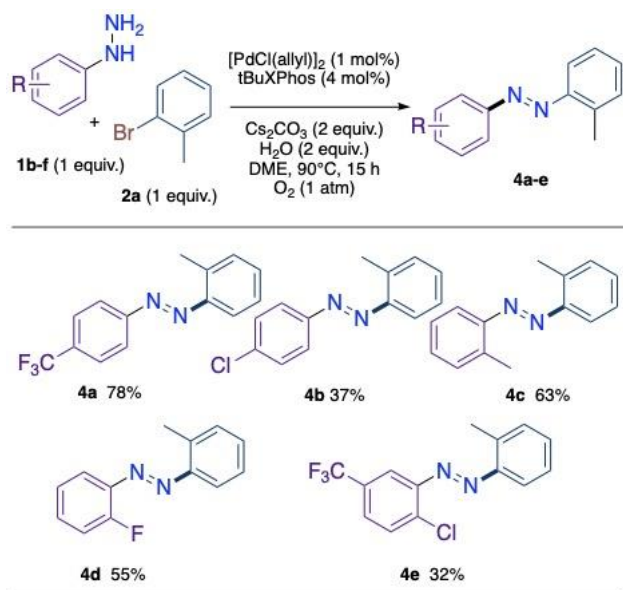
Scheme 2: Scope of Arylhydrazines in Palladium-Catalyzed Dehydrogenative C–N Coupling with 2-Bromotoluene (**2a**).

As shown above, the steric hindrance plays a significant role in driving the reaction. For this reason, we have applied our novel Pd methodology to synthesize a series of tetra-, tri-, and di-*ortho*-substituted azobenzenes (Scheme 3). Notably, this method demonstrates remarkable efficiency, as the reaction proceeds smoothly even when both coupling partners possess sterically hindered substituents at the 2,6-positions. For example, the coupling of 2,6-difluorophenylhydrazine with 1-bromo-2,6-dimethoxybenzene yielded tetra-*ortho*-substituted azobenzene **5a** in a notable yield of 63%, surpassing the performance of traditional approaches in similar contexts. Similarly, tri-*ortho*-substituted azobenzenes **5b** and **5c** were prepared in 42% and 47% yields, respectively. However, the isolation of these compounds in pure form remains challenging due to contamination with biphenyl side products. Finally, di-*ortho*-substituted azobenzene **5d** was also successfully prepared using this approach, achieving an excellent yield of 80%.

5a 63%

5c 47%[a]

5b 42%[a]

5d 80%[a]
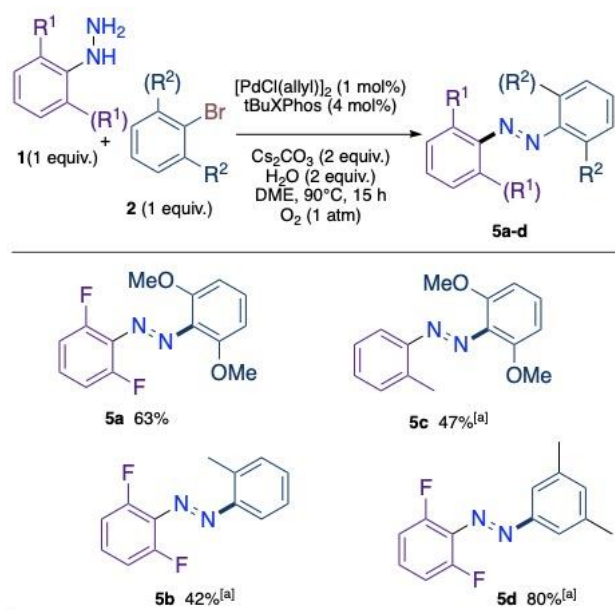
[a] Isolated with 85–95% purity.

Scheme 3: Application to the Synthesis of Tera-, Tri or Di-*Ortho*-Substituted Azobenzenes via Palladium-Catalyzed Dehydrogenative C–N Coupling.

The mechanism of the reaction was further outlined to explain the formation of all identified main and side products (Figure 2). A two-step cascade Pd-catalyzed reaction is proposed. In the first step a C–N coupling reaction with phenylhydrazine occurs [19]. The catalytic cycle starts by the formation of Pd(0) in situ through reduction facilitated by phosphine and water [20]. This is followed by the oxidative addition of aryl bromides, leading to the formation of the Pd(II)-aryl intermediate (**B**). Subsequently, ligand exchange occurs, generating hydrazido complexes (**C** and **C'**). When bulky substituents are present on the phosphine ligand and/or (both) coupling partner(s) has *ortho*-substituent(s), the hydrazido complex **C**, chelating on the terminal nitrogen, is preferentially formed to minimize steric clashes. Finally, reductive elimination leads to the formation of *N,N*-diarylhydrazine (**D**), which has been identified and characterized during the optimization process (see SI for details). In a second catalytic cycle, the N,N-diarylhydrazine (**D**) undergoes dehydrogenation via a mechanism involving Pd and O_2, similar to the process reported by Huan and co-workers [21]. Initially, Pd(0)

species (**E**) is oxidized to Pd(II) by O_2, forming a Pd-peroxo complex (**F**) [22]. Subsequently, ligand exchange occurs between the deprotonated N,N-diarylhydrazine and carbonate, yielding the Pd(II) intermediate (**G**). This intermediate then undergoes *β*–H elimination to afford the desired azobenzene product, along with a Pd(II) species (**H**). Finally, reductive elimination regenerates Pd(0), completing the catalytic cycle. Then, a general reaction pathway for the formation of product and side products is presented in Figure 2B. The first reaction to be inhibited is the Pd-catalyzed denitrogenative cross-coupling, which leads to the formation of an array of biphenyl products [16]. This can be controlled by selecting appropriate catalysts and solvents. For instance, PdCl(allyl)$_2$ in DME with strong base (Cs_2CO_3) favors C–N bond coupling, which may yield products resulting from arylation at either the terminal or internal nitrogen atoms. The selectivity can be influenced by the steric hindrance of the phosphine ligands and/or the substrates. Once *N,N*-diarylhydrazine is formed, minimizing the disproportionation side reaction [23] becomes crucial, as this reaction produces the desired azobenzene along with equimolar amounts of aniline partners. These aniline derivatives can further participate in Pd-catalyzed cross-coupling, generating a range of diarylamines as side products. The presence of oxidants such as O_2 mitigates this pathway by promoting oxidative dehydrogenation as the dominant pathway.
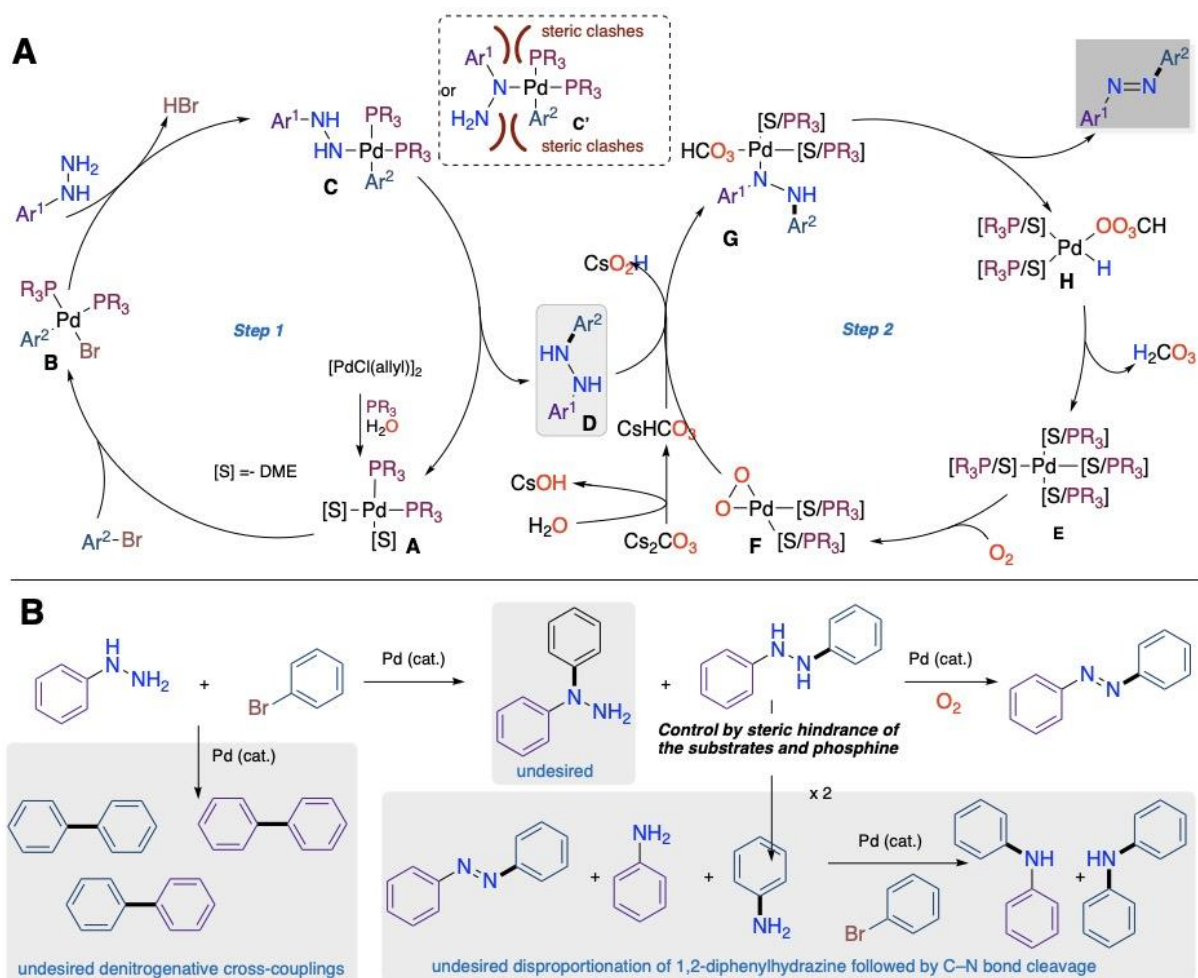
Figure 2: (**A**) Proposed Catalytic Cycle for the One-Pot Palladium-Catalyzed Dehydrogenative C–N Coupling for the Synthesis of Azobenzene from Arylhydrazine and Aryl Bromide. (**B**) Proposed Chemical Pathway for Azobenzene Synthesis, Including Side Product Formation as Determined by GC/MS Analysis

Conclusion

In summary, we have developed robust and efficient conditions for the preparation of azobenzenes via C–N coupling and dehydrogenation, employing [PdCl(C$_3$H$_5$)]$_2$ with *t*BuXPhos to promote selective C–N bond formation. This approach makes use of commercially available starting materials and displays broad functional group tolerance. Notably, it enables access to sterically demanding tetra-*ortho*-substituted

azobenzenes in moderate to good yields. The results demonstrate that aryl hydrazines can serve as practical amine partners in Pd-catalyzed C–N coupling reactions, with regioselectivity toward arylation of the less nucleophilic terminal nitrogen governed by the steric profile of the substrates and the choice of phosphine ligand. These conditions represent a valuable addition to existing methodologies and open further opportunities for applications in molecular probe design, functional materials, and photoresponsive systems, where *ortho*-substitution is often critical.

Supporting Information

Details of optimization experiments, full characterization data, and NMR spectra (^{1}H, ^{13}C, ^{19}F) for all products.

Acknowledgements

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