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Oxidative Coupling of Aromatic Amines and Nitrosoarenes: Iodine-Mediated Formation of Unsymmetrical Aromatic Azoxy Compounds

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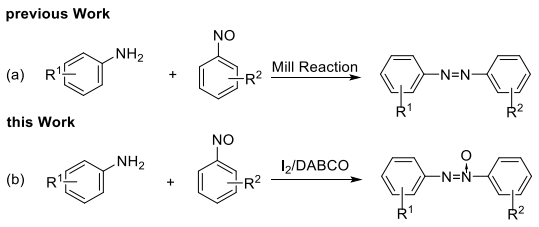
Abstract. I_2/DABCO (iodine/1,4-diazabicyclo[2.2.2]octane)-mediated oxidative coupling of nitrosobenzenes with aromatic amines was revealed to lead to the production of unsymmetrical aromatic azoxy compounds, instead of azo compounds reported previously in Mills reaction. Our study illustrates that various aromatic amines can be efficiently coupled with nitrosobenzenes to produce unsymmetrical azoxy product, in which more than thirty unsymmetrical azoxybenzenes have been successfully prepared. The applicability to a broad range of substrates, scalability to large scales and mild reaction conditions make this new synthetic protocol very practical, providing a convenient and direct access to unsymmetrical azoxybenzenes.

Keywords: Unsymmetrical azoxybenzenes; Nitrosoarenes; Aromatic amines; Iodine; Oxidative coupling

Aromatic azoxy compounds are versatile intermediates and precursors in the preparation of dyes, pigments and pharmaceuticals, and have also been used as reducing agents, chemical stabilizers, and food additives.[1] Selective oxidation of aromatic amines and reduction of nitroarenes are the most common methods for the preparation of azoxy compounds. Attempts have been made for oxidative coupling of aromatic amines using different oxidants such as H_2O_2,[2] O_2,[3] peracetic acid,[4] lead salts,[5] mangances salts,[6] ferrates,[7] mercury salts,[8] etc. A variety of reduction processes have also been developed to obtain the desired products, in which alcohol,[9] H_2,[9a,10] $NH_2NH_2{\cdot}H_2O$[11] or other reductant such as zinc [12] and bimuthium[12b,13] were utilized as the reducing reagents.

Despite the tremendous amounts of efforts towards the synthesis of azoxy derivatives, azoxy compounds provided by these two routes are symmetric, and unsymmetrical aromatic azoxy compounds could not be prepared via them. Meanwhile, the complexity of the oxidation of aromatic amines and reduction process of aromatic nitro make it very challenging to achieve high yields and selectivity.

So far, several methods have been developed for the synthesis of unsymmetrical azoxybenzenes. The reaction of Gringard reagent with *N*-substituted tosyloxydiimide *N*-oxide needs inert atmosphere protection and anhydrous condition.[14] Moreover, *N*-hydroxy-*N*-phenylnitrous amide, as the starting material for the synthesis of *N*-substituted–tosyloxydiimide *N*-oxide, its preparation process is tedious. Other methods such as oxidation of unsymmetrical azoarenes,[15] selective substitution of azoxybenzes,[16] condensation of nitrosoarens with *N*-arylhydroxylamines,[17] and condensation of nitroarenes with aryliminodimagnesium[18] suffer from the use of expensive metal,[16] poor selectivities,[15,17] availability of starting material,[17] and harsh reaction conditons.[18] All of these issues greatly limit the utilities of the methods and make them not so practical. Therefore, a convenient access to unsymmetrical azoxybenzenes is highly desirable.



Scheme 1. Different products from the reaction of aromatic amines with nitrosoarenes.

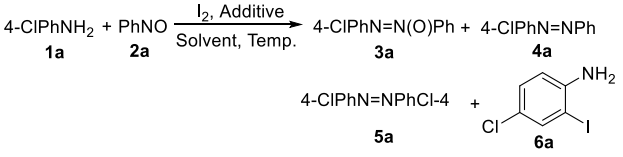
In Mills reaction aromatic nitroso derivatives react with aromatic amines and give the corresponding unsymmetrical azobenzenes in good yield, which involves the attack of aromatic amines on the nitroso derivatives that leads to azobenzenes after

dehydration of the intermediate [Scheme 1a].[1d] In this study, we found unsymmetrical azoxy compounds were formed [Scheme 1b] through the reactions of aromatic nitroso derivatives with aromatic amines using I_2/DABCO as the promoters. To the best of our knowledge, it is the first convenient and practical process for unsymmetrical azoxy compounds from aromatic amines with nitrosobenzenes under mild conditions.

The condensation of 4-chloroaniline **1a** and nitrosobenzene **2a** was chosen as a model reaction to optimize reaction parameters (Table 1). In the initial attempt, **1a** was treated with **2a** in the presence of I_2 (1.5 equiv.) in toluene at 65 °C under air for 24 hr, and 4-Chloro-2-iodoaniline **6a** was formed as a major product in 75% GC yields (Table 1, entry 1). Various bases such as CH_3COONa, NaOH, pyridine, CH_3ONa, DABCO, TEA (triethylamine), piperidine, EDA (ethylenediamine), and HMTA (hexamethylene tetramine) were screened. It was found that the reaction selectivity was very different with respect to the added base. Specifically, When CH_3COONa was added, the formation of **6a** was decreased greatly, companied with the substantial increase of Mills product **4a** (Table 1, entry 2). When NaOH was employed, there was no iodinated product, while **4a** and **5a** (oxidative dehydrogenative coupling product of **1a**) formed (Table 1, entry 3). Interestingly, when DABCO was employed as base, dehydrogenative coupling compound **3a,** unsymmetrical azoxybenzene was formed as a major product (96% selectivity with 94% conversion) (Table 1, entry 6). The molecular structure of product **3g**[19] was confirmed by single crystal X-ray diffraction analysis (SI, Figure S1) and NMR spectra. In the next step, the loadings of I_2 and DABCO were optimized (SI, Table S1 and S2). To obtain satisfactory conversion, 1.5 equivalent of I_2 and 3.0 equivalent of DABCO were needed for this transformation. Increasing reaction temperature led to lower selectivity. Good conversion with a high selectivity can be obtained with a low reaction temperature and long reaction time (SI, Table S3). Screening the solvent indicates that the selectivity of the reaction is independent of the solvent polarity, while the conversion rate is sensitive to it in this transformation (SI, Table S4).

At the above optimized reaction conditions, the I_2/DABCO system were then applied to various aromatic amines (Table 2). The results show that the method tolerates various functional groups. Halo, methoxy, and alkyl substituted aromatic amines, including the sterically more hindered ortho-substituted ones, reacted efficiently to give the target unsymmetrical aromatic azoxy compounds with a good yield (**3a-3d**, **3h-3m**). It is noteworthy that halogens survived well, leading to the production of halo-substituted unsymmetrical azoxybenzene. These substance are potentially useful in other synthesis, as they bear chloro, bromo and iodo groups. The reactions of electron-deficient aromatic amines, such as CH_3OCO-, NO_2-, and CF_3-, were not efficient (Table 2, **3e-3g**), in which their target products have only moderate yields with an elevated reaction temperature and longer reaction time (80°C and 48hr). And some unreacted amines were detected by GC, possibly because strongly electron-withdrawing substituted aromatic amines are less basic and nucleophilic, resulting in less efficient condensation reactions. Naphthalen-1-amine was not a suitable substrate, its reaction led to the product in 57% GC yields (Table 2, **3n**), accompanied with a Mills product (5%), unidentified product (20%), and unreacted material (18%). Similar to electron-withdrawing substituted phenylamines, the reaction between heteroaromatic amines with nitrosobenzene is not efficient and only forms the corresponding products with a moderate yield at a high temperature and long reaction time (80°C and 48hr) (Table 2, **3o**, **3q-3t**). Pyridin-4-amine failed to react with nitrosobenzene, and was recovered intact. This is most likely due to a combination of electronic effect and solubility, as pyridin-4-amine is not soluble in toluene. Quinolin-3-amine was not a suitable substrate neither, and only 27% GC yield of product was detected, accompanied with Mills product (9%), iodinated byproduct (41%), and unreacted amine (23%)(Table 2, **3u**).

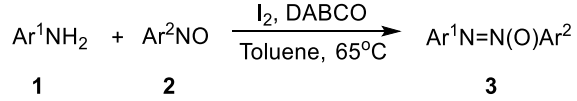
Table 1. Bases screening for the synthesis of unsymmetrical azoxybenzene.

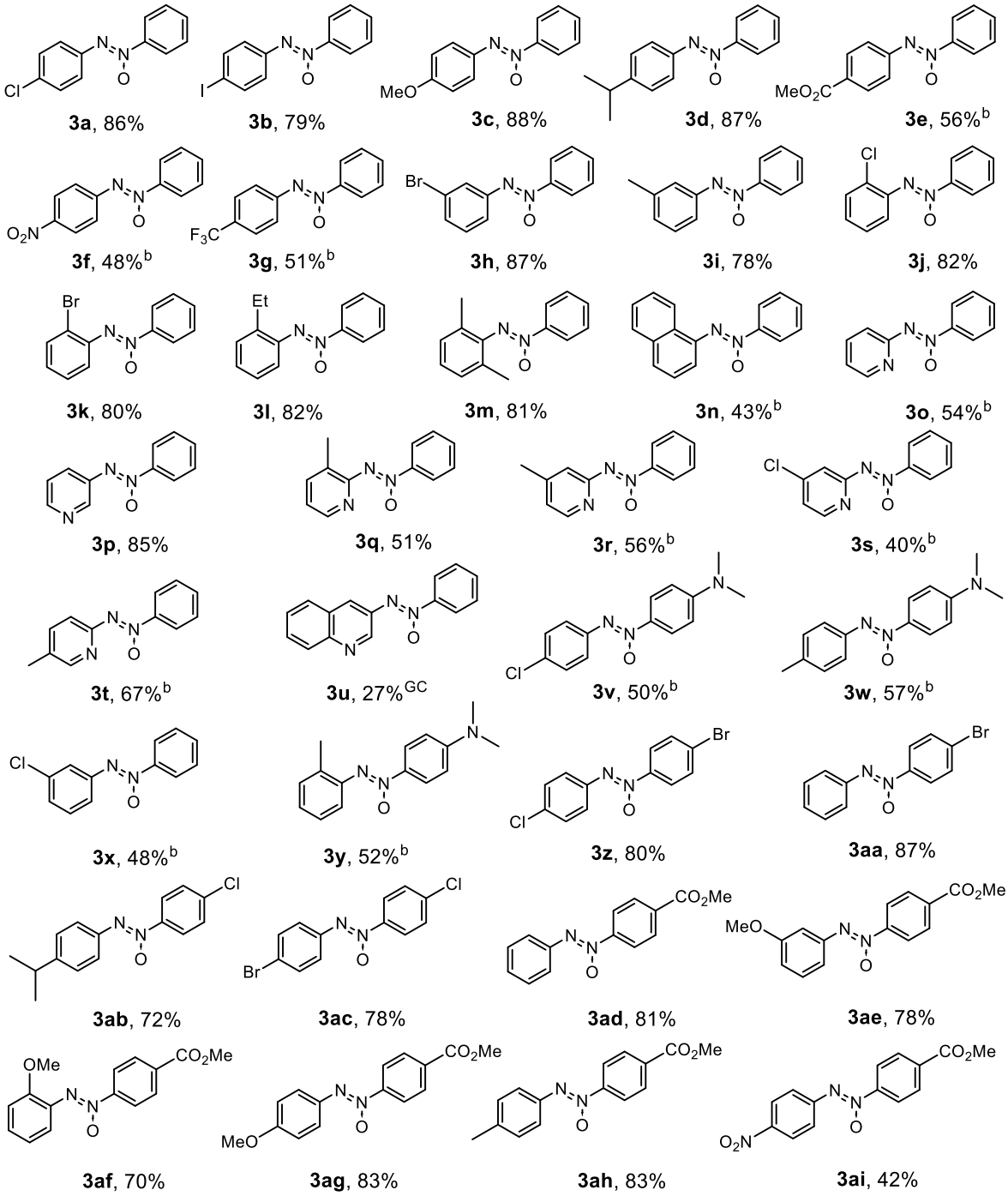


Entry[a]	Base	Conv.(%)[b]	Sel.(%)[b]			
			3a	**4a**	**5a**	**6a**
1	-	92	-	18	-	82
2	CH_3COONa	82	10	49	-	41
3	NaOH	80	-	40	60	-
4	Pyridine	90	-	52	-	48
5	TEA	52	-	-	-	100
6	DABCO	94	96	2	-	2
7	CH_3ONa	96	-	39	12	49
8	Piperidine	8	-	-	-	100
9	Piperazine	15	25	7	-	68
10	EDA	5	28	12	-	60
11	HMTA	44	-	-	-	100

[a] All the experiments were carried out with *p*-$ClC_6H_4NH_2$ (0.2 mmol), C_6H_5NO (0.22 mmol), I_2 (0.3 mmol), Base (0.6 mmol), Toluene (1 mL), 65°C, air, 24hr, unless otherwise noted. [b] Conversion and selectivity based on *p*-$ClC_6H_4NH_2$ and measured by GC-MS.

Table 2. The oxidative coupling reactions of aromatic amines and nitrosobenznes for synthesis of unsymmetrical azoxybenzenes in the presence of I_2/DABCO.

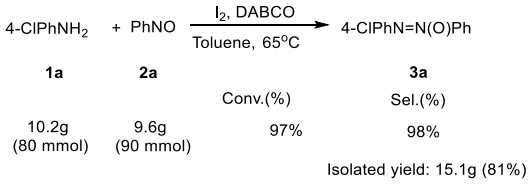




[a] All the experiments were carried out with Ar^1NH_2 (0.2 mmol), Ar^2NO (0.22 mmol), I_2 (0.3 mmol), Base (0.6 mmol), Toluene (1 mL), 65°C, air, 24hr, unless otherwise noted. [b] 80°C, 48hr.

Several nitrosoarenes were also employed to react with substituted aromatic amines. The electronic effect of substitutent on nitrosobenzenes was observed again. Electron-donating substituted

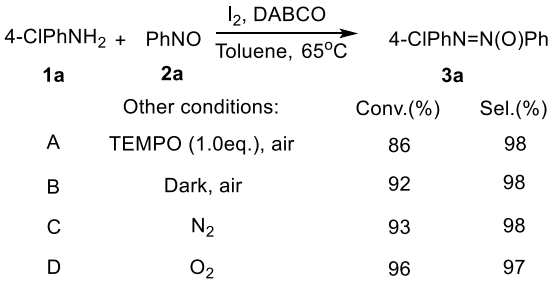
nitrosobenzenes showed a negative response to the oxidative coupling reaction. For example, when *N*,*N*-dimethylamino was attached to the nitrosobenzene, its reaction was not so efficient and only afforded the products with a moderate yield with 80°C and 48hr period (Table 2, **3v-3y**). In contrast, electron-withdrawing group substituted ones showed a positive effect on this transformation. For example, the reaction of ethyl 4-nitrosobenzoate produces azoxybenzenes with a good yield (Table 2, **3ad-3ah**).



Scheme 2. Large scale reaction for the synthesis of unsymmetrical azoxybenzene.

The reaction was then carried out on a much larger scale to examine the scalability and practicality of the above oxidative coupling of aromatic amines with nitrosobenzene. As shown in Scheme 2**,** 80-mmol scale reaction of **1a** and **2a** successfully provides 81% isolated yield of **3a** under the optimized reaction conditions. All the above experimental results clearly revealed the generality, practicality and synthetic potential of the present method.

To decipher the reaction mechanism, control experiments were carried out. The addition of TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) to the standard reaction, which is a representative radical inhibitor, did not affect the product yield (Scheme 3-A). It was also observed that conducting the reaction in the dark or under daylight (Scheme 3-B**)** had no impacts on the reaction yield and selectivity. These results suggest that the process involves the formation of ionic rather than radical intermediates.



Scheme 3. Control experiments for exploration reaction mechanism.

The reactions of **1a** with **2a** under optimized conditions were also investigated under N_2 or O_2 atmosphere, respectively. Similar GC yields of **3a** were obtained in both of cases (Scheme 3-C, D). All these results implicate that the oxygen atom of product comes from the oxygen of nitrosobenzene.

Throughout our exploration, it was noticed that both iodine and DABCO are essential for the reaction. No reaction occurred in the absence of iodine. It was also observed that the selectivity of the reaction was very different with or without DABCO. To understand how DABCO and I_2 worked in the reaction, we deployed ^{1}H NMR techniques to monitor the above reaction as shown in Figure 1. It was seen that upon the addition of 0.5 equivalents of I_2 into a [D6]DMSO solution of DABCO (1.0 equiv.), the singlet signal (2.6 ppm) of DABCO disappeared, accompanied with the appearance of a broad multiplet (2.77-2.95 ppm) and a triplet (3.14 ppm) signal, which resulted from the interaction between I_2 with DABCO. When 1.5 equivalents of I_2 was added to a [D6]DMSO solution of **1a** (1.0 equiv.), the two doublet signals (6.53 and 7.00 ppm) of aromatic hydrogen atoms of **1a** disappeared, and **6a** was formed in 65% (^{1}H NMR yield). Another unidentified compound was produced, which also has two doublet signals (7.32 and 7.54 ppm). It was speculated to be the *N*-iodinated product such *p*-ClC_6H_4NHI, an unstable intermediate, and could also be converted into **1a** through a hydrogen-iodine exchange, since we detected only **6a** (85%) and **1a** (15%) after 24 hr through GC-MS.[20] However, once DABCO was added into mixture [D6]DMSO solution of **1a** and I_2, not only did the iodinated product **6a** decrease greatly but *N*-iodinated product of **1a** could not be detected, while the interaction signals of I_2 with DABCO still unchanged. We suggest that the above result was due to nucleophilicity difference of nitrogen in DABCO and **1a**. DABCO has stronger nucleophilicity than **1a**, and the bond between iodine and nitrogen of DABCO is formed more easily than a bond between iodine and nitrogen of **1a**, moreover, this formed bond is so strong that electrophilic aromatic iodination product **6a** cannot occur efficiently and its yield decreases greatly. We did another experiment in which we added *N*-iodosuccinimide (NIS) to the reaction of **1a** with **2a** instead of I_2. It was found that similar results were obtained that the GC yields of iodinated products (**6a** and diiodoaniline) were 71% without addition of DABCO, while their yields decreased greatly with the addition of DABCO (SI, Table S5). When nitrosobenzene was added to the mixture solution of iodine, DABCO and **1a**, the oxidative coupling reaction occured immediately.

Based on those control experiments, a plausible mechanism for the oxidative dehydrogenative is proposed in Scheme 4. First, nucleophilic attack on nitrosobenzene by the lone pair electrons of an aromatic amines occurs, affording a nucleophilic addition intermediate. Subsequently, DABCO

10.1002/adsc.201800495

abstracted a proton from the resulted ammonium ion, yielding the intermediate **A**. The nitrogen lone pair electron of **A** attacked iodine atom of DABCO-I_2 ion pair**,** followed by deprotonation of the initially formed ammonium ion of intermediate **B** which undergoes elimination of iodide anion (I^-) and gives a unsymmetrical azoxy compound.

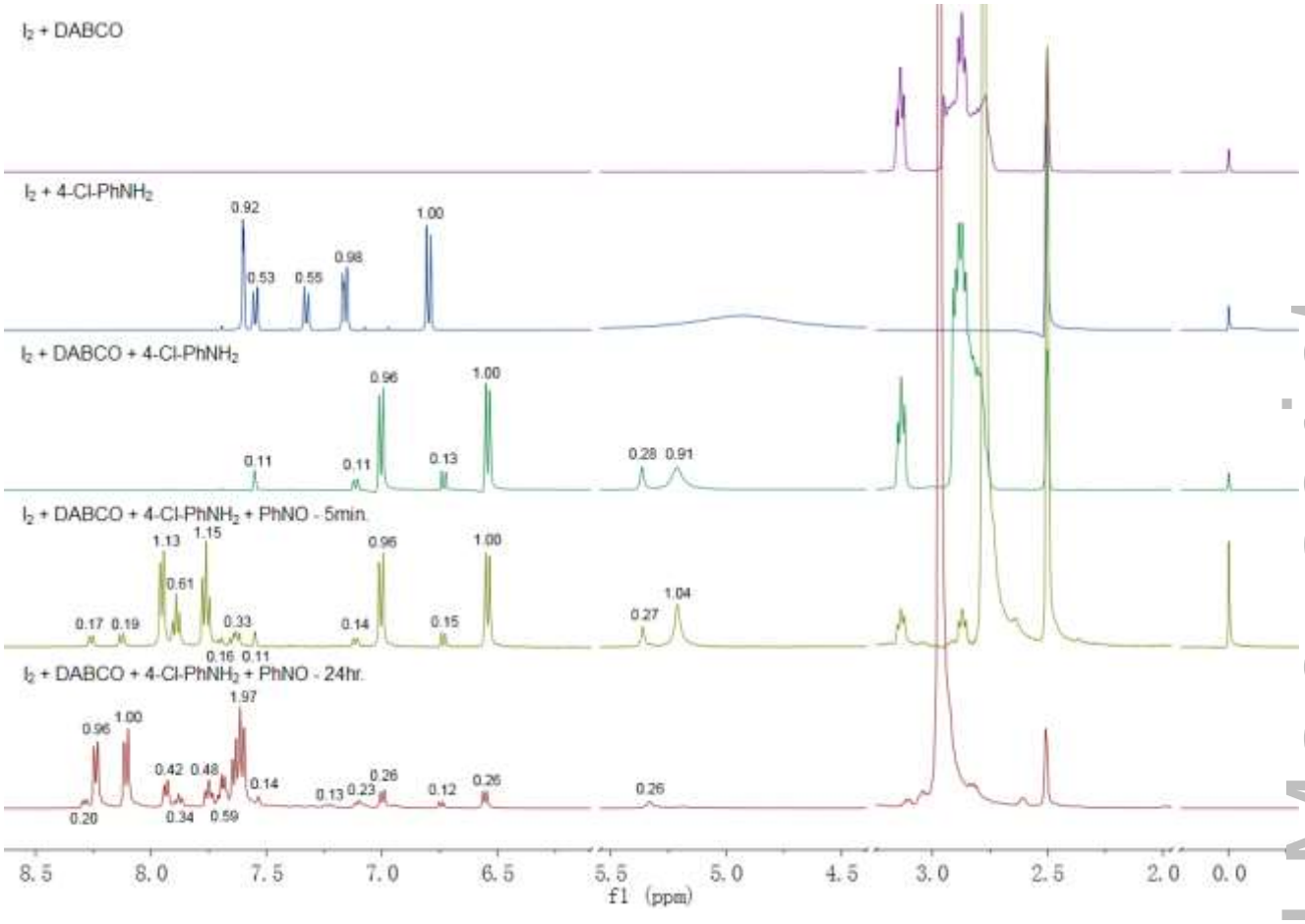
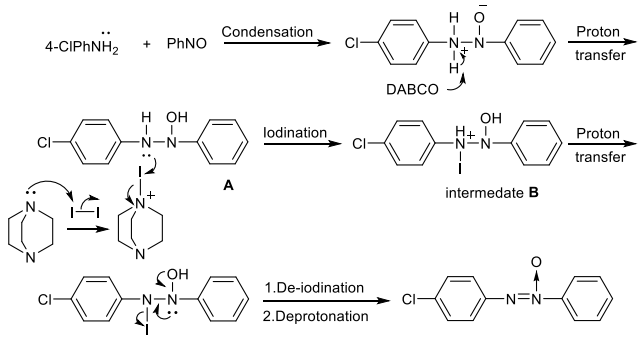
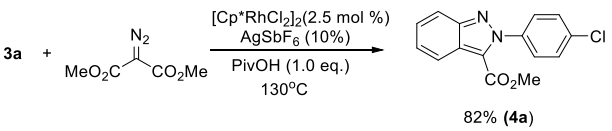


Figure 1. Contrast ^{1}H NMR spectrum with different reactants.



Scheme 4. A plausible mechanism for the oxidative dehydrogenative coupling.

As shown in Scheme 5, we finally investigated the synthetic potential of this reaction. Based on the literature report,[14d] **3a** could undergo a region- and chemoselective [4+1] annulation with diazoester for the synthesis of 3-acyl-2*H*-indazole **4a** with 82% isolated yield, which was a useful intermediate and could be utilized to prepare 4-aminoquinoline derivative.[21]



Scheme 5. Transformation of **3a** into 3-acyl-2*H*-indazoles **4a**.

In summary, we discovered a novel approach to the preparation of unsymmetrical aromatic azoxy compounds. A series of unsymmetrical azoxy compounds have been conveniently prepared through the oxidative coupling reaction of nitrosobenzenes and aromatic amines mediated by I_2/DABCO. As far as we know, it is the first example for the synthesis of

unsymmetrical azoxy compounds directly from aromatic amines and nitrosobenzenes. The reaction is operationally simple and is amenable to large scale, greatly reducing the difficulty in synthesis of unsymmetrical azoxy compounds. Further study of this new route would open a new chapter of research that brings more reactions to the synthesis and application of unsymmetrical azoxy compounds.

Experimental Section

General Procedure for the Synthesis of 3

A solution of **1** (0.2 mmol, 1.0 equiv.), **2** (0.22 mmol, 1.1 equiv.), I_2 (0.3 mmol, 1.5 equiv.) and DABCO (0.6 mmol, 3.0 equiv.) in toulune (1 mL) in a sealed 10 ml Schlenk tube was stirred at 65 °C. The progress of reaction was monitored by TLC and/or GC-MS. After completion of reaction, the crude reaction mixture was cooled to room temperature, and the solvent was then removed under reduced pressure. Then, the residue was purified by column chromatography on silica gel with EtOAc and petroleum ether as eluent to give **3**. The characterization data of the products are given in the Supporting Information.

Typical Procedure for the Synthesis of 4a

Into a dried 100 ml round bottom flask equipped with a magnetic stir bar, was added $[Cp^*RhCl_2]_2$ (15.4 mg, 0.025 mmol), $AgSbF_6$ (34.6 mg, 0.1 mmol), **3a** (232.0 mg, 1.0 mmol). The vessel was evacuated and backfilled with N_2 before PivOH (114.9μL, 1.0 mmol), dimethyl 2-diazomalonate (237.0 mg, 1.5 mmol), and 1.0 ml of 1,2-dichloroethane were added. The mixture was heated to 130 °C and stirred overnight. After completion of reaction, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Then the residue was purified by column chromatography on silica gel (PE/EtOAc = 10/1, v/v) to afford **4a** as a light yellow solid (234.5 mg, 82% yield).

Acknowledgements

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[19] CCDC 1581058 (**3g**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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UPDATE

Oxidative Coupling of Aromatic Amines and Nitrosoarenes: Iodine-Mediated Formation of Unsymmetrical Aromatic Azoxy Compounds

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