Dinickel-Catalyzed N=N Coupling Reactions for the Synthesis of Hindered Azoarenes

Christopher J. Rybak, Chengyi Fan, Parijat Sharma, Christopher Uyeda*

Department of Chemistry, Purdue University; 560 Oval Dr., West Lafayette, IN 47907, USA.

ABSTRACT: Azoarenes are the largest class of photoswitching molecules, and they have a broad range of applications in photopharmacology and materials science. Azoarenes possessing *ortho*-substitution often display improved properties, including isomerization under visible light irradiation, near quantitative switching, and long thermal half-lives in the *cis* form. The synthesis of hindered *ortho*-substituted azoarenes is often low-yielding using established oxidative or reductive coupling methods. Here, we describe the design and synthesis of a new dinickel complex that catalyzes the dimerization of *ortho*-substituted aryl azides in high yield. Applications of this method in the synthesis of high performance photoswitches, photoactive peptide cross-linkers, hindered diazocines, and main-chain azoarene polymers are described.

INTRODUCTION

Azoarenes are a century-old class of organic dye molecules that have seen a resurgence of interest due to their photoswitching properties.[1] Excitation at the π→π* or n→π* transition induces *cis–trans* isomerization, and the associated change in conformation can be leveraged in the design of light-responsive materials[2] and bioactive molecules.[3] The *trans*-to-*cis* isomerization of parent azobenzene requires UV irradiation at the higher energy π→π* band (λ_{max} = 313 nm).[4] An emerging research priority is the discovery of new derivatives that can be isomerized using visible light at the lower energy n→π* transition. Tetra-*ortho*-substituted azobenzenes represent a recent breakthrough in this regard.[5] Due to interactions between the N=N lone pair and the *ortho* substituent, the n→π* transition of the *trans* isomer is red-shifted from that of the *cis* isomer, allowing for near-quantitative photoswitching at longer wavelengths. In some cases, these compounds can be isomerized using red light, which is a prerequisite for applications in biomedical research where tissue penetration is needed.[6]

Ortho-substituted azoarenes are commonly synthesized by the oxidative dimerization of anilines (Figure 1A). However, these reactions often proceed in low to moderate yields, particularly for complex and highly functionalized derivatives.[5b, 6-7] The principal challenge is that the desired N=N bond formation requires condensation of an aniline with an *in situ* generated aryl nitroso intermediate. The rate of this condensation decreases with steric hindrance, leading to side reactions such as over-oxidation of the azobenzene to the corresponding azoxy compound. Azoarenes can also be synthesized by the reductive dimerization of nitroarenes.[8] However, this approach is rarely viable for the synthesis of *ortho*-substituted azoarenes.

RESULTS AND DISCUSSION

In principle, the limitations associated with oxidative or reductive N=N coupling processes could be addressed by considering an alternative redox neutral dimerization of aryl nitrenes generated from an appropriate precursor.[9] Recently, we reported that a dinickel catalyst, (NDI)$Ni_2(C_6H_6)$ (**1**), can promote the dimerization of aryl azides to form azoarenes.[10] The reaction is effective for a broad scope of substrates, requires no additional stoichiometric reagents, and produces gaseous N_2 as the only byproduct. Unfortunately, attempts to apply this catalyst to the synthesis of tetra-*ortho*-substituted azobenzenes were largely unsuccessful. Mesityl azide could be coupled in high yield at elevated temperatures, but substrates containing larger alkyl groups or heteroatom functional groups in the *ortho* position provided little to no yield of product.

The poor yields of coupling for hindered aryl azides using catalyst **1** appear to be an issue of product displacement rather than the N=N coupling process itself (Figure 1B). For example, 2,6-*i*-$PrPhN_3$ (**2**) (2.0 equiv) reacts stoichiometrically with complex **1** within minutes at room temperature to yield **3**. However, complex **3** is incapable of catalytic turnover and does not react with additional equivalents of azide **2**. Space-filling models of **3** indicate that the Ni_2 site is entirely shielded by the *i*-Pr groups of the ligand and the azoarene, preventing incoming ligands from binding. Ligand substitution at the 16 e^- Ni centers occurs by an associative substitution mechanism and is thus highly sensitive to steric effects.[10a, 11]

To accommodate hindered aryl azides, we reasoned that a catalyst with a more sterically accessible active site would be required. To that end, we pursued the synthesis of dinickel catalysts based on an alternative naphthyridine–bis(oxazoline) (NapBox) framework,[12] which would not contain the large aryl substituents that were required in the NDI ligand system. Initial metallation attempts of NapBox **4** with $Ni(COD)_2$ (2.0 equiv) in C_6H_6 only generated a mononickel complex (**5**). There was no evidence for incorporation of a second nickel, even at long reaction times and elevated temperatures. An evaluation of alternative exchangeable ligands to C_6H_6 revealed that diazocine (**6**) could mediate the successful assembly of the dinickel active site. The optimized synthetic procedure entails reacting ligand **4** (1.0 equiv) with $Ni(COD)_2$ (2.0 equiv) and diazocine **6** (1.0 equiv) in THF for 4 h at room temperature.

In the solid-state structure of complex **7**, the Ni–Ni distance is 2.3423(8) Å, which is within the range expected for a Ni–Ni single bond (Wiberg bond index = 0.6502) (Figure 1C). The calculated HOMO is highly delocalized and displays most of its electron density in the NapBox π-system and the N=N bond of the bound diazocine. Accordingly, the experimental bond metrics for the NapBox ligand are moderately distorted in a manner consistent with ligand-centered reduction. The N=N bond of the bound diazocine is 1.352(2) Å, which is significantly longer than that of free diazocine. Buried volume analysis was used to compare the steric properties of the NDI and NapBox complexes.[13] In the crystal structure of (NDI)$Ni_2(C_6H_6)$ (**1**), the *i*-Pr_2Ph groups of the ligand occupy a large fraction of the active site, and the $\%V_{bur}$ is calculated to be 42.3%. Complex **7** has a lower $\%V_{bur}$ of 34.7%, and the active site is notably more exposed above and below the ligand plane.

The (NapBox)Ni_2(diazocine) catalyst (**7**) proved to be effective in the coupling of hindered mono- and di-*ortho*-substituted aryl azides (Figure 2). Alkyl substitution as large as 2,6-*i*-Pr_2 and 2-*t*-Bu could be accommodated (products **8** and **14**). *Ortho*-fluoro and alkoxy groups, which are commonly found in high-performance photoswitches,[5a, b] were well-tolerated in various combinations (products **9**, **11**, and **15**–**20**). Substrates containing heterocycles in the *ortho* position were evaluated and found to react in high yield (products **21**–**26**). The most significant limitation of this reaction are substrates containing coordinating or reactive functional groups in the *ortho* position. For example, carbonyl and chloro groups were well-tolerated in the *para* position but could not be incorporated as *ortho* substituents.

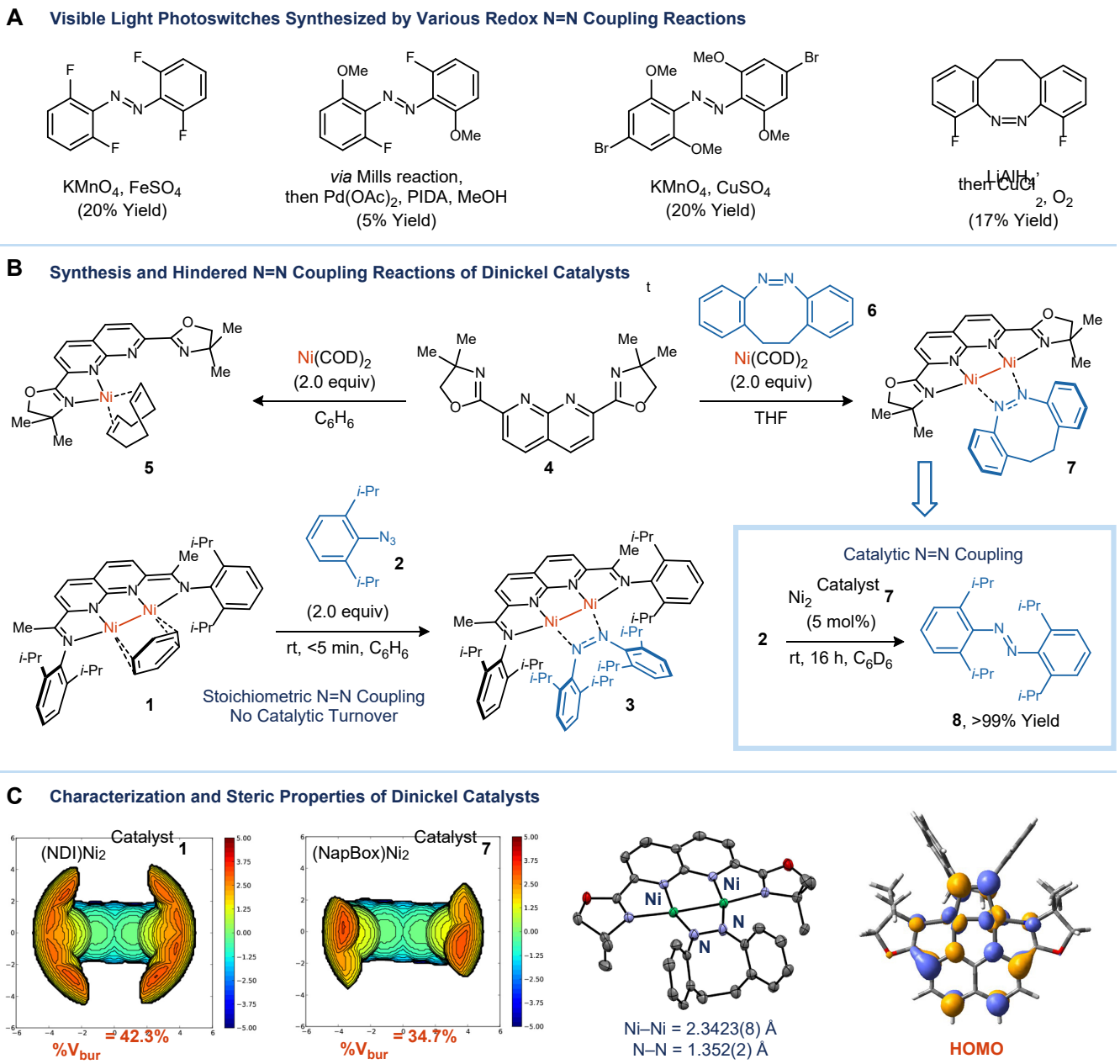

Figure 1. A catalytic redox-neutral dimerization of aryl azides to form *ortho*-substituted azoarenes. A) Oxidative N=N coupling reactions of hindered anilines often proceed in low to moderate yields. B) Development of a dinickel catalyst for the coupling of di-*ortho*-substituted aryl azides. C) Steric, structural, and electronic properties of the (NapBox)Ni_2(diazocine) catalyst **7**.

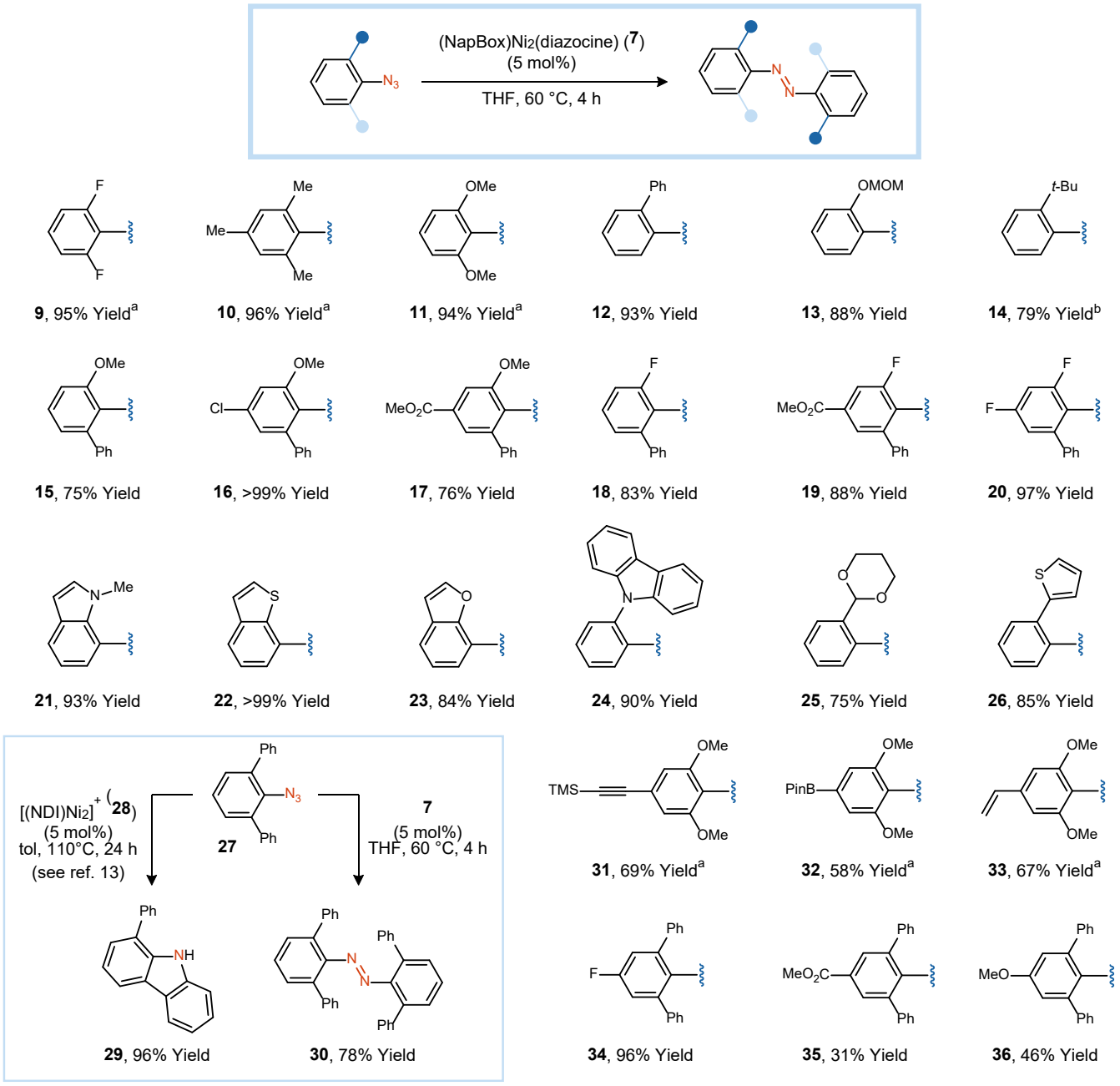

Figure 2. Substrate scope studies. Standard conditions: aryl azide (0.3 mmol), (NapBox)Ni_2(diazocine) (**7**) (5 mol%), THF, 60 °C, 4 h. [a]25 °C instead of 60 °C. [b]10 mol% instead of 5 mol% **7.**

We previously examined the reactivity of *m*-terphenylazide (**27**) using a cationic (NDI)Ni_2 catalyst (**28**) and found that the predominant reaction was an intramolecular C–H amination process to form carbazole **29** (110 °C, 24 h, 96% yield).[14] By contrast, the (NapBox)Ni_2 catalyst **7** mediates N=N coupling in 78% yield with minimal competing C–H amination. As a point of comparison to other methods reported in the literature, the synthesis of **30** was attempted by both the oxidative coupling of an aniline and the reductive coupling of a nitro compound. Across six sets of conditions, **30** was obtained in only 0–9% yield (See Supplementary Information).

Finally, a series of tetra-*ortho*-methoxy azoarenes containing useful functional handles at the *para* position were synthesized (products **31**–**33**).[5a, 6] These compounds display red-shifted absorbances that fall within the bio-optical window.[3c, 15] They are also stable toward reduction by glutathione and are resistant to photobleaching, making them a privileged class of compounds for biological photoswitching applications. The synthesis of functionalized tetra-*ortho*-methoxy azoarenes has been a significant challenge, and oxidative couplings of their corresponding anilines often proceed in low yield.

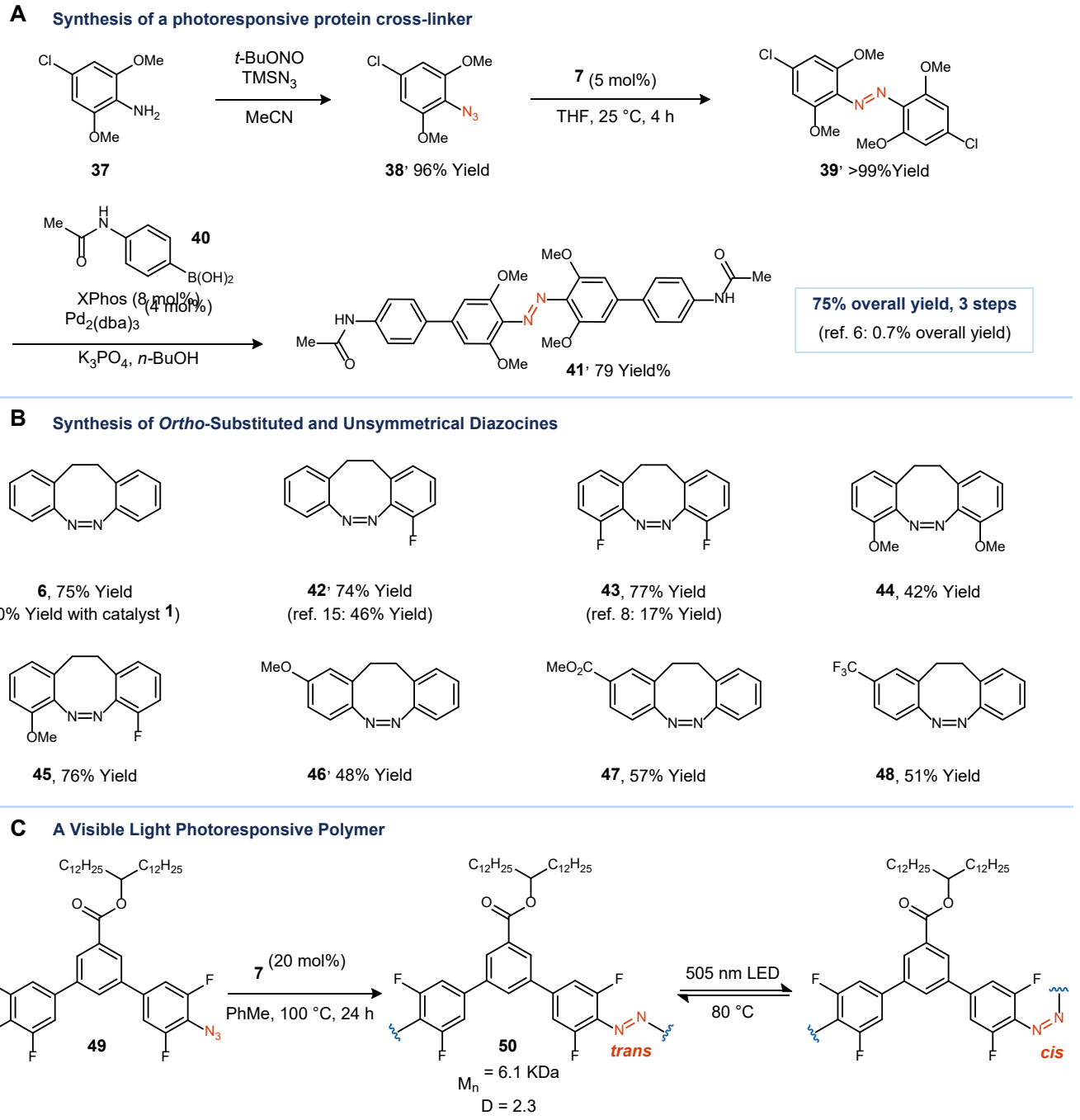

Figure 3. Synthetic applications of the catalytic N=N coupling. A) A photoactive peptide linker. B) *Ortho*-substituted and unsymmetrical diazocines. C) A visible light photoresponsive polymer.

To demonstrate the synthetic utility of the catalytic aryl azide dimerization, we examined the preparation of **41**, a photoresponsive peptide cross-linker reported by Woolley (Figure 3A).[6] The established synthetic route produced **41** in only 0.7% yield after four steps, with the N=N coupling proceeding in 20% yield. Using catalyst **7**, the N=N coupling of azide **38** provided **39** in >99% yield, and linker **41** was prepared in 75% overall yield in three steps from commercially available starting materials.

Diazocines are another class of compounds that display improved photoswitching properties relative to parent azobenzene.[16] Eight-membered diazocines are more stable in the *cis* form due to the geometric constraints of the ring, and a photostationary state of >90% *trans* can be accessed using blue light. The first reported synthesis of diazocine **6** involved a low-yielding intramolecular reductive coupling of a dinitro precursor (4% yield; $BaOH_2$, Zn, EtOH; Pb ball mill).[16] Recently, Trauner reported a more reliable oxidative N=N coupling approach.[17] However, unsymmetrical diazocines presented a challenge, and only one *ortho*-substituted diazocine was demonstrated.

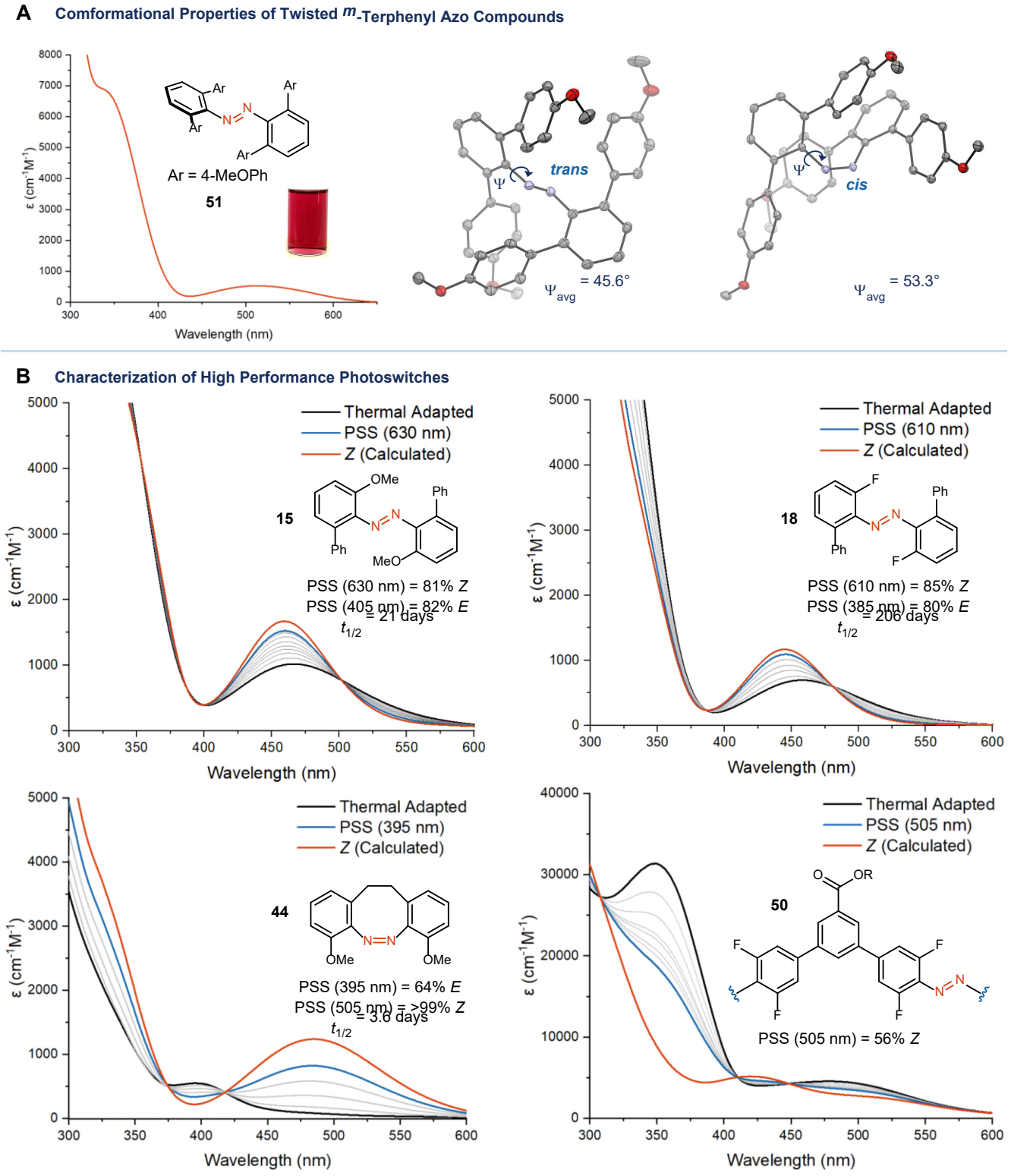

Figure 4. Photoswitching properties of *ortho*-substituted azoarenes. A) *meta*-Terphenyl azo compounds adopt twisted conformations in both the *trans* and *cis* forms. B) Visible light photoswitchable small molecules and polymers. Thermally adapted samples were heated at 90 °C in the dark for 18 h.

Using catalyst **7**, parent diazocine **6** was obtained in 75% yield from the corresponding diazide starting material (Figure 3B). To maximize intramolecular coupling over potential competing polymerization, the reaction was run at twofold dilution relative to the standard reaction conditions. Notably, the (NDI)Ni_2 catalyst **1** provided no yield of **6**, likely due to the

same issue of product displacement that was observed for di-*ortho*-substituted aryl azides. The solid-state structure of diazocine **6** bound to the (NDI)Ni_2 platform reveals that the ethylene bridge of the diazocine entirely blocks one face of the Ni_2 site, while the *i*-Pr_2-Ph groups shield the other.[18] The di-*ortho*-fluoro diazocine **43** was previously only generated in 17% yield from the reductive coupling of a dinitro precursor.[8] Using the catalytic azide dimerization, **43** was obtained in 77% yield. Novel doubly *ortho* substituted derivatives **44** and **45** were also prepared efficiently. Finally, intramolecular couplings of unsymmetrical substrates were viable to form products **46**–**48**.

Polymers containing main chain azoarene repeat units have attracted interest due to their ability to undergo large conformational changes in response to light.[19] Reported polymers do not incorporate *ortho* substitution and are thus limited to photoswitching using UV or near-UV light. To assess the utility of the catalytic N=N coupling process for the incorporation of di-*ortho* substitution into azopolymers, the diazide monomer **49** was prepared (Figure 3C). Catalytic polymerization followed by Soxhlet purification yielded a material with an average molecular weight of 6.1 kDa and a dispersity of 2.3 by GPC analysis, which is consistent with the expected step growth mechanism. Upon irradiation with a 505 nm LED, a photostationary state was reached where 56% of the azo bonds were in the *cis* form.

Whereas most azoarenes are red to yellow in color, *m*-terphenyl azoarene **51** is magenta due to a red-shifted n→π* transition (Figure 4A). Irradiation of ***trans*-51** using 630 nm red light generated a mixture that was enriched in the *cis* form (21% *cis*). Crystals of both ***trans*-51** and ***cis*-51** were obtained from saturated solutions in $CHCl_3$. Due to extreme steric hindrance, the aryl groups are not coplanar with the N=N double bond in either of the two isomers. In the *trans* form, the average CCNN dihedral angle is 45.6°. The ***cis*-30** compound adopts a conformation with pseudo-C_2 symmetry. The average CCNN dihedral angle is 53.3°, and the flanking aryl rings are within the range of a π-stacking interaction (4.30 Å between the centroids of the two rings).

Tetra-*ortho*-methoxy azoarenes can achieve >80% population of the *cis* form at >550 nm irradiation.[5a, 6] However, the half-lives of the *cis*-azoarenes are typically less than one day at room temperature, which limits applications where thermal bistability is needed. Steric hindrance generally increases the barrier for bond rotation. We therefore hypothesized that a Ph-containing azoarene, such as **15**, may display longer thermal half-lives and benefit from the red-shifted n→π* transition seen in the *m*-terphenyl series. Accordingly, **15** has a λ_{max} of 467 nm in DMSO, which is significantly longer than that of **11**, and the tail of the absorbance band reaches >600 nm (Figure 4B). Irradiation using a 630 nm red LED yielded a photostationary state of 81% *cis*, and the thermal half-life at room temperature is 21 days. Additionally, irradiation of *cis*-enriched samples of **15** at 405 nm, produced a photostationary state of 82% *trans*. F/Ph-substituted azoarene **18** exhibits similar photoswitching properties and has an even longer half-life of 206 days in the *cis* form. Finally, the impact of *ortho* substitution on the photoswitching properties of diazocine was examined. The dimethoxy diazocine **44** undergoes photoswitching from the *cis* to the *trans* form under 395 nm light, and ***trans*-44** has a half-life of 3.6 days, which is significantly longer than previously studied diazocines that lack *ortho* substitution (minutes to 15 h).

CONCLUSION

In summary, a (NapBox)Ni_2 catalyst promotes the dimerization of hindered aryl azides that were unreactive using the (NDI)Ni_2 system. Heteroatom-containing functional groups in the *ortho* position are tolerated, and substrates as hindered as di-*ortho*-isopropyl and di-*ortho*-phenyl-substituted aryl azides couple efficiently. In the latter case, the extreme steric hindrance of the *m*-terphenyl group causes the azoarene product to adopt a twisted conformation in the *trans* form, which leads to an n→π* transition that is red shifted relative to that of parent azobenzene. The method also provides a viable route to high performance photoswitches that were previously only accessible in low yields. New derivatives that display visible light *trans*-to-*cis* isomerization and long thermal half-lives in the *cis* form are demonstrated. Finally, the N=N coupling can be used to generate main-chain azo polymers that are responsive to visible light. Future directions are aimed at using this method to access materials that can be used in energy storage and electronics applications.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge at https://pubs.acs.org

Experimental details, characterization data, and computational details (PDF)

AUTHOR INFORMATION

Corresponding Author

*cuyeda@purdue.edu

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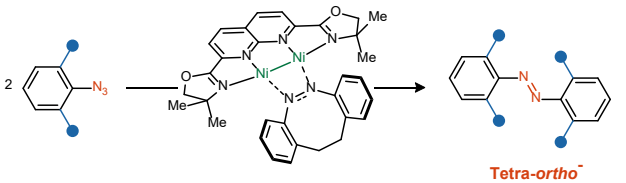
Sterically Accessible Dinickel Catalyst



Tetra-*ortho*[-] substituted azoarenes