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Oxidative Dimerization of (Hetero)aromatic Amines Utilizing *t*-BuOI Leading to (Hetero)aromatic Azo Compounds: Scope and Mechanistic Studies

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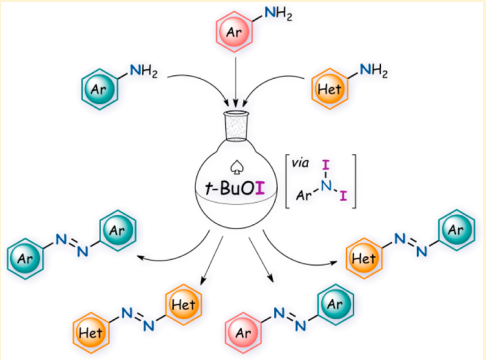
Supporting Information

ABSTRACT: A straightforward synthetic method of both symmetric and unsymmetric aromatic azo compounds through an efficient and cross-selective oxidative dimerization of aromatic amines using *tert*-butyl hypoiodite (*t*-BuOI) under metal-free and mild conditions has been developed. This method was also found applicable to the synthesis of heteroaromatic azo compounds. The spectroscopic study indicates the involvement of *N*,*N*-diiodoanilines in the oxidative reaction as the key intermediate.



INTRODUCTION

For over a century, azobenzene derivatives have been utilized as organic dyes in industry.[1] In addition to such traditional use of azobenzenes, over the past few decades, there has been a rapid growth in interest in their next-generation applications as photoresponsive soft materials such as smart polymers,[2] liquid crystals,[3] photochromic ligands for optochemical genetics,[4] and photoswitches in biological systems,[5] owing to their intrinsic ability of photochemical *cis*/*trans*-isomerization.[6] In terms of their preparation, a myriad of synthetic methods are available nowadays.[7] However, an appropriate choice of synthetic method would mostly depend on the structural symmetry of azobenzenes of interest (i.e., *symmetric* or *unsymmetric* types). As for the preparation of symmetric azobenzenes, direct synthetic methods starting from readily available organic compounds involve reductive homodimerization of nitrobenzenes[8] and oxidative homodimerization of aromatic amines.[9] Nonetheless, the former often confronts the difficulty in controlling product distribution of the azo-/azoxybenzene ratio, and the latter suffers from the stoichiometric use of environmentally unfriendly heavy-metal oxidants such as $BaMnO_4$, $Pb(OAc)_4$, AgO, and HgO. Although Cu-catalyzed homodimerization processes of aromatic amines using air as the co-oxidant have been developed to avoid the use of heavy-metal salts,[10] incompatibility of functional groups and low yields of desired products are still inevitable. On the other hand, unsymmetric aromatic azo compounds have been exclusively synthesized by diazonium coupling[11] and the Mills reaction.[12] These reactions require the preparation of explosive diazonium salts or toxic nitrosobenzenes as substrates from commercially available organic compounds. More specifically, the main problem of these approaches lies in the substrate scope, which is limited to the combination of electron-rich and -deficient aromatic amines, because of their reaction mechanisms. To address these issues, recently, catalytic approaches using oxygen as an oxidant have been developed.[13] While Grirrane, Corma, and García realized the air-oxidation system by employing Au/TiO_2 nanoparticles,[13a,b] He and Li utilized Ag nanoparticles as a heterogeneous catalyst.[13c] The Jiao's group reported Cu/pyridine-catalyzed aerobic oxidative dimerization of aniline derivatives.[13d] Furthermore, an organocatalytic approach using hypervalent iodine(III) has also been developed by Ma and Lei.[14] Although these reports succeeded in synthesizing a series of unsymmetric azobenzenes, there still remains considerable room for improvement in each method: the harsh conditions employing high pressurized O_2 (5 bar) and a high temperature (100 °C) in the Au/TiO_2 system, the stoichiometric use of a strong base (KOH) in the Ag-nanoparticle system, and the use of excess amounts of the electron-deficient aromatic amines in the Cu/pyridine system. Therefore, the development of robust synthetic methods of azobenzene derivatives with high efficiency, wide diversity, and high functional compatibility is significantly desirable.

In this regard, we have recently reported an efficient, lower-energy-consuming, and metal-free synthetic method for both symmetric and unsymmetric aromatic azo compounds through oxidative dimerization of aromatic amines (Scheme 1),[15] utilizing a unique monovalent iodine-containing reagent, *tert*-butyl

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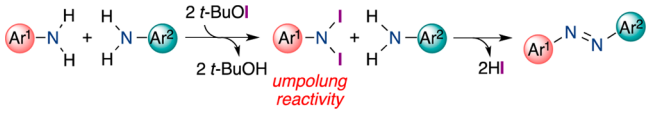
Scheme 1. Oxidative Dimerization of Aromatic Amines Using *t*-BuOI

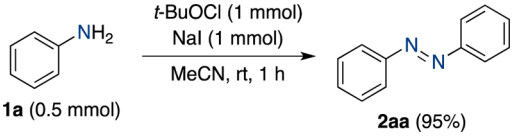


hypoiodite (*t*-BuOI).[16] The key concept of the oxidative reaction involves the umpolung reactivity of aromatic amines, converting $ArNH_2$ as a nucleophile into $ArNI_2$ as an electrophile through an efficient H/I exchange process mediated by *t*-BuOI (Scheme 1).[17] Our preliminary study revealed that the reaction conditions were applicable to a wide range of anilines with high functional compatibility under mild reaction conditions. The successful results prompted us to further expand the substrate scope to heteroaromatic amines: heteroaromatic azo compounds can find new applications such as nonliner optical (NLO) materials[18] and photodissociable ligands (PDLs).[19] We also became interested in the application of our method to the practical preparation of functional materials. Furthermore, we continued to pursue mechanistic details of the oxidative reaction. Herein, we disclose the detailed course of reaction development, the full scope of substrates, and the synthetic applications to efficient preparation of photochemical switches. Furthermore, mechanistic aspects probed by NMR and MS spectroscopy are discussed.

RESULTS AND DISCUSSION

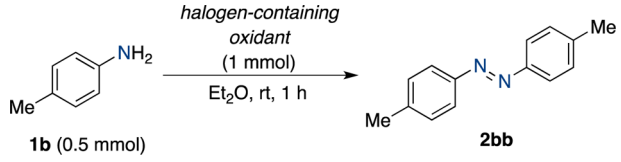
Development of Oxidative Homodimerization of (Hetero)aromatic Amines. The reagent *t*-BuOI was readily generated in situ from commercially available and inexpensive reagents, *tert*-butyl hypochlorite (*t*-BuOCl) and sodium iodide (NaI).[17] Initially, we examined an oxidative homodimerization of aniline (**1a**) as the model reaction. When **1a** (0.5 mmol) was treated with 2 equiv of *t*-BuOI (1 mmol) in acetonitrile at room temperature for 1 h, oxidative homodimerization forming a N═N double bond was found to smoothly proceed to give *trans*-azobenzene **2aa** in 95% yield (Scheme 2).

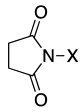
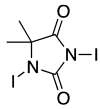
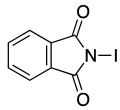
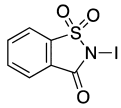
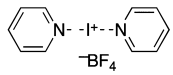
Scheme 2. Homodimerization of Aniline (1a)



To confirm the superiority of the system, we examined other electrophilic halogen-containing oxidants in the homodimerization of *p*-toluidine (**1b**) (Table 1). Whereas the use of *t*-BuOI afforded azo product **2bb** in 97% yield (entry 1), *t*-BuOCl was found to be ineffective for the reaction (entry 2). Iodinating reagents composed of diatomic interhalogen molecules (I_2, ICl, IBr) and the combination of I_2/Et_3N failed to give the product (entries 3−6). Widely used halogenating reagents, *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), and *N*-iodosuccimide (NIS) also did not give satisfactory yields of **2bb** in any of the cases (entries 7−9). The employment of *N*-iodopyrrolidin-2-one, 1,3-diiodo-5,5-dimethylhydantoin (DIH), *N*-iodophthalimide (NIPI), and *N*-iodosaccharin (NISac) resulted in rather low yields of **2bb** (entries 10−13). The use of a highly electrophilic iodonium reagent, IPy_2BF_4 (BPIT), failed to provide the desired product (entry 14). The order of the addition of

Table 1. Effect of Halogen-Containing Oxidants[a]



entry	oxidant		yield [%][b]
1	*t*-BuOI		97[c]
2	*t*-BuOCl		4
3	I_2		0
4	I_2 + Et_3N		0
5	ICl		0
6	IBr		0
7		X = Cl	4
8		Br	0
9		I	10
10			5
11[d]		**DIH**	15
12		**NIPI**	8
13		**NISac**	trace
14		**BPIT**	0

[a]Reaction conditions: **1b** (0.5 mmol) and halogen-containing oxidant (1 mmol) in Et_2O (3 mL) at room temperature for 1 h. [b]^1H NMR yields. [c]Isolated yield. [d]0.5 mmol of DIH was used.

reagents also turned out to be a quite important factor: when *t*-BuOCl was first added prior to NaI, no dimerized product was produced and only monochlorinated amine was detected. This result suggests that in situ generation of *t*-BuOI is much faster than the chlorination of the amine by *t*-BuOCl.

Having confirmed the superiority of *t*-BuOI, the substrate scope of the oxidative homodimerization was investigated (Table 2). Anilines bearing an electron-donating substituent such as methyl-, methoxy-, and *N*,*N*-dimethylamino groups at the *para* position were readily transformed into the corresponding aromatic azo compounds **2bb**−**2dd** in moderate to high yields (entries 2−4). Halo-substituted anilines were applicable to the reaction conditions to give the corresponding products in high yields (entries 5−8). Although the homodimerization of electron-deficient aromatic amines required prolonged times compared to the reactions of electron-rich amines, the corresponding azo compounds were produced in excellent yields

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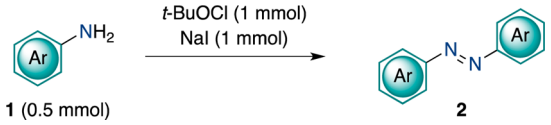
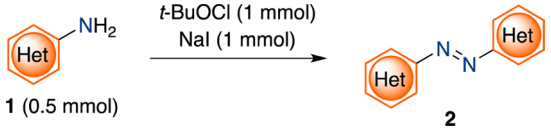
Table 2. Homodimerization of Aromatic Amines[a]

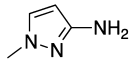
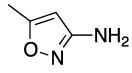
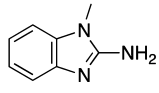
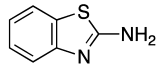
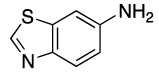
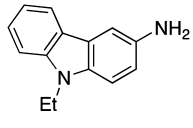


entry	1	Ar	conditions	2	yield [%][b]
1	**1a**	Ph	MeCN, rt, 1 h	**2aa**	95
2	**1b**	*p*-Me-C_6H_4	Et_2O, rt, 1 h	**2bb**	97
3	**1c**	*p*-MeO-C_6H_4	MeCN, rt, 0.25 h	**2cc**	87
4	**1d**	*p*-Me_2N-C_6H_4	DMF, 0 °C, 6 h	**2dd**	69
5	**1e**	*p*-F-C_6H_4	acetone, rt, 6 h	**2ee**	95
6	**1f**	*p*-Cl-C_6H_4	Et_2O, −20 °C, 12 h	**2ff**	96
7	**1g**	*p*-Br-C_6H_4	acetone, rt, 3 h	**2gg**	83
8	**1h**	*p*-I-C_6H_4	Et_2O, −20 °C, 12 h	**2hh**	88
9	**1i**	*p*-EtO_2C-C_6H_4	Et_2O, rt, 3 h	**2ii**	95
10	**1j**	*p*-Me(O)C-C_6H_4	Et_2O, −20 °C, 12 h	**2jj**	91
11	**1k**	*p*-NC-C_6H_4	THF, rt, 12 h	**2kk**	89
12[c]	**1l**	*p*-O_2N-C_6H_4	THF, rt, 6 h	**2ll**	79
13	**1m**	*p*-(Ph-N═N)-C_6H_4	THF, −20 °C, 24 h	**2 mm**	67
14	**1n**	*m*-Cl-C_6H_4	acetone, rt, 3 h	**2nn**	86
15	**1o**	*m*-O_2N-C_6H_4	THF, −20 °C, 12 h	**2oo**	78
16	**1p**	*o*-Ph-C_6H_4	Et_2O, −20 °C, 36 h	**2pp**	44
17	**1q**	*o*-NC-C_6H_4	Et_2O, rt, 24 h	**2qq**	73
18	**1r**	3,4-$Me_2C_6H_3$	Et_2O, rt, 1 h	**2rr**	89
19	**1s**	3,5-$(F_3C)_2C_6H_3$	THF, rt, 12 h	**2ss**	94
20	**1t**	F_5C_6	Et_2O, rt, 12 h	**2tt**	67

[a]Reaction conditions: **1** (0.5 mmol), *t*-BuOCl (1 mmol), and NaI (1 mmol) in solvent (3 mL). [b]Isolated yields. [c]2 mmol of *t*-BuOCl and NaI were used.

Table 3. Homodimerization of Heteroaromatic Amines[a]



entry	1		conditions	2	yield [%][b]
1		**1u**	DME, –40 °C, 12 h then, –20 °C, 12 h	**2uu**	83
2		**1v**	MeCN, rt, 24 h	**2vv**	76
3		**1w**	DME, –20 °C, 24 h	**2ww**	76
4		**1x**	MeCN, rt, 48 h	**2xx**	72
5		**1y**	acetone, 0 °C, 48 h	**2yy**	62
6		**1z**	DME, –20 °C, 3 h	**2zz**	70

[a]Reaction conditions: **1** (0.5 mmol), *t*-BuOCl (1 mmol), and NaI (1 mmol) in solvent (3 mL). [b]Isolated yields.

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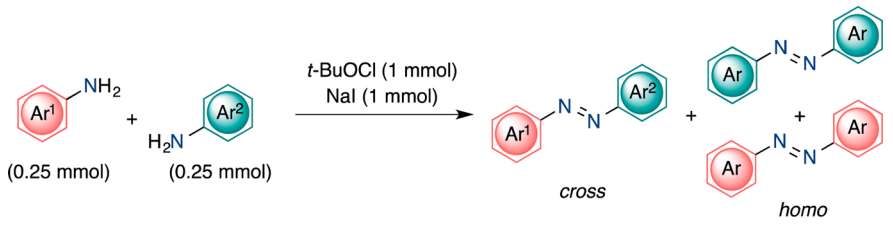
Table 4. Cross-dimerization of Aromatic Amines[a]



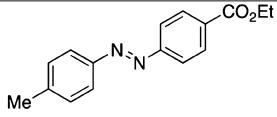
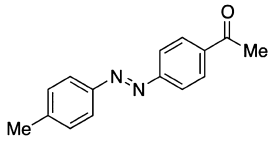
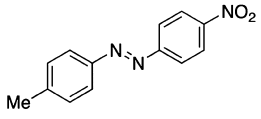
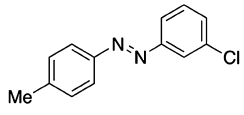
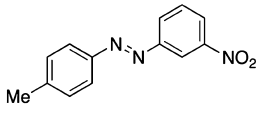
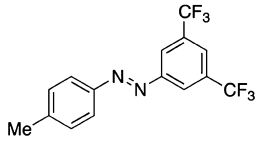
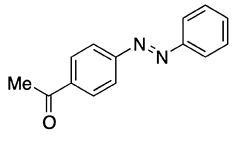
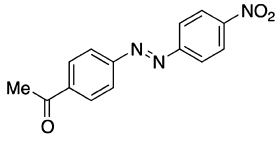
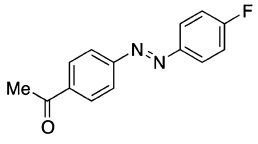
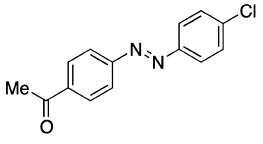
entry	1	conditions	*cross-product*	yield [%][b]	
				cross	*homo*
1	**1b** + **1i**	THF, 0 °C, 6 h		62 (**2bi**)	32 (**2bb**) 30 (**2ii**)
2[c]	**1b** + **1j**	THF, –20 °C, 24 h		58 (**2bj**)	60 (**2bb**) 24 (**2ij**)
3	**1b** + **1l**	THF, 0 °C, 3 h Then, rt, 1 h		64 (**2bl**)	27 (**2bb**) 20 (**2ll**)
4	**1b** + **1n**	acetone, 0 °C, 3 h		52 (**2bn**)	34 (**2bb**) 21 (**2nn**)
5	**1b** + **1o**	THF, –20 °C, 24 h		60 (**2bo**)	32 (**2bb**) 16 (**2oo**)
6	**1b** + **1s**	THF, rt, 12 h		66 (**2bs**)	27 (**2bb**) 20 (**2ss**)
7	**1a** +**1 j**	THF, rt, 12 h		54 (**2aj**)	40 (**2aa**) 30 (**2jj**)
8	**1j** + **1l**	MeCN, –20 °C, 24 h		72 (**2jl**)	25 (**2jj**) 22 (**2ll**)
9	**1e** + **1j**	DME, rt, 3 h		61 (**2ej**)	30 (**2ee**) 20 (**2jj**)
10	**1f** + **1j**	MeCN, 0 °C, 18 h		65 (**2fj**)	31 (**2ff**) 26 (**2jj**)

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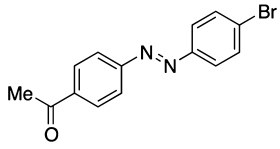
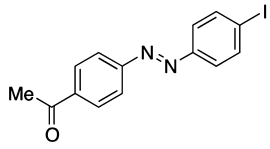
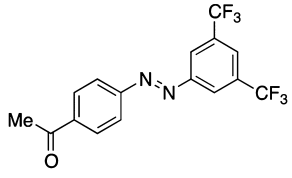
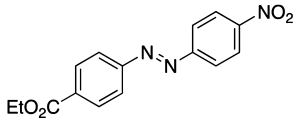
Table 4. continued

entry	1	conditions	*cross-product*	yield [%][b] *cross*	yield [%][b] *homo*
11	**1g** + **1j**	DME, –20 °C, 24 h		58 (**2gj**)	38 (**2gg**) 31 (**2jj**)
12	**1h** + **1j**	THF, rt, 12 h		53 (**2hj**)	35 (**2hh**) 41 (**2jj**)
13	**1j** + **1s**	MeCN, –20 °C, 24 h		63 (**2js**)	29 (**2jj**) 33 (**2ss**)
14[d]	**1i** + **1l**	MeCN, 0 °C, 24 h		66 (**2il**)	25 (**2ii**) 54 (**2ll**)

[a]Reaction conditions: Ar^1NH_2 (0.25 mmol), Ar^2NH_2 (0.25 mmol), *t*-BuOCl (1 mmol), and NaI (1 mmol) in solvent (3 mL). [b]Isolated yields. [c]**1b** (0.5 mmol), **1j** (0.25 mmol), *t*-BuOCl (1.5 mmol), and NaI (1.5 mmol). [d]**1i** (0.25 mmol), **1l** (0.5 mmol), *t*-BuOCl (1.5 mmol), and NaI (1.5 mmol).

(entries 9–12). Notably, the employment of amino-azobenzene **1m** under the oxidative conditions gave homodimerized product **2 mm**, which is regarded as an aza-analogue of oligo(*p*-phenylenevinylene)s. *meta*-Substitution on the benzene ring did not significantly affect the yields of the products (entries 14 and 15). Anilines having a substituent at the *ortho* position were successfully transformed into the corresponding azobenzenes in moderate yields, despite requiring extended reaction times (entries 16 and 17). It should be noted that the homodimerization of multiply substituted aromatic amines gave the corresponding azo products in high yields (entries 18–20).

Motivated by the successful results of the homodimerization of aniline derivatives, we then extended substrate scope to heteroaromatic amines (Table 3). To our delight, the reaction conditions were applicable to five-membered heteroaromatic amines such as pyrazine and oxazole, which are much more electron-rich than aniline and labile toward oxidative conditions, affording the corresponding products **2uu** and **2vv** in good yields (entries 1 and 2). Benzene-fused heteroaromatic amines also successfully dimerized to give homodimers (entries 3–5). Carbazole-containing amine **1z** was also applicable to the reaction (entry 6). In addition to the potential applications as NLO materials and PDLs, these heteroaromatic compounds can serve as an oxidant in the Mitsunobu reaction.[20] In respect to the limitation of the scope of heteroaromatic amines, electron-poor heteroaromatic amines such as 2-methylquinolin-5-amine and isoquinolin-5-amine did not give the homodimerized products at all or resulted in rather low yields of the products (e.g., in the case of 4-aminopyridine, the corresponding product was formed in less than 50% ^{1}H NMR yield and was difficult to isolate).

Scope of Oxidative Cross-dimerization of (Hetero)-aromatic Amines. The successful homodimerization of aromatic amines into symmetric azo compounds prompted us to apply the reaction conditions to cross-dimerization (Table 4). Initially, we examined the cross-dimerization of *p*-toluidine (**1b**) with an equimolar amount of ethyl 4-aminobenzoate (**1i**). It was revealed that the corresponding unsymmetric azo compound **2bi** was dominantly produced in 62% yield over the homodimers **2bb** and **2ii** (32% and 30% yields, respectively) (entry 1). Considering the difficulty in achieving cross-dimerization of aromatic amines in an oxidative way, this result demonstrates the high superiority of our method.[21] The cross-dimerization of **1b** with **1j** and **1l** also proceeded to give push–pull-type aromatic azo compounds **2bj** and **2bl** in high yields in both cases (entries 2 and 3). When *p*-toluidine (**1b**) was treated with *meta*-substituted anilines **1n**, **1o**, and **1s**, the corresponding aromatic azo compounds **2bn**, **2bo**, and **2bs** were obtained in moderate to good yields (entries 4–6). Cross-dimerization reactions of an electron-deficient aniline, 4-aminoacetophenone (**1j**), with various aromatic amines were also examined (entries 7–13). Aniline (**1a**) selectively reacted with **1j**, leading to the monoacetylated azo compound **2aj** in good yield (entry 7). Anilines containing electron-withdrawing and halogen groups were also applicable to the reaction conditions to afford the corresponding unsymmetric azobenzenes in high yields (entries 8–13). Cross-dimerization of highly electron-deficient anilines **1i** and **1l** also proceeded to give unsymmetric azobenzene **2il** in a selective way, albeit requiring longer time (entry 14). Since it is difficult to synthesize unsymmetric aromatic azo compounds bearing two electron-deficient aromatic rings by conventional methods, this result clearly highlights the advantage of our method.

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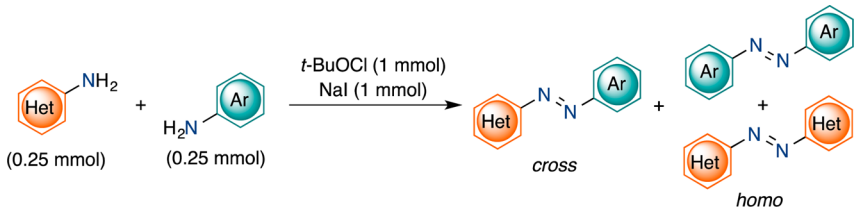
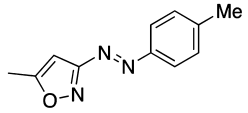
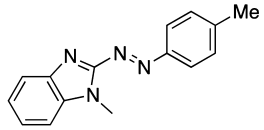
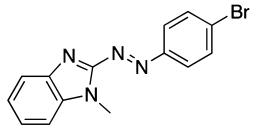
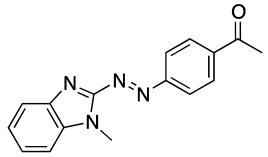
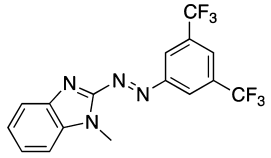
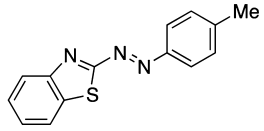
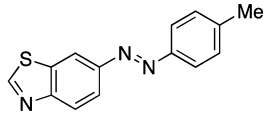
Table 5. Cross-dimerization of Heteroaromatic Amines with Aniline Derivatives[a]



entry	1	conditions	*cross*-product	yield [%][b]	
				cross	*homo*
1[c]	**1b** + **1v**	THF, rt, 24 h		58 (**2bv**)	50 (**2bb**) 29 (**2vv**)
2	**1b** + **1w**	DME, rt, 12 h		61 (**2bw**)	30 (**2bb**) 31 (**2ww**)
3	**1g** + **1w**	acetone, rt, 6 h		58 (**2gw**)	32 (**2gg**) 28 (**2ww**)
4	**1j** + **1w**	acetone, –20 °C, 24 h		56 (**2jw**)	32 (**2jj**) 27 (**2ww**)
5	**1s** + **1w**	acetone, rt, 12 h		50 (**2sw**)	22 (**2ss**) 31 (**2ww**)
6	**1b** + **1x**	MeCN, rt, 12 h		48 (**2bx**)	38 (**2bb**) 15 (**2xx**)
7	**1b** + **1y**	acetone, rt, 12 h		44 (**2by**)	38 (**2bb**) 30 (**2yy**)

[a]Reaction conditions: Ar^1NH_2 (0.25 mmol), Ar^2NH_2 (0.25 mmol), *t*-BuOCl (1 mmol), and NaI (1 mmol) in solvent (3 mL). [b]Isolated yields. [c]**1b** (0.5 mmol), **1v** (0.25 mmol), *t*-BuOCl (1.5 mmol), and NaI (1.5 mmol).

The scope of the cross-dimerization of heteroaromatic amines with aniline derivatives is shown in Table 5. Five-membered heteroaromatic amine **1v** smoothly reacted with **1b** to give the corresponding product **2bv** in good yield (entry 1). The reaction of 2-amino-1-methyl benzimidazole (**1w**) with various anilines (**1b**, **1g**, **1j**, and **1s**) proceeded to provide unsymmetric azo products in moderate to high yields (entries 2–5). This method was also applicable to the cross-dimerization reactions of **1b** with 2-aminobenzothiazole (**1x**, entry 6) and 6-aminobezothiazole (**1y**, entry 7). In all cases, unsymmetric azobenzenes were dominantly produced over homodimers and easily separated by column chromatography.

Synthetic Applications of the Oxidative Dimerization. To demonstrate the practicality of the oxidative dimerization method, a gram-scale synthesis of azo product was conducted (Scheme 3). When 10 mmol of ethyl 4-aminobenzoate (**1i**) was treated with a 20 mmol of *t*-BuOI in 60 mL of Et_2O at room temperature for 3 h, the homodimerized product **2ii** was successfully synthesized in 93% yield without any significant

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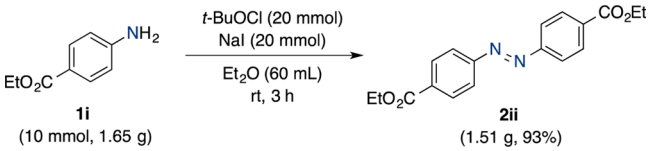
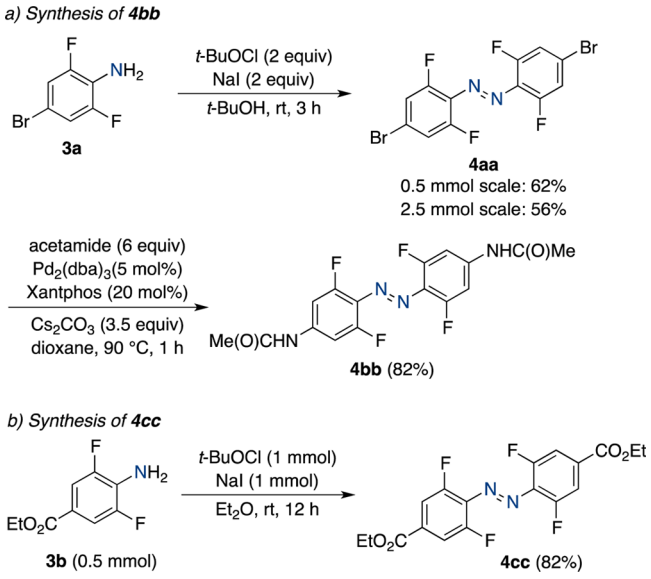
Scheme 3. Gram-Scale Synthesis of Azobenzene 2ii



loss of reaction efficiency, compared with the small-scale run (0.5 mmol).

Taking advantage of this straightforward and efficient synthetic method, highly improved syntheses of azobenzene-based photoswitches[22] were demonstrated (Scheme 4).

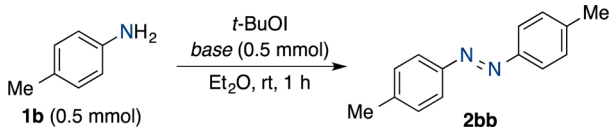
Scheme 4. Efficient Syntheses of Photoswitches 4bb and 4cc



Recently, Bléger, Brouwer, and Hecht have developed a new class of photoswitches **4bb** and **4cc**, which can undergo *E*/*Z* isomerization under visible light irradiation of in a nearly quantitative efficiency.[22b] When 4-bromo-2,6-difluoroaniline (**3a**) was treated with 2 equiv of *t*-BuOI in *t*-BuOH at room temperature for 3 h, tetrafluoroazobenzene **4aa** was obtained in 62% yield (Scheme 4a). Additionally, this reaction was applicable to a 5-fold scale operation, producing **4aa** in 56% yield. Two bromo functionalities of **4aa** were then efficiently substituted with two acetamide groups through Pd-catalyzed amidation,[22b] leading to azobenzene **4bb**. Homodimerization of **3b** also smoothly proceeded to give **4cc** in a high yield (Scheme 4b). According to the literature,[22b] the conventional synthetic method for **4aa** and **4cc** required excess amounts of heavy metal oxidants ($KMnO_4/FeSO_4{\cdot}7H_2O$), and **4aa** and **4cc** were produced in rather low yields (22% and 23% yield, respectively). Therefore, our oxidative method allows for much more efficient access to these useful functional molecules.

Mechanistic Studies. For deeper understanding of the reaction mechanism, several experiments were conducted. The pH of the aqueous layer extracted from the reaction mixture of homodimerization of *p*-toluidine (**1b**) indicated 4.75, suggesting that hydrogen iodide (HI) was liberated during the reaction.[23] Hydrogen iodide could be trapped by *t*-BuOI to generate *t*-BuOH and I_2. If the generated acid (HI) is efficiently trapped by an adventitious base, the stoichiometry of *t*-BuOI should be reduced by half. To verify the assumption, the addition of bases

Table 6. Effect of Base on the Homodimerization[a]



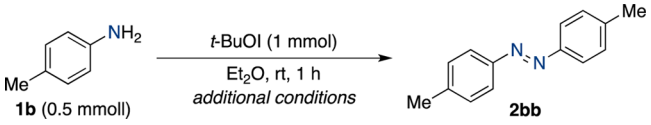
entry	*t*-BuOI [mmol]	base	yield [%][b]
1	1		97[c]
2	0.5		16
3	0.5	2,6-lutidine	18
4	0.5	*t*-BuOK	50
5	0.5	$(Me_3Si)_2NH$[d]	53

[a]Reaction conditions: **1b** (0.5 mmol), *t*-BuOCl (0.5−1 mmol), NaI (0.5−1 mmol), and base (0.5 mmol) in Et_2O (3 mL). [b]^1H NMR yields. [c]Isolated yield. [d]0.25 mmol of hexamethyldisilazane was used.

was examined, with the amount of *t*-BuOI being reduced by half (Table 6). A blank experiment resulted in rather low yield of product **2bb** (entry 2). The addition of 2,6-lutidine did not significantly affect the efficiency of the reaction (entry 3). In contrast, the employment of stronger bases such as *t*-BuOK (entry 4) and hexamethyldisilazane (entry 5) resulted in much higher product yields, albeit much lower than with the standard conditions (entry 1). These results suggest that *t*-BuOI serves as the most appropriate trapping agent against HI in the actual system.

Table 7 shows the results of the homodimerization of **1b** conducted under radical-inhibiting conditions. Clearly, radical

Table 7. Homodimerization under Radical-Inhibiting Conditions[a]



entry	additional conditions	yield [%][b]
1		97[c]
2	addition of TEMPO	94[c]
3	addition of Galvinoxyl	88[c]
4	under O_2 atmosphere	89
5	in the dark	92

[a]Reaction conditions: **1b** (0.5 mmol), *t*-BuOCl (1 mmol), NaI (1 mmol), and additive (1 mmol, entries 2 and 3) in Et_2O (3 mL). [b]^1H NMR yields. [c]Isolated yield.

scavengers (TEMPO and Garvinoxyl, entries 2 and 3), oxygen (entry 4), and light shielding (entry 5) did not affect the product yields, suggesting that it is not likely to involve the radical species in the dimerization reaction.

On the basis of our preliminary assumption, we pursued the possibility of the involvement of $ArNI_2$ as the key intermediate. The results of NMR monitoring of aromatic amines under the effect of *t*-BuOI are summarized in Scheme 5, and representative NMR spectra of the experiments are also provided in Figures 1−3. When 2 equiv of *t*-BuOI were added to the d_6-DMSO solution of **1e**, the signal corresponding to the two N−H hydrogens (δ = 4.93 ppm) disappeared, and aromatic hydrogens (δ = 6.51 and 6.82 ppm) shifted to the lower field (δ = 6.65 and 6.87 ppm, respectively) (eq 1 in Scheme 5, Figure 1a, and b). Similar phenomena were observed in the

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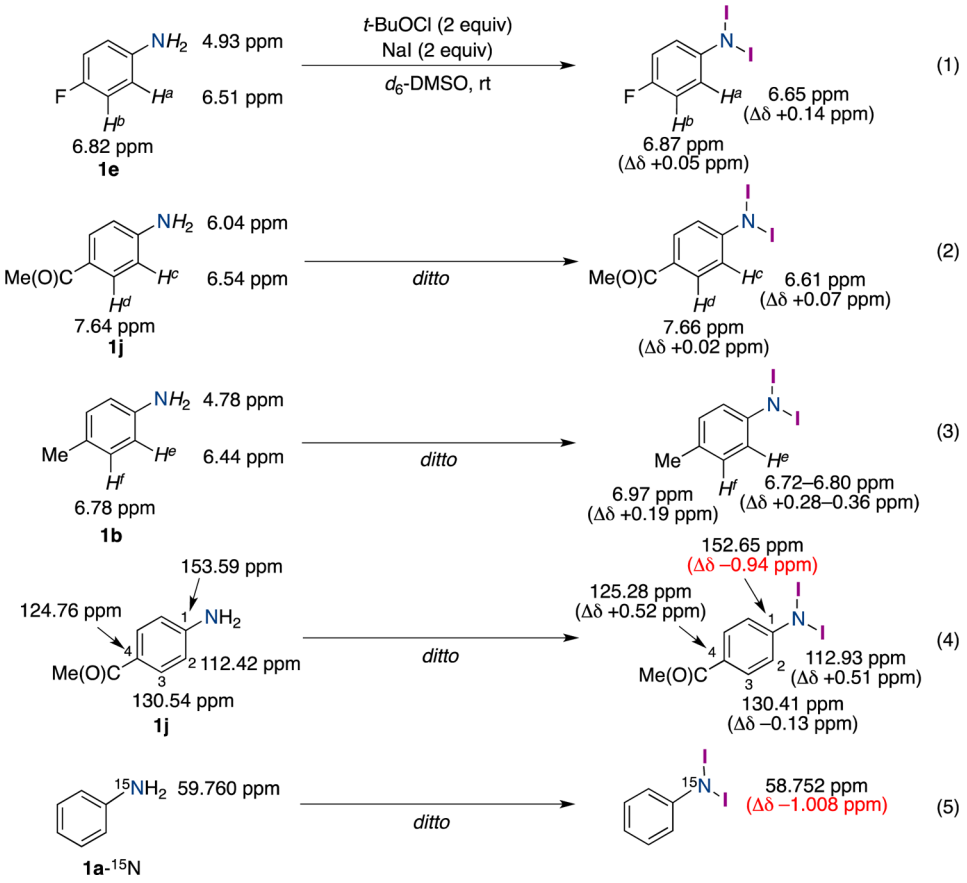
Scheme 5. Summary of NMR Monitoring of H/I Exchange of Aromatic Amines



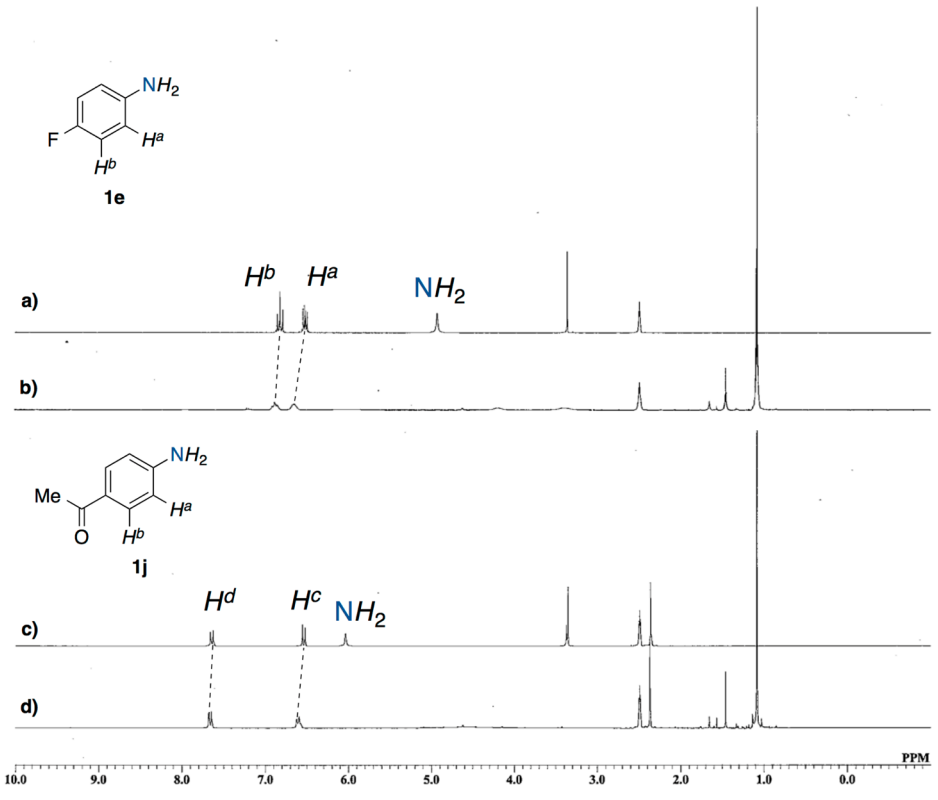


Figure 1. ^{1}H NMR spectra of **1e** and **1j** in d_6-DMSO recorded at room temperature: (a, c) the mixture of aromatic amine (0.05 mmol) and NaI (0.1 mmol); (b, d) the mixture after adding *t*-BuOCl (0.1 mmol).

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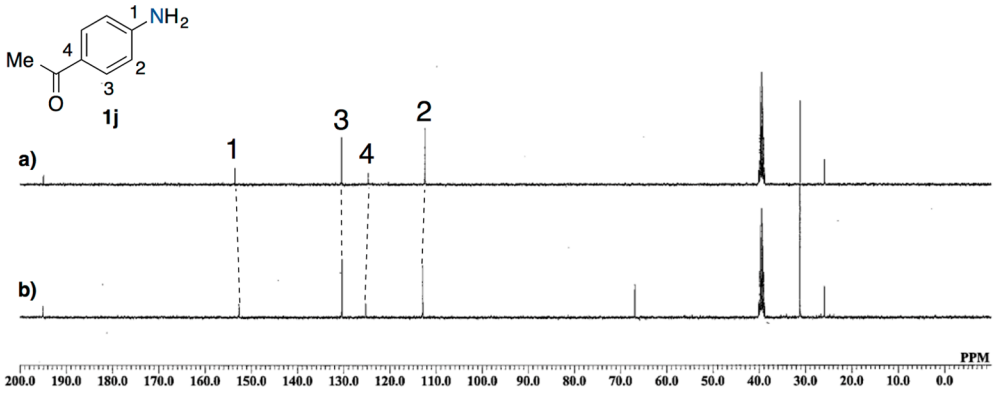


Figure 2. ^{13}C NMR spectra of **1j** in d_6-DMSO recorded at room temperature: (a) the mixture of **1j** (0.05 mmol) and NaI (0.1 mmol); (b) the mixture after adding *t*-BuOCl (0.1 mmol).

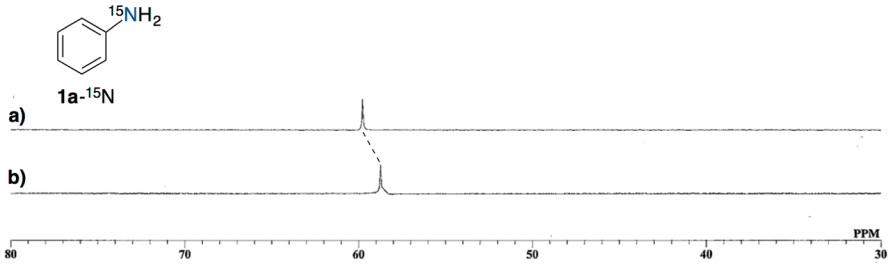
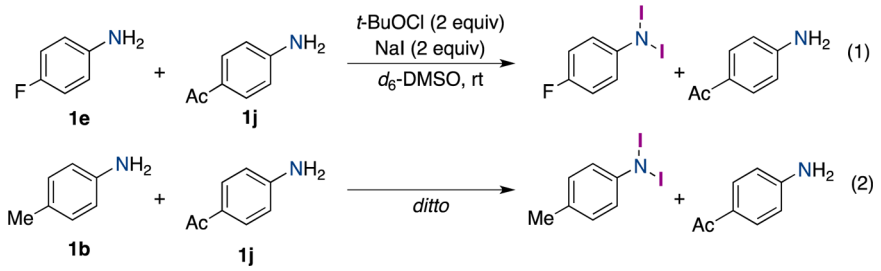


Figure 3. ^{15}N NMR spectra of **1a**-^{15}N in d_6-DMSO recorded at room temperature: (a) the mixture of **1a**-^{15}N (0.1 mmol) and NaI (0.2 mmol); (b) the mixture after adding *t*-BuOCl (0.2 mmol).

Scheme 6. Competitive Study of H/I Exchange



cases of **1j** and **1b** (eqs 2 and 3 in Scheme 5, Figure 1c, and d). These results suggested that the double proton exchange process is very rapid. Furthermore, ^{13}C and ^{15}N NMR analyses of the chemical species generated as the result of the proton exchange were also conducted (eqs 4 and 5 in Scheme 5, Figures 2 and 3). Notably, upon treating separately **1j** and **1a** labeled with ^{15}N (**1a**-^{15}N) with *t*-BuOI, the chemical shifts of the C1 of **1j** and the N of **1a**-^{15}N were moved to the upper regime by 0.94 and 1.00 ppm, respectively (Figures 2 and 3), which implies the presence of some sort of "heavy atoms" on the N atom.[24] This was also partly supported by the observation of a singlet peak of **1a**-^{15}N under the nondecoupled conditions.[25] To further prove the generation of *N*,*N*-diiodoaniline,[26] ESI-MS analysis of the reaction system was conducted using **3a** as a reactant. Although the molecular ion peak of *N*,*N*-diiodoaniline was not detected, the mass fragment of $C_6H_3BrF_2NI$, which corresponds to a radical cation of *N*-monoiodinated **3a**, was detected. This radical cation species could generate through the homolytic cleavage of the N–I bond of the corresponding ammonium form of *N*,*N*-diiodoaniline ($ArNI_2H^+$),[27,28] probably due to the rather small dissociation energy of N–I bond (~130 kJ/mol).[29,30] Taken together, *N*,*N*-diiodoanilines most likely to generate through an efficient H/I exchange process.

To further gain insights into the H/I exchange process, an equimolar mixture of **1e** and **1j** was treated with *t*-BuOI (2 equiv). As the result, ^1H NMR spectra indicated the exclusive generation of *p*-fluoro-*N*,*N*-diiodoaniline from **1e** with keeping **1j** intact (eq 1 in Scheme 6 and Figure 4). Likewise, the similar experiment using **1b** and **1j** also suggested the exclusive generation of *N*,*N*-diiodoaniline derived from **1b**, while **1j** remained unreacted (Scheme 6, eq 2). Taking into account the Hammett constants (σ_p) of F, Ac, and Me being 0.06, 0.50, and −0.17,[31] respectively, the H/I exchange proceeded more predominantly with the electron-richer aniline than with the electron-poorer aniline, at least on the NMR time scale.

Based on these experimental results, a plausible reaction mechanism is illustrated in Scheme 7. On the basis of the fact that the electron-richer aniline was preferentially diiodinated, we propose H/I exchange mechanism through "halogen bonding"[32] formation between the nitrogen and iodine atoms (**A**) to generate intermediate **B**. Based on this concept, the exchange process of a strong Lewis base (an electron-richer amine) would be more favorable than that with a weak base (an electron-poorer amine), which is in good agreement with the results of NMR experiments. The resulting ammonium salt **B**

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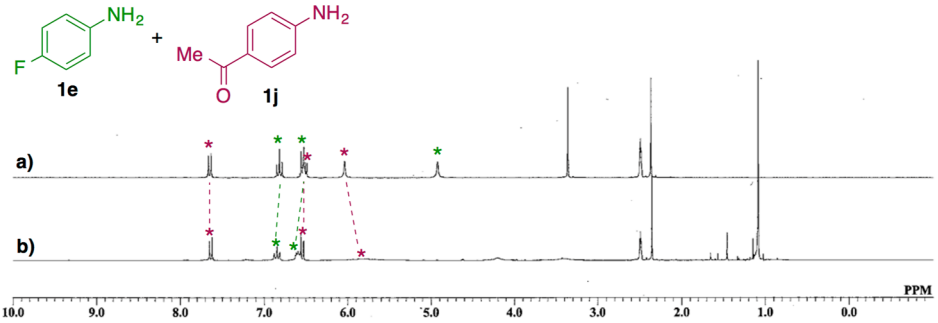
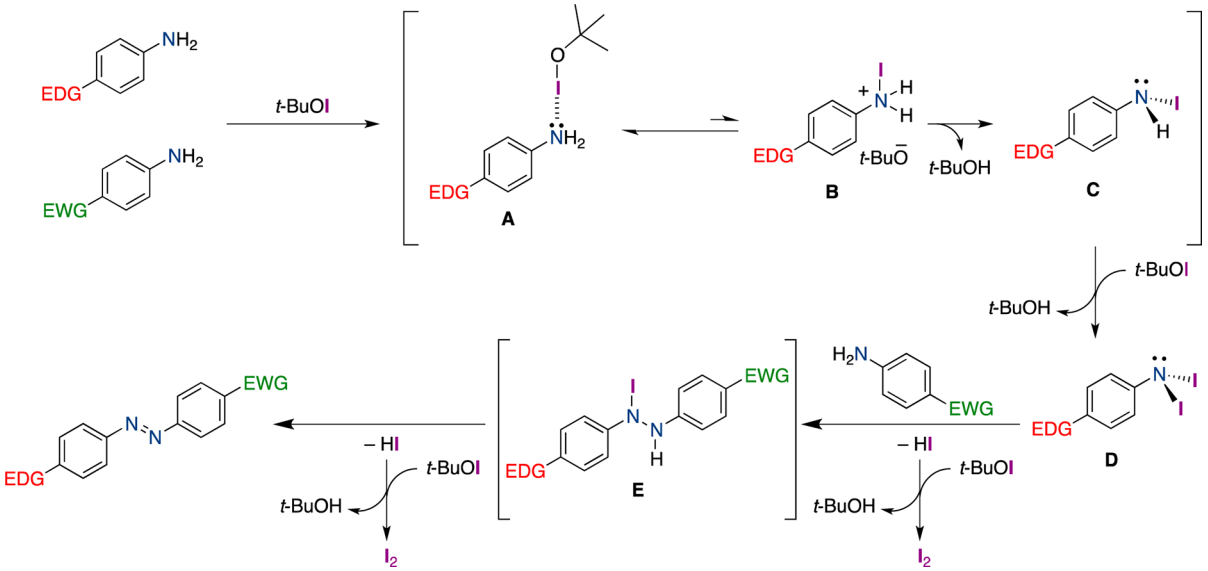
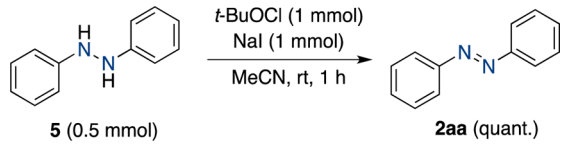


Figure 4. ^{1}H NMR spectra of the mixture of **1e** (indicated in green) and **1j** (indicated in violet) in d_6-DMSO recorded at room temperature: (a) the mixture of **1e** (0.05 mmol), **1j** (0.05 mmol), and NaI (0.2 mmol); (b) the mixture after adding *t*-BuOCl (0.1 mmol).

Scheme 7. Plausible Reaction Mechanism



Scheme 8. Oxidation of Hydrazine 5 with *t*-BuOI



would be deprotonated by *t*-BuO$^-$ to produce monoiodinated aniline **C**. The following iodination of **C** would afford *N*,*N*-diiodoaniline **D** in a similar manner. It should be noted that the second iodination of **C** proceed more preferentially than the monoiodination of the electron-poorer aniline. This is possibly because the nucleophilicity of monoiodinated intermediate **C** is higher than that of the unreacted electron-deficient aniline as the result of slight pyramidalization of the N-center partly facilitated by steric repulsion.[34] The diiodinated aniline **D** would then serve as an electrophile to form the N–N single bond to afford **E** that accompanies liberation of HI. Lastly, elimination of another equivalent of HI would give aromatic azo product, which was supported by the experiment illustrated in Scheme 8. Liberated HI would be trapped by 2 equiv of *t*-BuOI, thus resulting in I_2 and *t*-BuOH as discussed in the early part of this section.

CONCLUSION

In summary, we have developed a new synthetic method for both of symmetric and unsymmetric aromatic azo compounds through an oxidative dimerization of aromatic amines under metal-free and mild conditions. This efficient, low energy-consuming, and straightforward method allowed us easy access to diverse azobenzenes including heteroaromatic azo compounds, which would have high degree of potential for the use as various functional molecules. Furthermore, mechanistic aspects of this new oxidative dimerization have been elucidated.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a NMR spectrometer (^{1}H NMR, 270 or 400 MHz; ^{13}C NMR, 68 or 100 MHz) using tetramethylsilane as an internal standard. ^{15}N NMR spectra were recorded on a NMR spectrometer (^{15}N NMR, 40 MHz) using liquid ammonia as an external standard. ^{19}F NMR spectra were recorded on a NMR spectrometer (^{19}F NMR, 376 MHz) using benzotrifluoride as an internal standard. Products were purified by chromatography on silica gel (200–400 mesh) or aluminum oxide (active stage I, 0.063–0.200 mm). Analytical thin-layer chromatography (TLC) was performed on precoated silica gel glass plates (silica gel, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

Materials. Aromatic Amines except for **1y** and **3b** were purchased from commercial sources and distilled or recrystallized before using. Aromatic amines **1x**[35], **1y**[36] and **3b**[22b] were prepared according to the literature. Sodium iodide and *tert*-butyl hypochlorite were purchased from commercial sources and used as received. *N*-Iodophthalimide

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(NIPI)[37] and *N*-iodosaccharin (NIsac)[38] were prepared according to the literature. All other reagents were commercially available and used as received.

Typical Procedure for Comparative Study of Halogen-Containing Oxidants (Table 1). To a solution of *p*-toluidine (0.5 mmol, 53.6 mg) in diethyl ether (3 mL) was added halogen-containing oxidant (1.0 mmol) under N_2 atmosphere at room temperature. The mixture was stirred for 1 h and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give a crude product. The yield of product was calculated by ^{1}H NMR integration of the crude product using 1,1,2,2-tetrachloroethane as an internal standard.

Typical Procedure for the Synthesis of Symmetric Azo Compounds Using *t*-BuOI (Table 2 and 3). To a mixture of aromatic amine (0.5 mmol) and NaI (1.0 mmol, 150.0 mg) in an appropriate solvent (3 mL) was added *t*-BuOCl (1.0 mmol, 108.6 mg) under N_2 atmosphere at the appropriate temperature. The mixture was stirred for the indicated time and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: ethyl acetate in hexane) gave homodimerized product.

(*E*)-1,2-Diphenyldiazene (2aa). Spectroscopic data were in agreement with those previously reported.[13d] Purified by silica gel column chromatography (hexane/EtOAc 99:1); red solid (43.0 mg, 95%); mp 67.3−68.2 °C; R_f 0.53 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41−7.53 (m, 6H), 7.89−7.94 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 122.7, 129.0, 130.9, 152.5; IR (ATR) ν 1580, 1481, 1450, 1298, 1068, 926, 773 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 182 ([M]$^+$, 57), 77 ([C_6H_5]$^+$, 100), 105 ([$N_2C_6H_5$]$^+$, 26); HRMS (EI) *m*/*z* calcd for $C_{12}H_{10}N_2$ (M) 182.0844, found 182.0841.

(*E*)-1,2-Di-*p*-tolyldiazene (2bb). Spectroscopic data were in agreement with those previously reported.[13d] Purified by silica gel column chromatography (hexane/EtOAc 99:1); yellow solid (51.2 mg, 97%); mp 137.6−140.9 °C; R_f 0.48 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.42 (s, 6H), 7.30 (d, 4H, *J* = 8.4 Hz), 7.81 (d, 4H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 122.6, 129.6, 141.1, 150.7; IR (ATR) ν 2922, 1597, 1500, 1151, 1109, 823 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 210 ([M]$^+$, 37), 91 ([$C_6H_4CH_3$]$^+$, 100), 119 ([$N_2C_6H_4CH_3$]$^+$, 15); HRMS (EI) *m*/*z* calcd for $C_{14}H_{14}N_2$ (M) 210.1157, found 210.1153.

(*E*)-1,2-Bis(4-methoxyphenyl)diazene (2cc). Spectroscopic data were in agreement with those previously reported.[13d] Purified by silica gel column chromatography (hexane/EtOAc 9:1); yellow solid (52.8 mg, 87%); mp 154.6−156.3 °C; R_f 0.25 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.88 (s, 6H), 6.99 (d, 4H, *J* = 8.9 Hz), 7.87 (d, 4H, *J* = 8.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 55.6, 114.1, 124.2, 146.9, 161.4; IR (ATR) ν 2920, 1728, 1575, 1240, 1139, 1101, 1022, 813 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 242 ([M]$^+$, 88), 107 ([$C_6H_4OCH_3$]$^+$, 100), 135 ([$N_2C_6H_4OCH_3$]$^+$, 41); HRMS (EI) *m*/*z* calcd for $C_{14}H_{14}N_2O_2$ (M) 242.1055, found 242.1059.

(*E*)-4,4′-(Diazene-1,2-diyl)bis(*N*,*N*-dimethylaniline) (2dd). Spectroscopic data were in agreement with those previously reported.[8b] Purified by silica gel column chromatography (hexane/EtOAc 9:1); red solid (40.3 mg, 60%); mp 264.7−265.2 °C (dec.); R_f 0.38 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 12H), 6.76 (d, 4H, *J* = 9.2 Hz), 7.81 (d, 4H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4, 111.8, 124.0, 144.1, 151.5; IR (ATR) ν 2916, 1726, 1591, 1362, 1146, 1130, 894 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 268 ([M]$^+$, 100), 120 ([$C_6H_4N(CH_3)_2$]$^+$, 79); HRMS (EI) *m*/*z* calcd for $C_{16}H_{20}N_4$ (M) 268.1688, found 268.1689.

(*E*)-1,2-Bis(4-fluorophenyl)diazene (2ee). Spectroscopic data were in agreement with those previously reported.[13d] Purified by silica gel column chromatography (hexane/EtOAc 99:1); yellow solid (52.1 mg, 95%); mp 97.1−99.8 °C; R_f 0.56 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.15−7.21 (m, 4H), 7.88−7.93 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 116.0 (d, *J* = 22.8 Hz), 124.7 (d, *J* = 9.0 Hz), 148.8 (d, *J* = 2.2 Hz), 164.2 (d, *J* = 251.7 Hz); IR (ATR) ν 2939, 1729, 1589, 1496, 1228, 1138, 839, 752 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 218 ([M]$^+$, 40), 95 ([C_6H_4F]$^+$, 100), 123 ([$N_2C_6H_4F$]$^+$, 25); HRMS (EI) *m*/*z* calcd for $C_{12}H_8F_2N_2$ (M) 218.0656, found 218.0660.

(*E*)-1,2-Bis(4-chlorophenyl)diazene (2ff). Spectroscopic data were in agreement with those previously reported.[13d] Purified by silica gel column chromatography (hexane/EtOAc 95:5); yellow solid (59.0 mg, 96%); mp 182.0−184.5 °C; R_f 0.50 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.48 (d, 4H, *J* = 8.9 Hz), 7.87 (d, 4H, *J* = 8.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 124.1, 129.3, 137.1, 150.6; IR (ATR) ν 1571, 1475, 1103, 1082, 1002, 842, 825, 715 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 250 ([M]$^+$, 31), 111 ([C_6H_4Cl]$^+$, 100), 139 ([$N_2C_6H_4Cl$]$^+$, 38); HRMS (EI) *m*/*z* calcd for $C_{12}H_8Cl_2N_2$ (M) 250.0065, found 250.0055.

(*E*)-1,2-Bis(4-bromophenyl)diazene (2gg). Spectroscopic data were in agreement with those previously reported.[13d] Purified by basic alumina column chromatography (hexane/EtOAc 95:5); red solid (70.7 mg, 83%); mp 201.3−203.7 °C; R_f 0.50 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.65 (d, 4H, *J* = 8.1 Hz), 7.79 (d, 4H, *J* = 8.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 124.3, 125.7, 132.3, 151.0; IR (ATR) ν 1726, 1568, 1469, 1396, 1269, 1062, 1004, 833, 709 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 340 ([M]$^+$, 33), 155 ([C_6H_4Br]$^+$, 100), 183 ([$N_2C_6H_4Br$]$^+$, 61); HRMS (EI) *m*/*z* calcd for $C_{12}H_8Br_2N_2$ (M) 337.9054, found 337.9053.

(*E*)-1,2-Bis(4-iodophenyl)diazene (2hh). Spectroscopic data were in agreement with those previously reported.[34] Purified by silica gel column chromatography (hexane/EtOAc 95:5); red solid (95.1 mg, 88%); mp 242.4−244.8 °C; R_f 0.50 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.64 (d, 4H, *J* = 8.6 Hz), 7.86 (d, 4H, *J* = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 98.1, 124.5, 138.4, 151.8; IR (ATR) ν 1560, 1467, 1390, 1296, 1278, 1095, 1049, 1001, 810, 713 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 434 ([M]$^+$, 72), 203 ([C_6H_4I]$^+$, 100), 231 ([$N_2C_6H_4I$]$^+$, 53); HRMS (EI) *m*/*z* calcd for $C_{12}H_8I_2N_2$ (M) 433.8777, found 433.8776.

(*E*)-Diethyl 4,4′-(Diazene-1,2-diyl)dibenzoate (2ii). Spectroscopic data were in agreement with those previously reported.[13d] Purified by silica gel column chromatography (hexane/EtOAc 9:1); red solid (77.9 mg, 95%); mp 139.7−142.6 °C; R_f 0.26 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.44 (t, 6H, *J* = 7.0 Hz), 4.42 (q, 4H, *J* = 7.0 Hz), 7.98 (d, 4H, *J* = 8.6 Hz), 8.22 (d, 4H, *J* = 8.6 Hz,); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.4, 61.4, 122.8, 130.5, 132.6, 154.7, 165.8; IR (ATR) ν 1711, 1265, 1095, 1006, 868, 779, 700 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 326 ([M]$^+$, 33), 149 ([$C_6H_4CO_2Et$]$^+$, 100), 177 ([$N_2C_6H_4$ CO_2Et]$^+$, 13); HRMS (EI) *m*/*z* calcd for $C_{18}H_{18}N_2O_4$ (M) 326.1267, found 326.1269.

(*E*)-1,2-Bis(4-acetylphenyl)diazene (2jj). Spectroscopic data were in agreement with those previously reported.[8b] Purified by basic alumina column chromatography (hexane/EtOAc 8:2); red solid (60.7 mg, 91%); mp 213.0−215.5 °C; R_f 0.16 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.68 (s, 6H), 8.01 (d, 4H, *J* = 8.6 Hz), 8.13 (d, 4H, *J* = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 27.0, 123.1, 129.3, 138.7, 154.6, 197.2; IR (ATR) ν 1672, 1404, 1354, 1307, 1258, 1223, 1109, 1006, 961, 856, 837 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 266 ([M]$^+$, 58), 119 ([$C_6H_4COCH_3$]$^+$, 100), 147 ([$N_2C_6H_4COCH_3$]$^+$, 14); HRMS (EI) *m*/*z* calcd for $C_{16}H_{14}N_2O_2$ (M) 266.1055, found 266.1053.

(*E*)-4,4′-(Diazene-1,2-diyl)dibenzonitrile (2kk). Spectroscopic data were in agreement with those previously reported.[8c] Purified by silica gel column chromatography (hexane/EtOAc 7:3); red solid (51.4 mg, 89%); mp 277.8−278.2 °C; R_f 0.05 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.86 (d, 4H, *J* = 8.6 Hz), 8.04 (d, 4H, *J* = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 115.1, 118.2, 123.7, 133.4, 153.9; IR (ATR) ν 2924, 2226, 1489, 1408, 1294, 1098, 1011, 851, 839 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 232 ([M]$^+$, 49), 102 ([C_6H_4CN]$^+$, 100), 130 ([$N_2C_6H_4CN$]$^+$, 22); HRMS (EI) *m*/*z* calcd for $C_{14}H_8N_4$ (M) 232.0749, found 232.0748.

(*E*)-1,2-Bis(4-nitrophenyl)diazene (2ll). Spectroscopic data were in agreement with those previously reported.[39] Purified by basic alumina column chromatography (hexane/EtOAc 7:3); red solid (54.3 mg,

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79%); mp 223.3−225.4 °C; R_f 0.10 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.11 (d, 4H, J = 8.9 Hz), 8.43 (d, 4H, J = 8.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 123.8, 124.7, 149.2, 154.8; IR (ATR) ν 1608, 1533, 1344, 1319, 1209, 1105, 1002, 862, 806, 758 cm^{-1}; MS (EI) m/z (relative intensity, %) 272 ([M]$^+$, 49), 122 ([$C_6H_4NO_2$]$^+$, 100), 150 ([$N_2C_6H_4NO_2$]$^+$, 61); HRMS (EI) m/z calcd for $C_{12}H_8N_4O_4$ (M) 272.0546, found 272.0547.

(*E*)-4,4′-Bis(phenylazo)azobenzene (2 mm). Spectroscopic data were in agreement with those previously reported.[40] Purified by basic alumina column chromatography (hexane/EtOAc 5:5); brown solid (65.1 mg, 67%); mp 237.0−237.8 °C; R_f 0.45 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 4H, J = 8.8, Hz), 8.10 (d, 4H, J = 8.8, Hz), 7.98 (d, 4H, J = 6.8 Hz), 7.54 (m, 6H); IR (ATR) ν 3065, 3044, 1942, 1692, 1587, 1306, 1213, 854, 759 cm^{-1}; MS (EI) m/z (relative intensity, %) 390 ([M]$^+$, 100), 105 ([$C_6H_5N_2$]$^+$, 41), 181 ([$C_6H_5N_2C_6H_4$]$^+$, 69), 285 ([$C_6H_5N_2C_6H_4N_2C_6H_4$]$^+$, 49); HRMS (EI) m/z calcd for $C_{24}H_{18}N_6$ (M) 390.1593, found 390.1595.

(*E*)-1,2-Bis(3-chlorophenyl)diazene (2nn). Spectroscopic data were in agreement with those previously reported.[34] Purified by silica gel column chromatography (hexane/EtOAc 95:5); yellow solid (53.8 mg, 86%); mp 100.2−101.6 °C; R_f 0.50 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43−7.45 (m, 4H), 7.70−7.88 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 121.8, 122.5, 130.1, 131.1, 135.1, 152.9; IR (ATR) ν 1584, 1566, 1462, 1198, 1067, 885, 790 cm^{-1}; MS (EI) m/z (relative intensity, %) 250 ([M]$^+$, 13), 111 ([C_6H_4Cl]$^+$, 100), 139 ([$N_2C_6H_4Cl$]$^+$, 18); HRMS (EI) m/z calcd for $C_{12}H_8Cl_2N_2$ (M) 250.0065, found 250.0061.

(*E*)-1,2-Bis(3-nitrophenyl)diazene (2oo). Spectroscopic data were in agreement with those previously reported.[41] Purified by basic alumina column chromatography (hexane/EtOAc 8:2); orange solid (53.3 mg, 78%); mp 149.8−151.6 °C; R_f 0.14 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.78 (dd, 2H, J = 8.1, 8.1 Hz), 8.34 (dd, 2H, J = 1.1, 8.1 Hz), 8.40 (dd, 2H, J = 1.1, 8.1 Hz), 8.79 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 117.1, 125.9, 129.6, 130.2, 148.9, 152.2; IR (ATR) ν 1528, 1344, 1312, 1070, 918, 808, 741 cm^{-1}; MS (EI) m/z (relative intensity, %) 272 ([M]$^+$, 39), 122 ([$C_6H_4NO_2$]$^+$, 100), 150 ([$N_2C_6H_4NO_2$]$^+$, 63); HRMS (EI) m/z calcd for $C_{12}H_8N_4O_4$ (M) 272.0546, found 272.0544.

(*E*)-1,2-Bis([1,1′-biphenyl]-2-yl)diazene (2pp). Purified by silica gel column chromatography (hexane/EtOAc 95:5); orange solid (36.5 mg, 44%); mp 133.5 °C; R_f 0.40 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.26−7.57 (m, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 116.3, 127.2, 127.6, 130.0, 130.6, 130.7, 130.8, 138.8, 141.4, 149.7; IR (ATR) ν 3048, 1586, 1470, 768, 732, 723 cm^{-1}; MS (EI) m/z (relative intensity, %) 334 ([M]$^+$, 60), 153 ([C_6H_4Ph]$^+$, 100), 181 ([$N_2C_6H_4Ph$]$^+$, 25); HRMS (EI) m/z calcd for $C_{24}H_{18}N_2$ (M) 334.1470, found 334.1471.

(*E*)-2,2′-(Diazene-1,2-diyl)dibenzonitrile (2qq). Purified by basic alumina column chromatography (hexane/EtOAc 7:3); red solid (42.1 mg, 73%); mp 233.1−234.7 °C; R_f 0.05 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.65 (ddd, 2H, J = 1.4, 7.6, 7.6 Hz), 7.75 (ddd, 2H, J = 1.6, 7.6, 7.6 Hz), 7.89 (dd, 2H, J = 1.6, 7.6 Hz), 8.06 (dd, 2H, J = 1.4, 7.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 114.8, 116.4, 116.8, 132.3, 133.5, 152.4; IR (ATR) ν 2232, 1589, 1481, 1227, 773, 743 cm^{-1}; MS (EI) m/z (relative intensity, %) 232 ([M]$^+$, 23), 102 ([C_6H_4CN]$^+$, 100), 130 ([$N_2C_6H_4CN$]$^+$, 34); HRMS (EI) m/z calcd for $C_{14}H_8N_4$ (M) 232.0759, found 232.0754.

(*E*)-1,2-Bis(3,4-dimethylphenyl)diazene (2rr). Purified by silica gel column chromatography (hexane/EtOAc 99:1); yellow solid (53.3 mg, 89%); mp 155.2−157.8 °C; R_f 0.50 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.31 (s, 6H), 2.34 (s, 6H), 7.23 (d, 2H, J = 7.8 Hz), 7.65 (d, 2H, J = 7.8 Hz), 7.68 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.9, 19.9, 120.7, 123.2, 130.2, 137.4, 139.9, 151.2; IR (ATR) ν 1602, 1443, 1242, 1101, 1022, 883, 827, 712 cm^{-1}; MS (EI) m/z (relative intensity, %) 238 ([M]$^+$, 45), 105 ([$C_6H_4(CH_3)_2$]$^+$, 81), 133 ([$N_2C_6H_4(CH_3)_2$]$^+$, 16); HRMS (EI) m/z calcd for $C_{16}H_{18}N_2$ (M) 238.1470, found 238.1469.

(*E*)-1,2-Bis(3,5-bis(trifluoromethyl)phenyl)diazene (2ss). Purified by silica gel column chromatography (hexane); yellow solid (109.3 mg, 94%); mp 115.2−117.2 °C; R_f 0.40 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.06 (s, 2H), 8.46 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 122.9 (q, J = 272.9 Hz), 123.4 (q, J = 2.8 Hz), 125.2 (m), 133.2 (q, J = 34.1 Hz), 152.1; IR (ATR) ν 1373, 1277, 1262, 1165, 1105, 1055, 935, 907, 847, 729 cm^{-1}; MS (EI) m/z (relative intensity, %) 454 ([M]$^+$, 20), 213 ([$C_6H_4(CF_3)_2$]$^+$, 100), 241 ([$N_2C_6H_4(CF_3)_2$]$^+$, 9); HRMS (EI) m/z calcd for $C_{16}H_6F_{12}N_2$ (M) 454.0339, found 454.0340.

(*E*)-1,2-Bis(pentafluorophenyl)diazene (2tt). Spectroscopic data were in agreement with those previously reported.[42] Purified by silica gel column chromatography (hexane/EtOAc 99:1); yellow solid (60.7 mg, 67%); mp 139.6−142.1 °C; R_f 0.55 (hexane/EtOAc 9:1); ^{19}F NMR (376 MHz, $CDCl_3$) δ −150.8 (m, 2F), −151.1 (m, 1F), −163.7 (m, 2F); IR (ATR) ν 1641, 1504, 1408, 1319, 1146, 999, 976 cm^{-1}; MS (EI) m/z (relative intensity, %) 362 ([M]$^+$, 43), 167 ([C_6F_5]$^+$, 100), 195 ([$N_2C_6F_5$]$^+$, 33); HRMS (EI) m/z calcd for $C_{12}F_{10}N_2$ (M) 361.9902, found 361.9904.

(*E*)-1,2-Bis(1-methyl-1*H*-pyrazol-3-yl)diazene (2uu). Purified by silica gel column chromatography (EtOAc); yellow solid (39.5 mg, 83%); mp 200.8−201.6 °C; R_f 0.28 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (s, 6H), 6.68 (d, 2H, J = 2.4 Hz), 7.36 (d, 2H, J = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.6, 95.3, 131.8, 164.0; IR (ATR) ν 3125, 2924, 1375, 1303, 1209, 869 cm^{-1}; MS (EI) m/z (relative intensity, %) 190 ([M]$^+$, 100), 109 ([$N_2C_4H_5N_2$]$^+$, 95); HRMS (EI) m/z calcd for $C_8H_{10}N_6$ (M) 190.0967, found 190.0966.

(*E*)-1,2-Bis(5-methylisoxazol-3-yl)diazene (2vv). Spectroscopic data were in agreement with those previously reported.[20c] Purified by basic alumina column chromatography (hexane/EtOAc 95:5); yellow solid (36.5 mg, 76%); mp 212.2−212.7 °C; R_f 0.38 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 6H), 6.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 92.0, 172.0, 173.8; IR (ATR) ν 3145, 1599, 1466, 1433, 1413, 1240, 1022, 1001, 929, 819, 740 cm^{-1}; MS (EI) m/z (relative intensity, %) 192 ([M]$^+$, 58), 110 ([$N_2C_4H_4NO$]$^+$, 100); HRMS (EI) m/z calcd for $C_8H_8N_4O_2$ (M) 192.0647, found 192.0644.

(*E*)-1,2-Bis(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)diazene (2ww). Purified by basic alumina column chromatography ($CHCl_3$/MeOH 99:1); red solid (55.4 mg, 76%); mp 282.9−283.3 °C; R_f 0.38 ($CHCl_3$/MeOH 99:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (s, 6H), 7.38−7.51 (m, 6H), 7.96 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 110.4, 122.4, 124.8, 125.4, 136.6, 142.4, 155.8; IR (ATR) ν 3051, 1573, 1483, 1458, 1325, 1246 cm^{-1}; FAB-MS m/z 291 ([M]$^+$+1); HRMS (FAB) m/z calcd for $C_{16}H_{15}N_6$ (M) 291.1358, found 291.1361.

(*E*)-2,2′-Azobenzothiazole (2xx). Purified by silica gel column chromatography (hexane/EtOAc 7:3); orange solid (53.4 mg, 72%); mp 293.7−294.6 °C; R_f 0.10 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.58 (m, 4H), 7.97 (m, 2H), 8.26 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 122.6, 125.8, 127.8, 128.9, 135.4, 153.2, 173.4; IR (ATR) ν 1548, 1474, 1452, 1313, 1244, 1192, 1153, 1115, 893 cm^{-1}; MS (EI) m/z (relative intensity, %) 296 ([M]$^+$, 3), 268 ([M − N_2]$^+$, 100), 130 ([C_7H_4NS]$^+$, 43); HRMS (EI) m/z calcd for $C_{14}H_8N_4S_2$ (M) 296.0190, found 296.0193.

(*E*)-1,2-Bis-benzothiazol-6-yl-diazene (2yy). Purified by silica gel column chromatography ($CHCl_3$/MeOH 100:0 to 8.2); yellow solid (46.2 mg, 62%); mp 250.2−251.1 °C; R_f 0.23 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, 2H, J = 2.0, 8.8 Hz), 8.27 (d, 2H, J = 8.8 Hz), 8.59 (d, 2H, J = 2.0 Hz), 9.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.7, 121.1, 124.1, 134.7, 150.2, 155.0, 156.4; IR (ATR) ν 3064, 1585, 1466, 1398, 1290, 889, 846 cm^{-1}; MS (EI) m/z (relative intensity, %) 296 ([M]$^+$, 49), 134 ([C_7H_4NS]$^+$, 100), 162 ([$N_2C_7H_4NS$]$^+$, 32); HRMS (EI) m/z calcd for $C_{14}H_8N_4S_2$ (M) 296.0190, found 296.0192.

(*E*)-9,9′-Diethyl-3,3′-azocarbazole (2zz). Spectroscopic data were in agreement with those previously reported.[43] Purified by basic alumina column chromatography (hexane/EtOAc 9:1); yellow solid (72.8 mg, 70%); mp 213.1−2136. °C; R_f 0.28 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (t, 6H, J = 7.2 Hz), 4.44 (q, 4H, J = 7.2 Hz), 7.31 (t, 2H, J = 6.8 Hz), 7.45−7.53 (m, 6H), 8,21 (m, 4H), 8.75 (d, 2H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 37.8, 108.6, 108.9, 116.0, 119.5, 120.7, 120.8, 123.3, 123.6, 126.1,

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140.6, 141.2, 146.5; IR (ATR) ν 2972, 1593, 1277, 1323, 1229, 1117, 746 cm^{-1}; MS (EI) m/z (relative intensity, %) 416 ($[M]^+$, 57), 194 ($[C_{14}H_{12}N]^+$, 100); HRMS (EI) m/z calcd for $C_{28}H_{24}N_4$ (M) 416.2001, found 416.2002.

Typical Procedure for the Synthesis of Asymmetric Azo Compounds Using *t*-BuOI (Table 4 and 5). To a mixture of two aromatic amines (Ar^1NH_2 and Ar^2NH_2, 0.25 mmol for each) and NaI (1.0 mmol, 150.0 mg) in an appropriate solvent (3 mL), was added *t*-BuOCl (1.0 mmol, 108.6 mg) under N_2 atmosphere at the appropriate temperature. The mixture was stirred for the indicated time and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: ethyl acetate in hexane) gave cross-dimerized product.

(*E*)-Ethyl 4-(*p*-Tolyldiazenyl)benzoate (2bi). Spectroscopic data were in agreement with those previously reported.[13d] Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); yellow solid (41.3 mg, 62%); mp 100.6−101.3 °C; R_f 0.43 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.43 (t, 3H, J = 7.0 Hz), 2.45 (s, 3H), 4.42 (q, 2H, J = 7.0 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.87 (d, 2H, J = 8.4 Hz), 7.92 (d, 2H, J = 8.6 Hz), 8.19 (d, 2H, J = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.4, 21.6, 61.2, 122.4, 123.1, 129.7, 130.4, 131.8, 142.3, 150.6, 155.1, 165.9; IR (ATR) ν 2922, 1715, 1601, 1265, 1103, 1094, 1008, 866, 822, 773, 709 cm^{-1}; MS (EI) m/z (relative intensity, %) 268 ($[M]^+$, 53), 91 ($[C_6H_4CH_3]^+$, 100), 119 ($[N_2C_6H_4CH_3]^+$, 33), 149 ($[C_6H_4CO_2Et]^+$, 25); HRMS (EI) m/z calcd for $C_{16}H_{16}N_2O_2$ (M) 268.1212, found 268.1214.

(*E*)-1-(4-Acetylphenyl)-2-*p*-tolyldiazene (2bj). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); red solid (34.7 mg, 58%); mp 128.7−130.0 °C; R_f 0.18 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.66 (s, 3H), 7.33 (d, 2H, J = 8.4 Hz), 7.86 (d, 2H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.6 Hz), 8.10 (d, 2H, J = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 26.8, 122.7, 123.2, 129.3, 129.8, 138.1, 142.5, 150.7, 155.1, 197.5; IR (ATR) ν 1676, 1595, 1354, 1263, 1003, 962, 853, 820, 707 cm^{-1}; MS (EI) m/z (relative intensity, %) 238 ($[M]^+$, 38), 91 ($[C_6H_4CH_3]^+$, 100), 119 ($[N_2C_6H_4CH_3]^+$, 35); HRMS (EI) m/z calcd for $C_{15}H_{14}N_2O$ (M) 238.1106, found 238.1109.

(*E*)-1-(4-Nitrophenyl)-2-*p*-tolyldiazene (2bl). Spectroscopic data were in agreement with those previously reported.[39] Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (38.5 mg, 64%); mp 180.2−181.3 °C; R_f 0.40 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.34 (d, 2H, J = 8.1 Hz), 7.87 (d, 2H, J = 8.1 Hz), 7.99 (d, 2H, J = 8.9 Hz), 8.35 (d, 2H, J = 8.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 123.1, 123.3, 124.5, 129.7, 143.1, 148.3, 150.4, 155.6; IR (ATR) ν 1605, 1589, 1522, 1339, 1306, 1134, 1105, 858, 826, 754 cm^{-1}; MS (EI) m/z (relative intensity, %) 241 ($[M]^+$, 34), 91 ($[C_6H_4CH_3]^+$, 100), 119 ($[N_2C_6H_4CH_3]^+$, 25); HRMS (EI) m/z calcd for $C_{13}H_{11}N_3O_2$ (M) 241.0851, found 241.0847.

(*E*)-1-(3-Chlorophenyl)-2-*p*-tolyldiazene (2bn). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (29.3 mg, 52%); mp 104.3−105.2 °C; R_f 0.45 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2,43 (s, 3H), 7.30−7.44 (m, 4H), 7.78−7.88 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 121.7, 122.2, 123.1, 129.8, 139.1, 130.4, 135.1, 142.2, 150.5, 153.5; IR (ATR) ν 2924, 1728, 1599, 1454, 1260, 1070, 823, 791, 710 cm^{-1}; MS (EI) m/z (relative intensity, %) 230 ($[M]^+$, 24), 91 ($[C_6H_4CH_3]^+$, 100), 111 ($[C_6H_4Cl]^+$, 17), 119 ($[N_2C_6H_4CH_3]^+$, 19); HRMS (EI) m/z calcd for $C_{13}H_{11}ClN_2$ (M) 230.0611, found 230.0608.

(*E*)-1-(3-Nitrophenyl)-2-*p*-tolyldiazene (2bo). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (38.0 mg, 60%); mp 113.2−115.9 °C; R_f 0.38 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.33 (d, 2H, J = 8.4 Hz), 7.67 (dd, 1H, J = 8.1, 8.1 Hz), 7.86 (d, 2H, J = 8.4 Hz), 8.21 (d, 1H, J = 8.1 Hz), 8.28 (d, 1H, J = 8.1 Hz), 8.69 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 116.9, 123.3, 124.5, 129.0, 129.8, 129.9, 143.0, 149.0, 150.3, 153.1; IR (ATR) ν 1601, 1584, 1518, 1346, 1146, 1076, 901, 828, 810, 739, 710 cm^{-1}; MS (EI) m/z (relative intensity, %) 241 ($[M]^+$, 27), 91 ($[C_6H_4CH_3]^+$, 100), 119 ($[N_2C_6H_4CH_3]^+$, 23); HRMS (EI) m/z calcd for $C_{13}H_{11}N_3O_2$ (M) 241.0851, found 241.0848.

(*E*)-1-(3,5-Bis(trifluoromethyl)phenyl)-2-*p*-tolyldiazene (2bs). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 9:1); orange solid (54.6 mg, 66%); mp 82.0−84.4 °C; R_f 0.28 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.34 (d, 2H, J = 8.1 Hz), 7.87 (d, 2H, J = 8.1 Hz), 7.95 (s, 1H), 8.33 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 122.8 (q, J = 3.3 Hz), 123.1 (q, J = 272.9 Hz), 123.5, 130.0, 132.6 (q, J = 34.1 Hz), 143.4, 150.2, 152.9; IR (ATR) ν 1600, 1504, 1363, 1275, 1261, 1172, 1124, 899, 828 cm^{-1}; MS (EI) m/z (relative intensity, %) 332 ($[M]^+$, 31), 91 ($[C_6H_4CH_3]^+$, 100), 119 ($[N_2C_6H_4CH_3]^+$, 19), 213 ($[C_6H_4(CF_3)_2]^+$, 11); HRMS (EI) m/z calcd for $C_{15}H_{10}F_6N_2$ (M) 332.0748, found 332.0745.

(*E*)-1-(4-Acetylphenyl)-2-phenyldiazene (2aj). Spectroscopic data were in agreement with those previously reported.[8b] Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); red solid (30.0 mg, 54%); mp 102.3−104.7 °C; R_f 0.24 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.66 (s, 3H), 7.50−7.56 (m, 3H), 7.93−7.99 (m, 4H), 8.10 (d, 2H, J = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.8, 122.8, 123.1, 129.2, 129.3, 131.7, 138.3, 152.5, 155.0, 197.4; IR (ATR) ν 2924, 1674, 1352, 1259, 961, 839, 771 cm^{-1}; MS (EI) m/z (relative intensity, %) 224 ($[M]^+$, 100), 77 ($[C_6H_5]^+$, 97), 105 ($[N_2C_6H_5]^+$, 26), 119 ($[C_6H_4COCH_3]^+$, 57); HRMS (EI) m/z calcd for $C_{14}H_{12}N_2O$ (M) 224.0950, found 224.0952.

(*E*)-1-(4-Acetylphenyl)-2-(4-nitrophenyl)diazene (2jl). Spectroscopic data were in agreement with those previously reported.[39] Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); red solid (48.2 mg, 72%); mp 160.0−161.6 °C; R_f 0.15 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.68 (s, 3H), 8.00−8.15 (m, 6H), 8.38 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.8, 123.4, 123.7, 124.7, 129.4, 139.3, 149.1, 154.5, 155.3, 197.1; IR (ATR) ν 1681, 1698, 1534, 1341, 1319, 1261, 1215, 1109 cm^{-1}, 860; MS (EI) m/z (relative intensity, %) 269 ($[M]^+$, 68), 119 ($[C_6H_4COCH_3]^+$, 100), 122 ($[C_6H_4NO_2]^+$, 35), 147 ($[N_2C_6H_4\ COCH_3]^+$, 29); HRMS (EI) m/z calcd for $C_{14}H_{11}N_3O_3$ (M) 269.0800, found 269.0803.

(*E*)-1-(4-Acetylphenyl)-2-(4-fluorophenyl)diazene (2ej). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (36.8 mg, 61%); mp 111.5−114.1 °C; R_f 0.24 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.66 (s, 3H), 7.18−7.27 (m, 2H), 7.93−8.02 (m, 4H), 8.08−8.13 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.8, 116.2 (d, J = 22.9 Hz), 122.8, 125.2 (d, J = 9.5 Hz), 129.3, 138.4, 149.0 (d, J = 2.8 Hz), 154.8, 164.8 (d, J = 253.3 Hz), 197.3; IR (ATR) ν 1680, 1591, 1489, 1406, 1358, 1233, 1138, 843 cm^{-1}; MS (EI) m/z (relative intensity, %) 242 ($[M]^+$, 62), 95 ($[C_6H_4F]^+$, 100), 119 ($[C_6H_4COCH_3]^+$, 41), 123 ($[N_2C_6H_4F]^+$, 36); HRMS (EI) m/z calcd for $C_{14}H_{11}FN_2O$ (M) 242.0855, found 242.0855.

(*E*)-1-(4-Acetylphenyl)-2-(4-chlorophenyl)diazene (2fj). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (42.0 mg, 65%); mp 149.8−152.3 °C; R_f 0.25 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.65 (s, 3H), 7.49 (d, 2H, J = 8.6 Hz), 7.88 (d, 2H, J = 8.6 Hz), 7.94 (d, 2H, J = 8.6 Hz), 8.09 (d, 2H, J = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.8, 122.9, 124.4, 129.3, 129.4, 137.7, 138.4, 150.7, 154.7, 197.3; IR (ATR) ν 1676, 1478, 1404, 1354, 1261, 1086, 1003, 852, 839 cm^{-1}; MS (EI) m/z (relative intensity, %) 258 ($[M]^+$, 86), 111 ($[C_6H_4Cl]^+$, 100), 119 ($[C_6H_4COMe]^+$, 69), 139 ($[N_2C_6H_4Cl]^+$, 43); HRMS (EI) m/z calcd for $C_{14}H_{11}ClN_2O$ (M) 258.0560, found 258.0570.

(*E*)-1-(4-Acetylphenyl)-2-(4-bromophenyl)diazene (2gj). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (44.2 mg, 58%); mp 168.3−169.4 °C; R_f 0.24 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.67 (s, 3H), 7.67 (d, 2H, J = 8.6 Hz), 7.83 (d, 2H, J = 8.6 Hz), 7.96 (d, 2H, J = 8.6 Hz), 8.10 (d, 2H, J = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.8, 123.0, 124.6, 126.3, 129.4, 132.4, 138.5, 151.2, 154.7, 197.4; IR (ATR) ν 2920, 1668, 1354, 1260, 1067, 1005, 839 cm^{-1}; MS (EI) m/z (relative intensity, %) 302 ($[M]^+$, 71), 119 ($[C_6H_4COMe]^+$, 100), 147 ($[N_2C_6H_4COMe]^+$, 25), 155 ($[C_6H_4Br]^+$, 95), 147 ($[N_2C_6H_4Br]^+$, 41); HRMS (EI) m/z calcd for $C_{14}H_{11}BrN_2O$ (M) 302.0055, found 302.0052.

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(*E*)-1-(4-Acetylphenyl)-2-(4-iodophenyl)diazene (2hj). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); red solid (46.3 mg, 53%); mp 190.0−192.3 °C; R_f 0.33 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.67 (s, 3H), 7.68 (d, 2H, J = 8.6 Hz), 7.89 (d, 2H, J = 8.6 Hz), 7.96 (d, 2H, J = 8.6 Hz), 8.11 (d, 2H, J = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.9, 98.8, 123.0, 124.7, 129.4, 138.5, 138.6, 151.8 154.7, 197.4; IR (ATR) ν 1665, 1354, 1298, 1263, 1003, 828 cm^{-1}; MS (EI) m/z (relative intensity, %) 350 ([M]$^+$, 100), 119 ([C_6H_4COMe]$^+$, 69), 147 ([$N_2C_6H_4COMe$]$^+$, 17), 203 ([C_6H_4I]$^+$, 99), 231 ([$N_2C_6H_4I$]$^+$, 43); HRMS (EI) m/z calcd for $C_{14}H_{11}IN_2O$ (M) 349.9916, found 349.9914.

(*E*)-1-(4-Acetylphenyl)-2-(3,5-bis(trifluoromethyl)phenyl)-diazene (2js). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); red solid (56.5 mg, 63%); mp 82.6−83.4 °C; R_f 0.25 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.70 (s, 3H), 8.02 (s, 1H), 8.05 (d, 2H, J = 8.6 Hz), 8.15 (d, 2H, J = 8.6 Hz), 8.41 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.9, 123.0 (q, J = 273.5 Hz), 123.2 (q, J = 3.4 Hz), 123.4, 124.4 (m), 129.5, 132.8 (q, J = 34.1 Hz), 139.4, 152.6, 154.2, 197.2; IR (ATR) ν 1694, 1369, 1358, 1277, 1258, 1206, 1163, 1126, 1103, 961, 903, 843 cm^{-1}; MS (EI) m/z (relative intensity, %) 360 ([M]$^+$, 52), 119 ([C_6H_4COMe]$^+$, 100), 147 ([$N_2C_6H_4COMe$]$^+$, 16), 213 ([$C_6H_3(CF_3)_2$]$^+$, 42), 241 ([$N_2C_6H_3(CF_3)_2$]$^+$, 2); HRMS (EI) m/z calcd for $C_{16}H_{10}F_6N_2O$ (M) 360.0697, found 360.0698.

(*E*)-Ethyl 4-((4-Nitrophenyl)diazenyl)benzoate (2il). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); red solid (49.3 mg, 66%); mp 159.7−160.9 °C; R_f 0.23 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.44 (t, 3H. J = 7.0 Hz), 4.43 (q, 2H, J = 7.0 Hz), 7.97 (d, 2H, J = 8.9 Hz), 8.05 (d, 2H, J = 8.6 Hz), 8.21 (d, 2H, J = 8.6 Hz), 8.39 (d, 2H, J = 8.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.4, 61.4, 123.0, 123.6, 124.6, 130.5, 133.3, 148.9, 154.4, 155.2, 165.5; IR (ATR) ν 1707, 1522, 1343, 1271, 1103, 862, 773 cm^{-1}; MS (EI) m/z (relative intensity, %) 299 ([M]$^+$, 54), 122 ([$C_6H_4NO_2$]$^+$, 33), 149 ([$C_6H_4CO_2Et$]$^+$, 100), 177 ([$N_2C_6H_4CO_2Et$]$^+$, 18); HRMS (EI) m/z calcd for $C_{15}H_{13}N_3O_4$ (M) 299.0906, found 299.0904.

(*E*)-5-Methyl-3-(*p*-tolyldiazenyl)isoxazole (2bv). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 8:2); yellow solid (29.2 mg, 58%); mp 97.3−98.0 °C; R_f 0.30 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.50 (s, 3H), 6.37 (s, 1H), 7.33 (d, 2H, J = 8.0 Hz), 7.89 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 21.6, 92.2, 123.6, 129.9, 143.7, 150.5, 171.0, 173.8; IR (ATR) ν 2926, 1726, 1602, 1470, 1153, 927, 823, 799 cm^{-1}; MS (EI) m/z (relative intensity, %) 201 ([M]$^+$, 26), 91 ([$C_6H_4CH_3$]$^+$, 100), 119 ([$N_2C_6H_4CH_3$]$^+$, 13); HRMS (EI) m/z calcd for $C_{11}H_{11}N_3O$ (M) 201.0902, found 201.0900.

(*E*)-2-(4′-Tolylazo)-1-methylbenzimidazole (2bw). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (38.3 mg, 61%); mp 175.4−176.0 °C; R_f 0.18 (hexane/EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 4.21 (s, 3H), 7.35−7.42 (m, 4H), 7.49 (d, 1H, J = 7.2 Hz), 7.91 (d, 1H, J = 7.2 Hz), 8.04 (d, 2H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 29.6, 109.8, 121.7, 123.7, 123.8, 124.1, 129.8, 135.9, 141.9, 143.7, 151.3, 155.0; IR (ATR) ν 1600, 1481, 1331, 1148, 817, 734 cm^{-1}; MS (EI) m/z (relative intensity, %) 250 ([M]$^+$, 4), 91 ([$C_6H_4CH_3$]$^+$, 34), 201 (100); HRMS (EI) m/z calcd for $C_{15}H_{14}N_4$ (M) 250.1218, found 250.1217.

(*E*)-2-(4′-Bromophenylazo)-1-methylbenzimidazole (2gw). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (45.8 mg, 58%); mp 205.8−206.2 °C; R_f 0.20 (hexane/EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 3H), 7.37−7.53 (m, 3H), 7.71 (d, 2H, J = 8.8 Hz), 7.92 (d, 1H, J = 7.2 Hz), 8.01 (d, 2H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.8, 110.0, 122.0, 124.2, 124.7, 125.0, 127.5, 132.5, 136.1, 142.1, 151.8, 154.8; IR (ATR) ν 1491, 1329, 1146, 1063, 849, 816, 734 cm^{-1}; MS (EI) m/z (relative intensity, %) 314 ([M]$^+$, 5), 287 (100); HRMS (EI) m/z calcd for $C_{14}H_{11}BrN_4$ (M) 314.0167, found 314.0168.

(*E*)-2-(4′-Acetylphenylazo)-1-methylbenzimidazole (2jw). Purified by silica gel column chromatography (CH_2Cl_2/EtOAc 99:1 to 9:1); red solid (39.2 mg, 56%); mp 228.1−228.8 °C; R_f 0.22 (CH_2Cl_2/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (s, 3H), 4.19 (s, 3H), 7.37−7.48 (m, 3H), 7.49 (d, 1H, J = 8.0 Hz), 8.11 (d, 1H, J = 8.8 Hz), 8.15 (d, 2H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 29.9, 110.1, 122.2, 123.7, 124.4, 125.0, 129.3, 136.1, 139.3, 142.1, 154.7, 155.2, 197.2; IR (ATR) ν 1678, 1392, 1355, 1329, 1256, 824 cm^{-1}; MS (EI) m/z (relative intensity, %) 278 ([M]$^+$, 7), 249 (100); HRMS (EI) m/z calcd for $C_{16}H_{14}N_4O$ (M) 278.1168, found 278.1166.

(*E*)-2-(3′,5′-Bis(trifluoromethyl)phenyl)-1-methylbenzimidazole (2jw). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 8:2); orange solid (46.8 mg, 50%); mp 194.7−195.2 °C; R_f 0.25 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (s, 3H), 7.40−7.49 (m, 2H), 7.51 (d, 1H, J = 7.6 Hz), 7.94 (d, 1H, J = 7.6 Hz), 8.06 (s, 1H), 8.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1 (s), 110.3 (s), 122.4 (s), 122.8 (q, J = 271.7 Hz), 123.4 (q, J = 3.3 Hz), 124.8 (s), 125.0 (m), 125.6 (s), 132.9 (q, J = 33.7 Hz), 136.3(s), 142.1 (s), 153.1 (s), 154.3 (s); IR (ATR) ν 1369, 1278, 1168, 1120, 901 cm^{-1}; MS (EI) m/z (relative intensity, %) 372 ([M]$^+$, 18), 213 ([$C_6H_4(CF_3)_2$]$^+$, 37), 343 (100); HRMS (EI) m/z calcd for $C_{16}H_{10}F_6N_4$ (M) 372.0810, found 372.0809.

(*E*)-1-(Benzothiazol-2-yl)-2-*p*-tolyldiazene (2bx). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (53.4 mg, 72%); mp 183.5−184.0 °C; R_f 0.40 (hexane/EtOAc 9:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.30 (d, 2H, J = 8.1 Hz), 7.49 (m, 2H), 7.88 (dd, 1H, J = 1.1, 7.3 Hz), 7.98 (d, 2H, J = 8.1 Hz), 8.17 (dd, 1H, J = 1.4, 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.8, 122.3, 124.4, 124.8, 126.6, 127.3, 130.1, 134.3, 144.9, 149.8, 152.6, 175.9; IR (ATR) ν 1730, 1597, 1494, 1421, 1147, 815, 758, 723 cm^{-1}; MS (EI) m/z (relative intensity, %) 253 ([M]$^+$, 14), 91 ([$C_6H_4CH_3$]$^+$, 100), 119 ([$N_2C_6H_4CH_3$]$^+$, 10); HRMS (EI) m/z calcd for $C_{14}H_{11}N_3S$ (M) 253.0674, found 253.0674.

(*E*)-6-(*p*-Tolyldiazenyl)benzothiazole (2by). Purified by silica gel column chromatography (hexane/EtOAc 99:1 to 7:3); orange solid (27.8 mg, 44%); mp 135.6−136.0 °C; R_f 0.38 (hexane/EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.32 (d, 2H, J = 8.0 Hz), 7.86 (d, 2H, J = 8.0 Hz), 8.12 (dd, 1H, J = 2.0, 8.8 Hz), 8.22 (d, 1H, J = 8.8 Hz), 8.17 (dd, 1H, J = 1.4, 7.3 Hz), 8.50 (d, 1H, J = 2.0 Hz), 9.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 117.0, 121.1, 123.0, 123.9, 129.8 (2), 141.9, 150.3, 150.6, 154.6, 156.1; IR (ATR) ν 3049, 1599, 1502, 1429, 1408, 1330, 1225, 846, 825 cm^{-1}; MS (EI) m/z (relative intensity, %) 253 ([M]$^+$, 78), 91 ([$C_6H_4CH_3$]$^+$, 100), 134 ([C_7H_4NS]$^+$, 74); HRMS (EI) m/z calcd for $C_{14}H_{11}N_3S$ (M) 253.0674, found 253.0676.

Procedure for the Gram-Scale Synthesis of 2ii (Scheme 3). To a mixture of ethyl 4-aminobenzoate (10 mmol, 1.65 g) and NaI (20 mmol, 3.00 g) in Et_2O (60 mL) was added *t*-BuOCl (20 mmol, 2.17 g) under N_2 atmosphere at room temperature. The mixture was stirred for 3 h and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 50 mL), and the solution was extracted with CH_2Cl_2 (100 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: hexane−EtOAc, 9:1) gave **2ii** in 93% yield (1.51 g).

Procedure for the Synthesis of 4aa and 4cc (Scheme 4a and b). To a mixture of aromatic amine (0.5 mmol) and NaI (1.0 mmol, 150.0 mg) in an appropriate solvent (3 mL) was added *t*-BuOCl (1.0 mmol, 108.6 mg) under N_2 atmosphere at the appropriate temperature. The mixture was stirred for the indicated time and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: ethyl acetate in hexane) gave homodimerized product.

Procedure for the Synthesis of 4bb (Scheme 4a). To a mixture of **4aa** (0.24 mmol, 98.9 mg), acetamide (1.44 mmol, 85.1 mg), cesium carbonate (0.84 mmol, 272.7 mg), and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) (0.012 mmol, 11.0 mg) in dioxane (2 mL) was added $Pd_2(dba)_3$ under argon atmosphere at room temperature. The mixture was heated at 90 °C and stirred for 1 h. The mixture was diluted with EtOAc (20 mL) and wash with brine. The organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. The crude product was washed with $CHCl_3$ to give **4bb**.

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(*E*)-2,2′,6,6′-Tetrafluoro-4,4′-dibromoazobenzene (4aa). Spectroscopic data were in agreement with those previously reported.[22b] Purified by silica gel column chromatography (hexane/EtOAc 95:5); red solid (63.9 mg, 62%); mp 169.5−170.4 °C; R_f 0.48 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, 4H, J = 1.2 Hz); IR (ATR) ν 3103, 3084, 1599, 1568, 1420, 1296, 1198, 1051, 874, 862, 839 cm^{-1}; MS (EI) m/z (relative intensity, %) 412 ([M]$^+$, 46), 112 (100), 191 ([$C_6H_2BrF_2$]$^+$, 70); HRMS (EI) m/z calcd for $C_{12}H_4Br_2F_4N_2$ (M) 409.8677, found 409.8680.

(*E*)-2,2′,6,6′-Tetrafluoro-4,4′-diacetoazobenzene (4bb). Spectroscopic data were in agreement with those previously reported.[22b] red solid (72.8 mg, 82%); mp 362.8−364.0 °C; R_f 0.08 (hexane/EtOAc 7:3); ^{1}H NMR (400 MHz, d_6-DMSO) δ 2.11 (s, 6H), 7.48 (d, 4H, J = 12.0 Hz), 10.63 (s, br, 2H); IR (ATR) ν 3302, 3271, 3121, 1678, 1599, 1539, 1420, 1371, 1348, 1265, 1150, 1053, 993, 841 cm^{-1}; MS (EI) m/z (relative intensity, %) 368 ([M]$^+$, 98), 170 ([$C_8H_6F_2NO$]$^+$, 100), 198 ([$N_2C_8H_6F_2NO$]$^+$, 65); HRMS (EI) m/z calcd for $C_{16}H_{12}F_4N_4O_2$ (M) 368.0896, found 368.0895.

(*E*)-Diethyl-4,4′-(2,2′,6,6′-tetrafluoro)azobenzene Dicarboxylate (4cc). Spectroscopic data were in agreement with those previously reported.[22b] Purified by silica gel column chromatography (hexane/EtOAc 9:1); red solid (81.7 mg, 82%); mp 145.8−146.0 °C; R_f 0.25 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, 6H, J = 6.8 Hz), 4.43 (q, 4H, J = 6.8 Hz), 7.75 (dd, 4H, J = 1.6, 10.4 Hz); IR (ATR) ν 3375, 3098, 2978, 1721, 1574, 1435, 1330, 1236, 1053, 1018, 887, 767 cm^{-1}; MS (EI) m/z (relative intensity, %) 398 ([M]$^+$, 47), 213 ([$N_2C_9H_7F_2O_2$]$^+$, 100); HRMS (EI) m/z calcd for $C_{18}H_{14}F_4N_2O_4$ (M) 398.0890, found 398.0891.

Procedure for pH Measurement. To a mixture of *p*-toluidine (0.5 mmol, 53.6 mg) and NaI (1.0 mmol, 150.0 mg) in diethyl ether (3 mL) was added *t*-BuOCl (1.0 mmol, 108.6 mg) under N_2 atmosphere at room temperature. The mixture was stirred for 1 h, and the resulting solution was extracted with water (10 mL). The pH measurement of the water layer indicated 4.75.

Procedure for the Base Addition Experiment (Table 6). To a mixture of *p*-toluidine (0.5 mmol, 53.6 mg), NaI (0.5 mmol, 75.0 mg), and base (0.5 mmol) in diethyl ether (3 mL) was added *t*-BuOCl (0.5 mmol, 54.3 mg) under N_2 atmosphere at room temperature. The mixture was stirred for 1 h and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. The yield of product was calculated by ^{1}H NMR integration of the crude product using 1,1,2,2-tetrachloroethane as an internal standard.

Procedure for the Homodimerization Reaction under Radical-Inhibiting Conditions (Table 7). To a mixture of *p*-toluidine (0.5 mmol, 53.6 mg), NaI (1.0 mmol, 150.0 mg), and radical scavenger (1.0 mmol) in diethyl ether (3 mL) was added *t*-BuOCl (1.0 mmol, 108.6 mg) under N_2 atmosphere at room temperature. The mixture was stirred for 1 h and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: ethyl acetate in hexane) gave **2bb**.

Procedure for the Reaction of 5 with *tert*-Butyl Hypoiodite (Scheme 8). To a mixture of 1,2-diphenylhydrazine (0.5 mmol, 92.1 mg) and NaI (1.0 mmol, 150.0 mg) in MeCN (3 mL) was added *t*-BuOCl (1.0 mmol, 108.6 mg) under N_2 atmosphere at room temperature. The mixture was stirred for 1 h and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: hexane−EtOAc, 99:1) gave **2ii** quantitatively (91.0 mg).

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of azo products, full NMR spectra of monitoring experiments, and ESI-MS spectra of iodoaniline. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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