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Construction of *meta*-Disubstituted Triaryls via Iodine-Catalyzed Oxidative Aromatization Coupling of Cycloalkenes with Indoles

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Abstract: *meta*-Disubstituted triaryls are privileged scaffolds in bioactive molecules and functional materials, but their efficient synthesis remains challenging, due to limitations in regioselectivity and reliance on prefunctionalized substrates or transition metals. Herein, an iodine-catalyzed oxidative aromatization strategy is reported for the construction of *meta*-triaryls via direct coupling of readily available cycloalkenes with indoles. This protocol enables regioselective C—C bond formation at the indole C3-position and a subsequent dehydrogenative desaturation of the cycloalkene component to form the *meta*-substituted arene motif. The method features broad substrate scope, accommodating diverse substituted cycloalkenes and indoles. Key advantages include economical catalyst (HI as iodine source), avoidance of precious metals, and operational simplicity. Additionally, the products can undergo an array of synthetic transformations, including heterocycle skeleton editing to quinolines, halogenations, and photoredox functionalizations, which highlight the potential applications of this strategy.

Keywords: aromatization, indole, iodine catalysis, *meta*-disubstituted triaryls, oxidation

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are nonpolar hydrocarbons with unique structures and photoelectric properties.[1] *meta*-Disubstituted triaryls represent a class of PAHs structural motifs prevalent in numerous biologically active molecules, pharmaceuticals, and functional materials.[2] Due to their significant conjugation effects and unique structures, these compounds typically exhibit significant application prospects in the fields of optoelectronic materials[3] and ligands[4] (**Figure 1**a). Therefore, the construction of *m*-terаryl and its derivatives is of great importance.

As a fundamental C—C bond formation method, the transition metal-catalyzed cross-coupling reaction[5] has been extensively utilized in the synthesis of *meta*-disubstituted triaryls (Figure 1b). For arenes containing two reactive sites, this approach enables the construction of *meta*-symmetric triarylated arenes.[6] However, the preparation of *meta*-unsymmetric triarylated arenes generally requires prefunctionalization of one reactive site. As an alternative method to construct C—C bonds, guided C—H functionalization[7] has been used for the synthesis of *meta*-disubstituted arenes.[8] However, these methods often face limitations including: the requirement for prefunctionalized starting materials, specific directing groups, potential regioselectivity issues, and the reliance on expensive or air-sensitive metal catalysts.

In addition, strategies involving cyclization or cycloaddition-oxidation sequences for assembling *meta*-disubstituted arenes have witnessed significant development[9] (Figure 1b). Nevertheless, this methodology faces challenges associated with reaction regioselectivity. Furthermore, access to the unsymmetrical *meta*-terаryls has also been demonstrated by using aryl acetylenes via a two-step procedure.[10] Consequently, the development of efficient, step-economical strategies for constructing *meta*-substituted arenes directly from

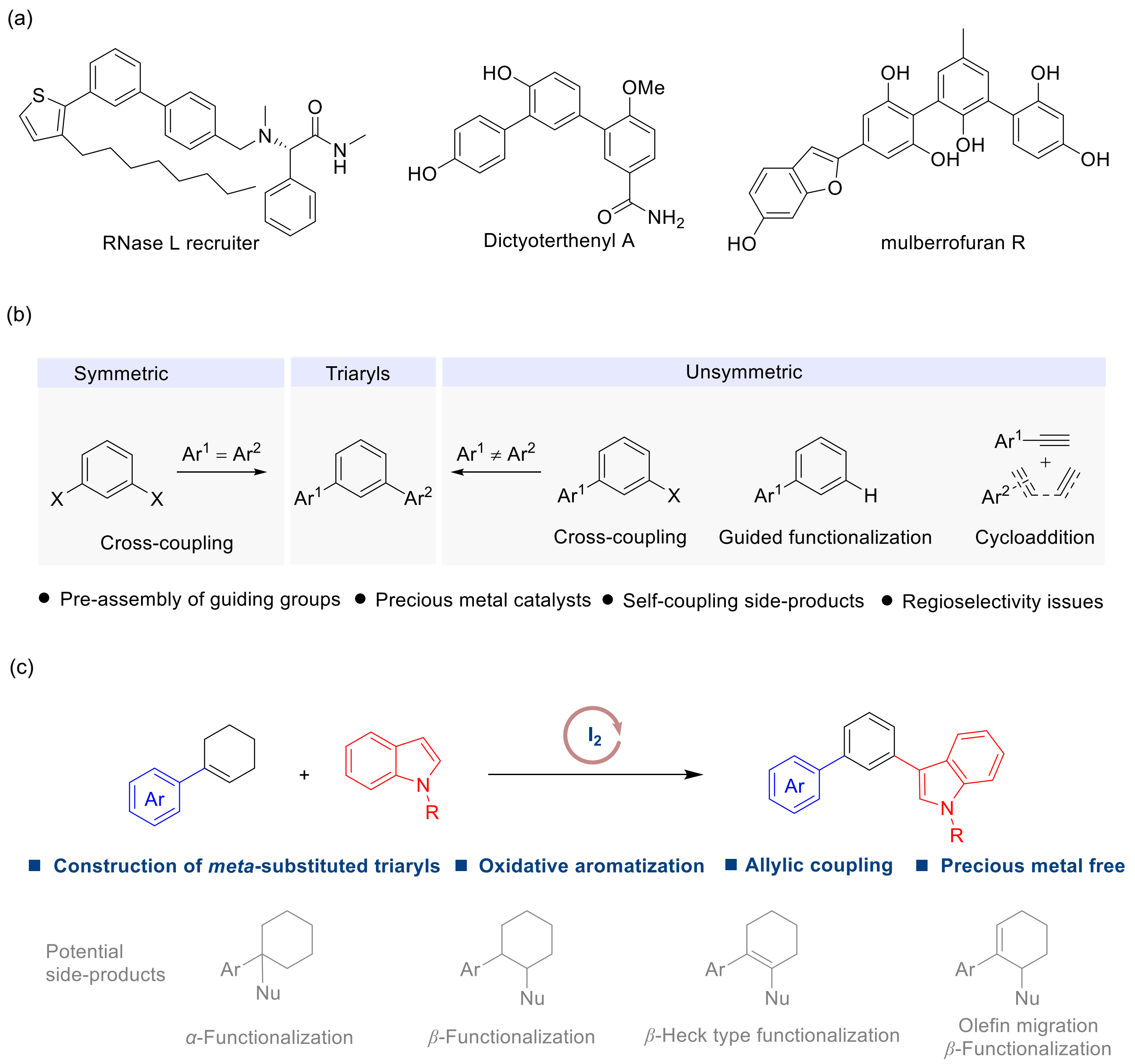


Figure 1. Construction of *meta*-substituted triaryls and their challenges. a) Representative example of *meta*-substituted triaryls. b) Methods for constructing *meta*-substituted triaryls. c) This work: oxidative aromatization coupling of cycloalkene with indole for construction of *meta*-substituted triaryls.

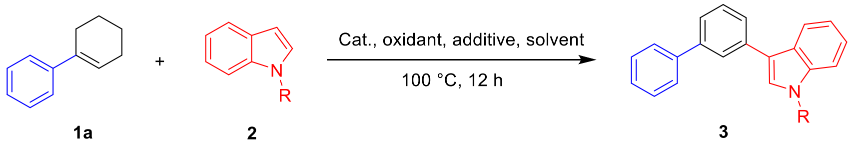
simple and readily available precursors remains a significant challenge.

Due to the influence of their spatial structure, the conversion of olefins (especially cycloalkenes) has faced certain challenges. Conceivable competitive reactions—such as α/β-functionalization of vinyl,[11] β-Heck-type functionalization of vinyl,[12] and functionalization of the β-site with olefin migration[13]—can cause considerable difficulties in redox- or regioselectivity control. To address these challenges and previous limitations, we envisioned a new strategy involving the oxidative aromatization coupling of readily accessible cycloalkenes with diverse indoles[14] (Figure 1c). By using an iodine-based catalytic system[15] to promote the C—C bond formation and a subsequent dehydrogenative desaturation, this protocol provides an efficient access to meta-disubstituted triaryls.

2. Results and Discussion

Our studies began with the reaction of phenyl cyclohexene (**1a**) and indole (**2p**) using I_2 as the catalyst. From the investigation of oxidants, potassium persulfate and hydrogen peroxide exhibited a similar reaction effect (**Table 1**, entries 1–2). The use of 2,5-di-*tert*-butyl-p-

Table 1. Optimization of reaction conditions.



Entry[a)]	Cat.	Oxidant	Additive	Solvent	3 [%]
1	I_2	$K_2S_2O_8$	–	THF	2
2	I_2	H_2O_2	–	THF	2
3	I_2	DMSO	–	THF	7
4	I_2	BQ	–	THF	17
5	I_2	BQ	–	Toluene	29
6	I_2	BQ	–	MeCN	8
7	I_2	BQ	–	CPME	34
8[b)]	I_2	BQ	–	CPME	55
9[b)]	I_2	BQ	$MnC_2O_4 \cdot 2H_2O$	CPME	55
10[b)]	I_2	BQ	MnO_2	CPME	60
11[b)]	I_2	BQ	$Mn(OAc)_2$	CPME	64
12[b)]	NIS	BQ	$Mn(OAc)_2$	CPME	60
13[b)]	DIDMH	BQ	$Mn(OAc)_2$	CPME	65
14[b)]	HI	BQ	$Mn(OAc)_2$	CPME	68
15[b,c)]	HI	BQ	$Mn(OAc)_2$	CPME	76

[a)] Conditions. **1a** (0.40 mmol), **2p** indole (0.20 mmol), [I] (0.04 mmol), oxidant (0.60 mmol), additive (0.10 mmol), solvent (1.0 mL), 100 °C, 12 h. Yields were determined by GC-FID analysis with mesitylene as the internal standard;

[b)] 140 °C;

[c)] **2a** 1-isopropyl-indole instead of **2p**, isolated yield. BQ: 2,5-di-*tert*-butyl-1,4-benzoquinone, DIDMH: 1,3-diiodo-5,5-dimethylhydantoin.

benzoquinone (BQ) gave a higher yield than DMSO (entries 3–4). Subsequently, different solvents were evaluated for this reaction (entries 4–7). When using cyclopentyl methyl ether (CPME) as reaction solvent, the target product could be obtained with a yield of 34% (entry 7). Meanwhile, it was found that a higher temperature favored the product formation (entry 8). Various manganese salts were investigated as additives in the reaction (entries 9–11). The addition of a catalytic amount of $Mn(OAc)_2$ increased the yield of the product from 55% to 64% (entry 11). Both NIS and 1,3-diiodo-5,5-dimethylhydantoin (DIDMH) were effective catalysts, yielding comparable results (entries 12 and 13). It was worth noting that HI as iodine source could yield the target product with 68% yield (entry 14). Finally, replacing indole **2p** with 1-isopropyl-indole (**2a**) as the substrate afforded the desired *meta*-disubstituted triaryl product **3aa** in 76% isolated yield (entry 15).

With the optimized conditions in hand, the scope of cycloalkenes **1** was investigated. A wide range of substituted cycloalkenes was applied and transformed to target products (**Figure 2**). It showed that both electron-donating and electron-withdrawing groups at the *para*-position of phenyl ring had no significant impact on the reactions and the desired products were obtained in 49%–82% yields (**3ba–3da**, **3ga–3ma**). In addition, naphthalene ring substituted cyclohexenes were amenable to the transformation as well (**3ea** and **3fa**). Notably, ortho-substituted benzene rings on cycloalkenes were compatible (**3na** and **3oa**). Additionally, 3,5-dimethoxy and 3,5-difluoro substituted aryl cycloalkenes were also found as good substrates in the reaction, giving the corresponding products in 62%–66% yields (**3pa**, **3qa**). Interestingly, heteroaromatic substituted cycloalkenes were found as competent substrates in the reaction, furan-, thiophene-, and benzofuran-substituted substrate affording the desired products (**3ra–3ta**) in 70%–80% yields.

Subsequently, the scope of indoles **2** was investigated in reactions with **1a** under standard conditions (Figure 2). The reactions of 4-position substituted indoles containing sterically hindered groups still gave the desired product (**3ab–3ae**, 53%–72%). The structure of **3ae** was confirmed by single-crystal X-ray crystallography (CCDC: 2,463,942). In addition, it showed that both electron-donating and electron-withdrawing groups on the phenyl ring, regardless of their positions, were well tolerated to afford the corresponding products **3af–3an**. The structure of **3af** was confirmed by single-crystal X-ray crystallography (CCDC: 2,456,031). It is noteworthy that common leaving groups, such as –Cl, –Br, and –I, which could offer useful handles for further synthetic manipulations, were also compatible to provide the corresponding products

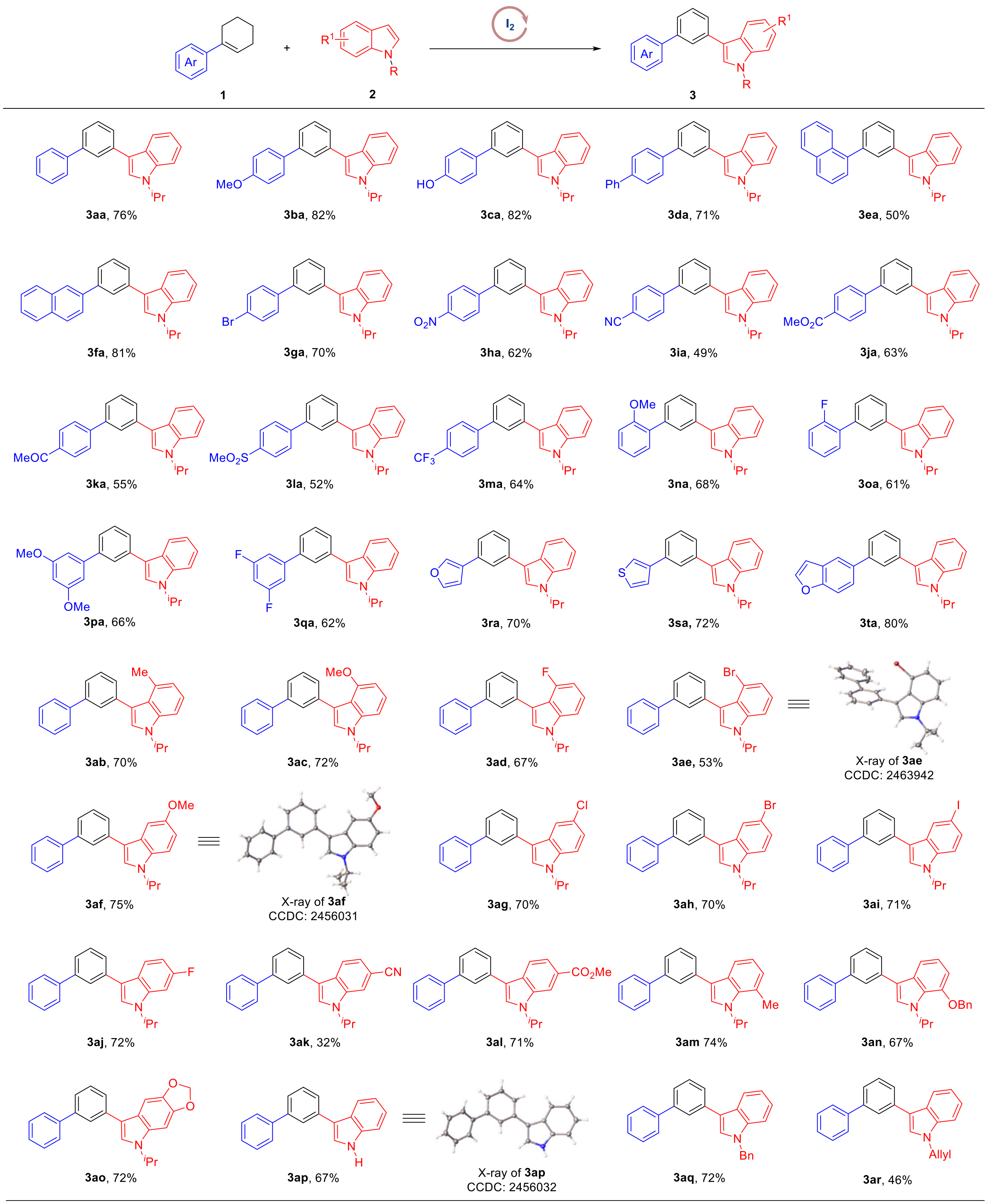


Figure 2. Substrate scope of cycloalkenes and indoles. Standard conditions: **1** (0.40 mmol), **2** (0.20 mmol), HI (20 mol%), Mn(OAc)$_2$ (50 mol%), BQ (3.0 eq.), CPME (1.0 mL), 140 °C, 12 h.

(**3ag–3ai**). 1,3-Dioxolane-substituted indole substrate **2o** also reacted smoothly as competent coupling partners in this reaction, giving the corresponding multisubstituted product **3ao** in good yields (72%). Subjecting unsubstituted indole **2p** to the standard conditions furnished oxidative coupling product **3ap** in

67% isolated yield. The structure of **3ap** was confirmed by single-crystal X-ray crystallography (CCDC: 2,456,032). Moreover, *N*-benzyl and *N*-allyl substituted indoles also worked smoothly to give *meta*-disubstituted triaryl products (**3aq** and **3ar**) in 72% and 46% yields.

To further demonstrate the synthetic applicability of this divergent protocol, a gram-scale (6.0 mmol) reaction was performed and gave *meta*-disubstituted triaryl product **3aa** in 72% yield (1.35 g, **Figure 3**). Subsequently, further synthetic transformations of **3** were carried out. The indole group of **3ap** could undergo skeleton editing to give quinoline compound **4** (80% yield),[16] which greatly enriches the diversity of product structures. In addition, TBAC and NBS as halogen sources, respectively, could achieve the synthesis of halogenated products **5** and **6**.[17] These compounds could then serve as versatile synthons in metal-catalyzed coupling reactions. The direct cyanomethylation of indoles at the 2-position was achieved via photoredox catalysis with a yield of 61% (**7**).[18] Furthermore, Friedel−Crafts C2-alkylation reactions of **3ap** with (2-nitrovinyl)benzene afforded the product **8** in moderate yield.[19] In the presence of PIFA, TBAC, and H_2O, the multifunctionalization of **3aa** motif could furnish product **9** with 56% yield through an oxidation process.[20]

To gain insights into the reaction mechanism, some preliminary mechanistic experiments have been performed. First, the dehydroaromatization of cycloalkene **1a** was performed in the presence of two equivalents of iodine (**Figure 4**a). By gas chromatography (GC) monitoring, 2% of diene **10a** and 4% of biphenyl **11** were formed at 60 °C for 1 h. In addition, when the reaction was carried out at 100 °C for 1 h, the yield of aromatization product **11** increased to 42%, and diene **10a** was not detected. We speculated that diene **10a** could not exist stably at high temperatures due to its structurally inherent instability. The reaction of diene **10a** or its isomer **10b** with indole **2p** gave the target product **3ap** in 68% and 49% yield, respectively (Figure 4a). This suggests that dienes **10a** and **10b** are probably the reaction intermediates. In the presence of one equivalent of hydrogen iodide, diene **10a** or **10b** could react with indole **2p** to afford cycloalkene **12** in moderate yields at room temperature (Figure 4a). Under standard conditions, cycloalkene **12** could be transformed to target product **3ap** in 82% yield (Figure 4a). These results indicate that cycloalkene **12** is probably another intermediate of this oxidative coupling reaction. Additionally, no conversion was observed in the reaction of biphenyl **11** with indole **2p** under standard conditions (Figure 4a). This rules out the possibility of **11** as an intermediate in the reaction. With the aid of one equivalent of hydrogen iodide conditions, dienes **10a** and **10b** could be converted to each other through an isomerization process at room temperature (Figure 4a).

Under standard conditions, the kinetic profiles of the reaction were obtained through GC monitoring. As depicted in Figure 4b, this was accompanied by a slower but steady growth in the amount of the oxidative aromatization product **11**. This further suggests that compound **11** exists only as a side-product in the reaction and can-not' participate in the oxidative coupling process of the reaction.

Based on these results and previous reports,[15g,15i] a possible reaction pathway is shown in Figure 4c. First, HI undergoes oxidation to generate I_2. Subsequently, iodonium species **B** is initially obtained from the reaction of cycloalkene **1a** with I_2. Through a nucleophilic attack by iodide, vicinal diiodide intermediate **C** is generated, which subsequently affords the compound **10a** via elimination of HI. And cyclic-diene **10b** can be obtained via the isomerization of diene **10a**.

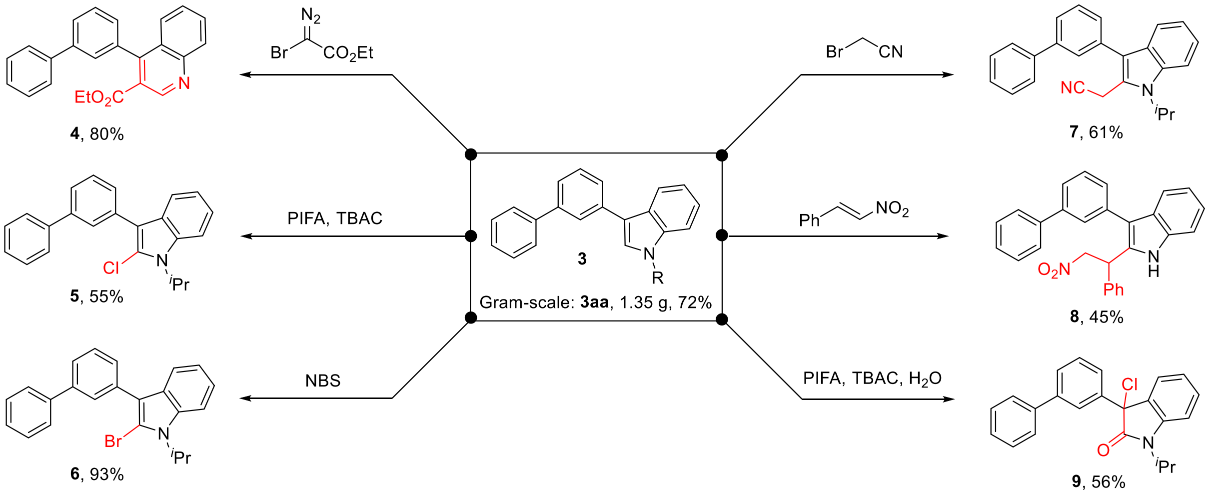


Figure 3. Synthetic transformations.

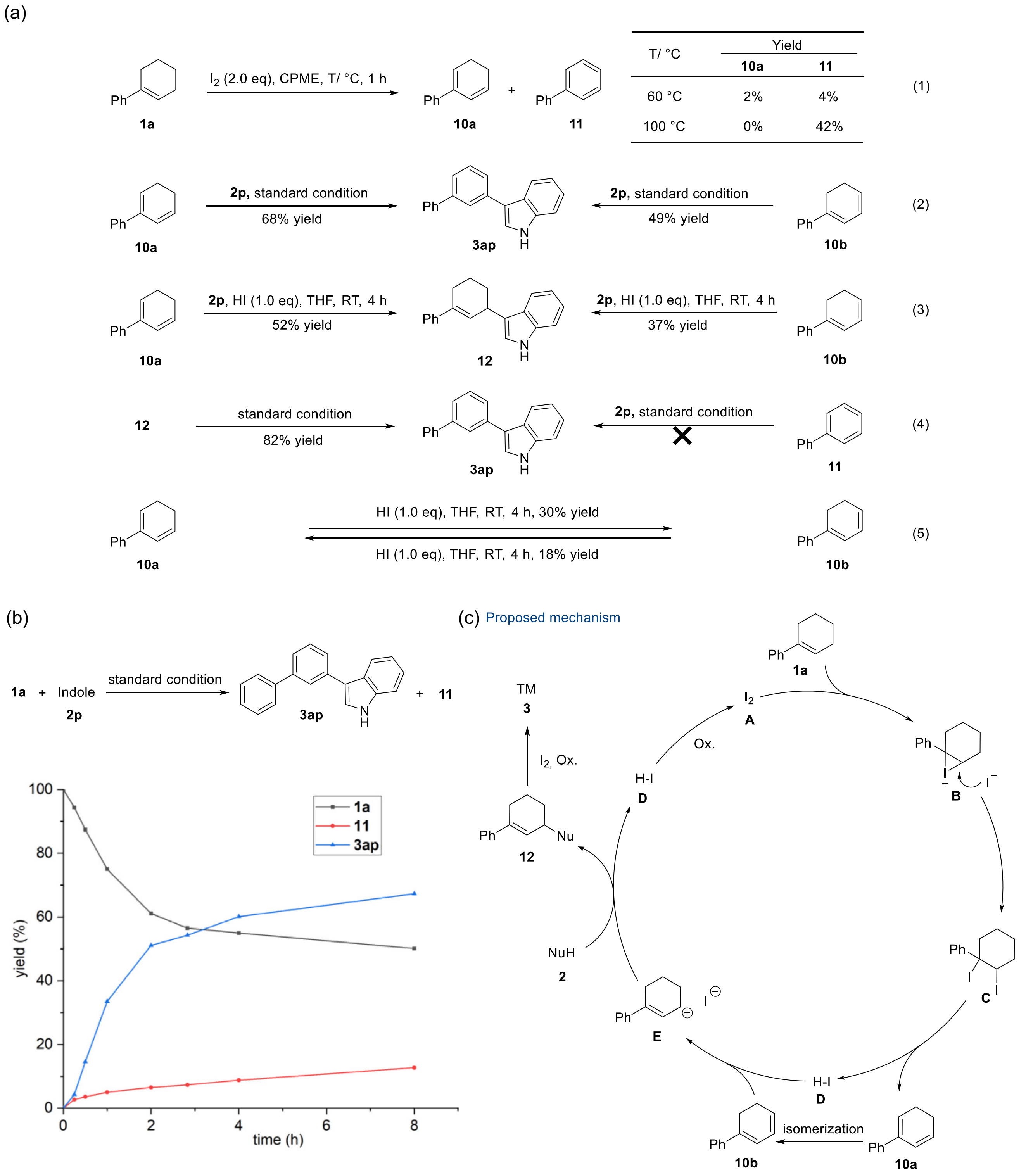


Figure 4. Mechanistic studies. a) Control experiments. b) Kinetic studies. c) Proposed mechanism.

Subsequently, a carbocation intermediate **E** is generated by the reaction of cyclic-diene **10b** and HI. Then, intermediate **E** reacts with indole **2** successfully to yield intermediate **4** and release HI. In the presence of oxidant BQ, HI undergoes oxidation to regenerate I_2. Finally, in the presence of iodide and oxidant, the desired product **3** is formed through oxidative aromatization of cycloalkene **12**.

3. Conclusions

In conclusion, we have developed an efficient strategy for the construction of *meta*-substituted unsymmetric triaryls. This approach simply employs iodine as the catalyst, with substituted cyclohexene and indole serving as coupling partners. Unlike traditional transition-metal-catalyzed approaches to *meta*-substituted unsymmetric triaryls, it avoids the need for precious metals, substrate prefunctionalization, and overcomes regioselectivity challenges. Furthermore, the reaction exhibits a notable substrate scope with tolerance toward various functional groups, providing access to numerous *meta*-disubstituted triaryl derivatives. Mechanistic studies reveal that it proceeds via a highly regioselective allylic coupling step followed by aromatization—thus removing the requirement for benzene ring prefunctionalization, a key limitation of conventional methods. Additionally, the products of this reaction can undergo diverse transformations, enabling straightforward synthesis of structurally varied triaryls. It is expected that this protocol may be of broad interest in the chemistry community and constitutes a practical alternative to the synthesis of natural products, pharmaceuticals, and functional materials.

4. Experimental Section

General Procedure: I_2 Catalyzed Oxidative Aromatization Coupling of Cycloalkenes with Indoles: Under air atmosphere, a sealed tube was charged with cycloalkene **1** (0.40 mmol, 2.0 eq.), indole **2** (0.2 mmol), BQ (0.60 mmol, 3.0 eq.), HI (55 wt% in H_2O, 0.04 mmol, 20 mol%), $Mn(OAc)_2$ (0.1 mmol, 50 mol%), and CPME (1.0 mL). The reaction tube was sealed with a Teflon screw cap. Then, the reaction mixture was stirred at 140 °C for 12 h. The reaction was washed with aq. NaOH, and extracted with ethyl acetate. After removing the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel to afford the target product **3**.

Safety Note: The operating temperature exceeds the boiling point of the solvent. All procedures must be conducted in a properly ventilated fume hood.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

***Heng Liu**, **Xiao-Feng Wu** and **Qing-An Chen** conceived and supervised the project. **Yang Yang**, **Heng Liu**, **Xiao-Feng Wu** and **Qing-An Chen** designed the experiments and wrote the paper. **Yang Yang**, **Zhi-Hui Wang**, **Yilitabaier Julaiti**, **Yanhua Lu** and **Boshun Wan** performed the experiments and analyzed the data. All authors discussed the results and commented on the manuscript.*

Data Availability Statement

*Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2463942 (**3ae**), 2456031 (**3af**), and 2456032 (**3ap**). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/. Data relating to the characterization data of materials and products, general methods, optimization studies, experimental procedures, mechanistic studies and NMR spectra are available in the Supplementary Information. All data are also available from the corresponding author upon request.*

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