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Palladium-Catalyzed Direct *ortho* Alkoxylation of Aromatic Azo Compounds with Alcohols

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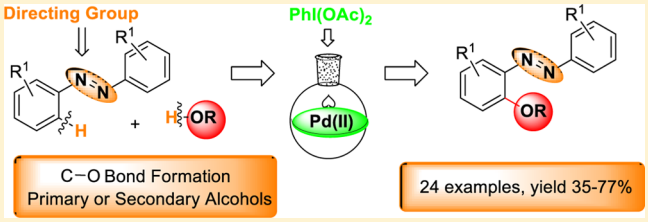
Supporting Information

ABSTRACT: An efficient and highly regioselective synthesis of 2-alkoxy aromatic azo compounds via palladium(II)-catalyzed alkoxylation of azobenzene derivatives directed by the azo group using alcohols as the alkoxylation reagents and $PhI(OAc)_2$ as the oxidant has been developed. The method is applicable to both primary and secondary alcohols and affords moderate to good yields.



In the past decade, transition-metal-catalyzed direct functionalization of unreactive C−H bonds has achieved great success and been applied in the syntheses of many useful polyfunctional compounds. A series of coordinating groups have been employed as the directing groups in this strategy.[1] Compared with the formation of C−C bonds, the reports of the formation of C−O bonds are less well established, maybe because of the electronegativities of the elements as well as the metal−ligand bond strengths.[2] Introducing an alkoxy group on the aromatic ring has great value in organic synthesis because of the strong electron-donating conjugation effect of this group. In addition, the aryl ether functionality is a common motif of pharmaceuticals, functional materials, and many other fine chemicals.[3] Therefore, the development of new methodologies for direct alkoxylation of C−H bonds is becoming a valuable and atom-economical strategy to construct this structural block.[4] A few research groups, including ours, have reported directed *ortho* alkoxylation of the $C(sp^2)$−H bonds of arenes or $C(sp^3)$−H bonds catalyzed by palladium using oxime ether, *N*-methoxyamide, amide, and cyano as the directing goups.[5] These successful results push us to continue to carry out our research in this area.

Aromatic azo derivatives, a group of important conjugated compounds, are widely used not only in the traditional chemical industry, such as dyes and pigments,[6] but more noticeably in many newly rising areas of science and technology, such as photochemical molecular switches, supermolecular chemistry of host−guest recognition, self-assembly of liquid-crystal materials, analysis of biomedical imaging, chemical light-driven molecular motors, energy conversion, and so on.[7] Therefore, the synthesis of aromatic azo derivatives and the modification and functionalization of these compounds in recent years have once again become the academic hot-spot. A few examples have concerned palladium-catalyzed functionalization of aromatic azo compounds.[8] Very recently, palladium-catalyzed *ortho* acylation and halogenation of aromatic azo compounds were reported.[9] A rhodium(III)-catalyzed C−H bond addition of azobenzenes to aldehydes was also developed.[10] Herein we describe a Pd-catalyzed *ortho* alkoxylation of $C(sp^2)$−H bonds on the aromatic ring directed by the azo group using alcohols as alkoxylation reagents to synthesize 2-alkoxy aromatic azo compounds.

We started to optimize the reaction conditions by using azobenzene (**1a**) as the substrate and methanol (**1b**) as both the alkoxylation reagent and the solvent (Table 1). In the absence of $Pd(OAc)_2$, the reaction did not proceed at all. The presence of $Pd(OAc)_2$ (10 mol %) and $PhI(OAc)_2$ as an oxidant led to a formation of the desired monomethoxylation product **3aa** with very high selectivity. In order to improve the yield, a series of oxidants were tested, and no conversion was observed when $Cu(OAc)_2$, AgOAc, benzoquinone (BQ), or O_2 was used (entries 12−15), while a very low yield was obtained when $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ was used (entries 10 and 11). $PhI(OAc)_2$ was proved to be the best oxidant, and the appropriate amount of it was 2 equiv (entries 1 and 9). Some additives such as AcOH, TFA, TsOH, and CH_3SO_3H were also tested. In the presence of AcOH, the yield did not increase evidently (entries 2−4), but the presence of TFA, TsOH, and CH_3SO_3H was obviously not favorable for this reaction (entries 5−7). Therefore, no additive was employed in our determined reaction conditions. Other palladium catalysts such as $PdCl_2$, $PdCl_2(CH_3CN)_2$, and $PdCl_2(PPh_3)_2$ showed low catalytic activity (entries 16−18), while the Ru and Rh catalysts $[RuCl_2(p\text{-cymene})]_2$ and $[RhCp^*Cl_2]_2$ demonstrated entirely no efficiency in this reaction (entries 19 and 20). Different reaction temperatures were also investigated. At 80 °C, the best result was obtained. Decreasing the temperature to 60 °C or room temperature brought a reduction in the yield. Also, there was no obvious promotion with an increase in the temperature to 100 °C (entry 1). Finally, the

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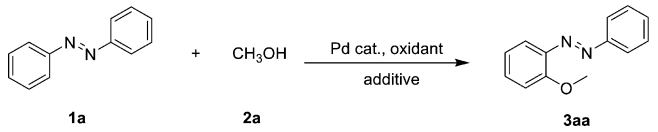
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa

entry	catalyst	oxidant (equiv)	additive (equiv)	yield (%)[b]
1	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	none	75 (23, 62, 73)[c]
2	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	AcOH (1)	73
3	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	AcOH (5)	70
4	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	AcOH (10)	71
5	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	TFA (1)	<10
6	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	TsOH (1)	<10
7	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	CH_3SO_3H (1)	<10
8	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	none	47[d]
9	$Pd(OAc)_2$	$PhI(OAc)_2$ (1)	none	43
10	$Pd(OAc)_2$	$K_2S_2O_8$ (2)	none	13
11	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$ (2)	none	23
12	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	none	0
13	$Pd(OAc)_2$	AgOAc (2)	none	0
14	$Pd(OAc)_2$	BQ (2)	none	0
15	$Pd(OAc)_2$	O_2 (1 atm)	none	0
16	$PdCl_2$	$PhI(OAc)_2$ (2)	none	55
17	$PdCl_2(CH_3CN)_2$	$PhI(OAc)_2$ (2)	none	25
18	$PdCl_2(PPh_3)_2$	$PhI(OAc)_2$ (2)	none	59
19	$[RuCl_2(p\text{-cymene})]_2$	$PhI(OAc)_2$ (2)	none	0
20	$[RhCp^*Cl_2]_2$	$PhI(OAc)_2$ (2)	none	0

[a]Unless otherwise specified, the reactions were carried out in a sealed tube in the presence of **1a** (0.50 mmol), **2a** (2 mL), catalyst (10 mol %), and oxidant (1 mmol) under an air atmosphere at 80 °C for 24 h. [b]Isolated yields. [c]At room temperature, 60 °C, and 100 °C, respectively. [d]$Pd(OAc)_2$ (5 mol %) was used.

yield decreased sharply when 5 mol % $Pd(OAc)_2$ was used (entry 8).

With suitable conditions for the methoxylation of azobenzene in hand, the reactivities of different alcohols as the alkoxylation reagents were investigated. The results are revealed in Table 2. To our delight, the alkoxylation with ethanol (**2b**) afforded product **3ab** in a yield of 63%. Unfortunately, propanol (**2c**) and isopropanol (**2d**) did not undergo the reaction smoothly to give corresponding alkoxylation products under the same conditions. Then we attempted to employ an additive. To our surprise, the propoxylation and isopropoxylation products **3ac** and **3ad** were obtained in yields of 77% and 55%, respectively, upon the addition of 20 equiv of AcOH. Under these reaction conditions, the alkoxylation products with some other primary or secondary alcohols such as butanol (**2e**), isobutanol (**2f**), and cyclopentanol (**2g**) were achieved in moderate yields with reaction times of 36−72 h (**3ae**−**ag**), while more sterically hindered *tert*-butyl alcohol failed to provide the desired product, which was similar to the results of previously reported alkoxylation reactions.[5] It was interesting that the reaction gave the monoalkoxylation products with very high selectivity for the alcohols we used.

After screening of different alcohols, we explored the scope of differently substituted azobenzenes. Substituents on the aromatic moiety of the aromatic azo compounds influenced the efficiency of this coupling reaction significantly. It was unfortunate that the method did not seem to be very efficient for the *ortho*- or *para*-substituted azobenzene derivatives under the present reaction conditions. For example, for the methoxylation of 2,2′-dimethylazobenzene and 4,4′-dimethylazobenzene, only trace desired products were generated. However, a range of *meta*-substituted azobenzenes could be adopted in our alkoxylation methodology. The reaction of azobenzene derivatives having an electron-donating group such as methyl or methoxy at the *meta* position of the phenyl ring proceeded smoothly to give the corresponding products. With primary alcohols (methanol, ethanol, propanol, isobutanol), satisfactory yields of 51−70% were obtained (**3ba**, **3bc**, **3bf**, **3eb**, and **3ec**), while secondary alcohols (isopropanol and cyclopentanol) gave lower yields (51% and 47% for **3bd** and **3bg**, respectively). Alkoxylation of aromatic azo compounds bearing a weak electron-withdrawing group (Cl, Br) at the *meta* position of the phenyl ring was less efficient apart from methoxylation reaction (**3ca**, **3da**). For example, the propoxylation and isopropoxylation reactions needed a higher temperature (100 °C) and longer reaction times (36−72 h) to afford the products (**3cc**, **3cd**, **3dc**, **3dd**). Other electron-withdrawing groups, such as acetyl, could also be functionalized to bring out the desired product, albeit with a relatively low yield (**3fa**).

On the basis of previous related studies[5,9] and our experiments, a possible mechanism of this palladium-catalyzed alkoxylation of aromatic azo compounds is proposed, as shown in Scheme 1. First, coordination of azobenzene (**1**) with the Pd(II) catalyst and subsequent C−H activation would result in cyclopalladation to form palladacycle **A**. The arylpalladium intermediate **A** would then be oxidized to Pd (IV) species **B** by $PhI(OAc)_2$ in the presence of alcohol. Next, the final product **3** would be obtained via reductive elimination of **B**, followed by regeneration of the Pd(II) catalyst. In addition, Ritter[11] proposed a Pd(II)/Pd(III) catalytic cycle through a bimetallic Pd(III) complex for a similar directed C−O bond formation reaction. Recently, Sunoj[5c] suggested a Pd(II)/Pd(0) process for direct

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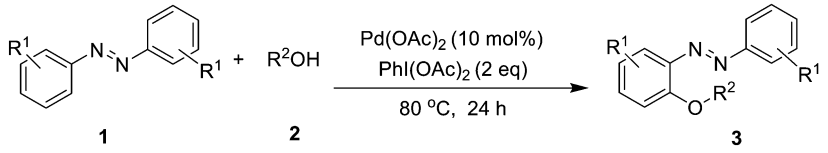
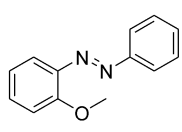
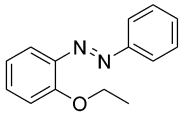
Table 2. The *ortho* Alkoxylation of Azobenzene Derivatives with Alcohols[a]



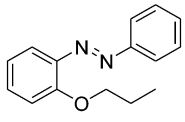
1 2 3



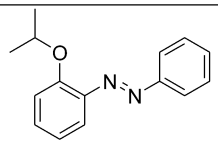
3aa 75%



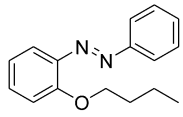
3ab 63%



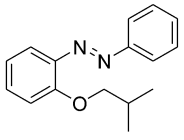
3ac 77%[b]



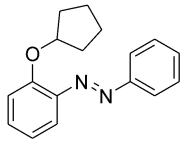
3ad 55%[b]



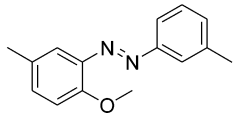
3ae 62% (36 h)[b]



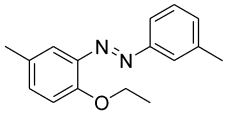
3af 65% (36 h)[b]



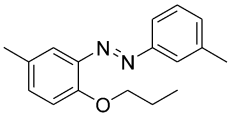
3ag 52% (72 h)[b]



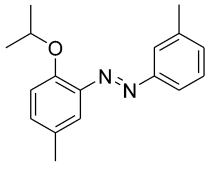
3ba 69%



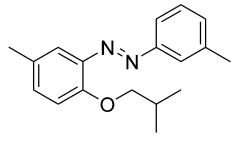
3bb 57%



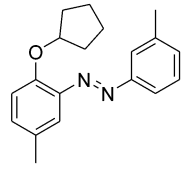
3bc 70%[b]



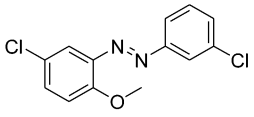
3bd 51%[b]



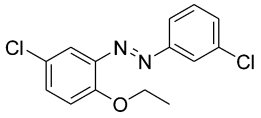
3bf 67%[b]



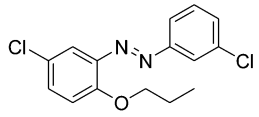
3bg 47%[b]



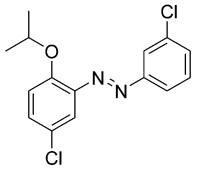
3ca 62%



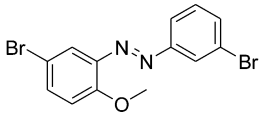
3cb 43%



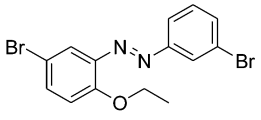
3cc 59% (100 °C, 48 h)[b]



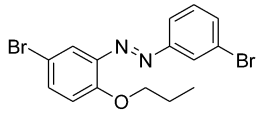
3cd 35% (100 °C, 72 h)[c]



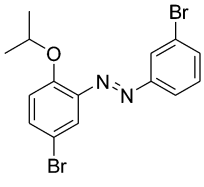
3da 66%



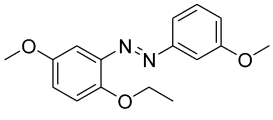
3db 47%



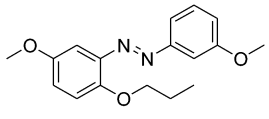
3dc 65% (100 °C, 36 h)[b]



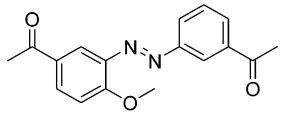
3dd 40% (100 °C, 72 h)[b]



3eb 55%



3ec 51%[b]



3fa 42%

[a]Unless otherwise specified, the reactions were carried out with aromatic azo compound **1** (0.5 mmol), alcohol **2** (2 mL), $Pd(OAc)_2$ (10 mol %), and $PhI(OAc)_2$ (1.0 mmol) under an air atmosphere at 80 °C for 24 h. All listed yields are isolated yields. [b]20 equiv of AcOH was used as an additive.

alkoxylation of *N*-methoxybenzamides. These possible mechanisms should not be excluded.

In summary, we have developed an efficient route for direct alkoxylation of aromatic azo compounds via Pd-catalyzed, azo-

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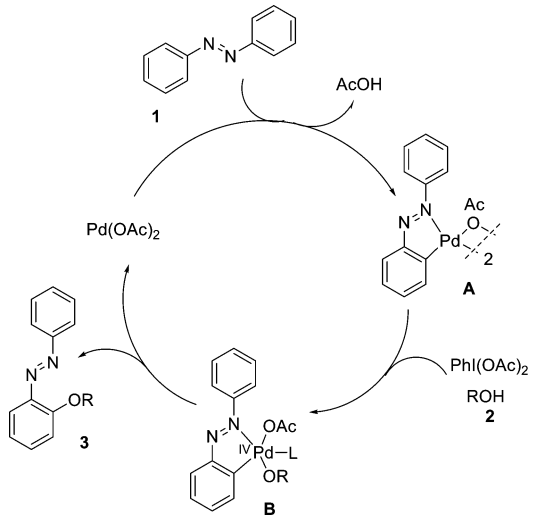
Scheme 1. Plausible Reaction Mechanism



group-directed C(sp^2)–H bond activation, in which PhI(OAc)$_2$ was found to be a particularly effective oxidant. The reaction exhibited functional group tolerance, as a series of azobenzene derivatives with either electron-donating or electron-withdrawing groups could be alkoxylated directly and efficiently. The method was applicable to both primary and secondary alcohols. This work provides a convenient method for the syntheses of 2-alkoxy aromatic azo compounds from readily accessible starting materials under mild reaction conditions and therefore is an important extension of the chemistry of azo compounds.

EXPERIMENTAL SECTION

General. All of the reactions were run in a sealed tube with a Teflon-lined cap under an air atmosphere. Chemicals were commercially available and used without purification. Aromatic azo compound substrates were prepared according to the literature procedure.[12] ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using $(CH_3)_4Si$ (for ^{1}H, δ = 0.00; for ^{13}C, δ = 77.00) as the internal standard. The following abbreviations are used to denote the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Melting points are uncorrected. HRMS data were obtained by ESI on a TOF mass analyzer.

General Experimental Procedures and Characterizations. Azobenzene (0.5 mmol), alcohol (2 mL), Pd(OAc)$_2$ (0.05 mmol), and PhI(OAc)$_2$ (1.0 mmol) were added to a 25 mL sealed tube with a Teflon lined cap. The mixture was heated at 80 °C (oil bath temperature) for 24 h. After the mixture was cooled to room temperature, the volatiles were removed under reduced pressure, and the residue was purified by a flash column chromatography on silica gel using hexane/ethyl acetate as the eluent to give the corresponding product.

*(E)-1-(2-Methoxyphenyl)-2-phenyldiazene (**3aa**).*[13] Yield: 75% (79 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95–7.93 (m, 2H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.55–7.45 (m, 4H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 0.6 Hz, 1H), 7.07–7.03 (m, 1H), 4.06 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.0, 153.2, 142.3, 132.5, 130.8, 129.0, 123.0, 120.8, 117.0, 112.7, 56.4.

*(E)-1-(2-Ethoxyphenyl)-2-phenyldiazene (**3ab**).* Yield: 63% (72 mg). Reddish-orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 1.2 Hz, 2H), 7.69 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.55–7.42 (m, 4H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.06–7.02 (m, 1H), 4.29 (q, J = 6.8 Hz, 2H), 1.55 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.5, 153.1, 142.6, 132.4, 130.7, 129.1, 123.0, 120.8, 117.0, 114.5, 65.3, 14.9. HRMS-ESI (m/z): calcd for $C_{14}H_{15}N_2O$ [M + H]$^+$ 227.1179, found 227.1168.

*(E)-1-Phenyl-2-(2-propoxyphenyl)diazene (**3ac**).* Yield: 77% (93 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97–7.94 (m, 2H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.56–7.42 (m, 4H), 7.12 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.06–7.02 (m, 1H), 4.20 (t, J = 6.4 Hz, 2H), 1.99–1.92 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.7, 153.2, 142.7, 132.3, 130.7, 129.0, 123.0, 120.8, 117.0, 114.7, 71.3, 22.7, 10.6. HRMS-ESI (m/z): calcd for $C_{15}H_{17}N_2O$ [M + H]$^+$ 241.1341, found 241.1346.

*(E)-1-(2-Isopropoxyphenyl)-2-phenyldiazene (**3ad**).* Yield: 55% (66 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 1.2 Hz, 2H), 7.69 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.56–7.48 (m, 3H), 7.44–7.40 (m, 1H), 7.14 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.08–7.04 (m, 1H), 4.72 (m, 1H), 1.45 (d, J = 4.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.0, 153.1, 144.1, 132.1, 130.7, 129.0, 123.0, 121.5, 118.5, 117.1, 73.8, 22.3. HRMS-ESI (m/z): calcd for $C_{15}H_{17}N_2O$ [M + H]$^+$ 241.1341, found 241.1338.

*(E)-1-(2-Butoxyphenyl)-2-phenyldiazene (**3ae**).* Yield: 62% (79 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96–7.94 (m, 2H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.56–7.42 (m, 4H), 7.12 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.06–7.02 (m, 1H), 4.22 (t, J = 6.4 Hz, 2H), 1.96–1.89 (m, 2H), 1.64–1.55 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.7, 153.2, 142.7, 132.3, 130.7, 129.0, 123.0, 120.8, 117.0, 114.7, 69.6, 31.4, 19.3, 13.9. HRMS-ESI (m/z): calcd for $C_{16}H_{19}N_2O$ [M + H]$^+$ 255.1497, found 255.1483.

*(E)-1-(2-Isobutoxyphenyl)-2-phenyldiazene (**3af**).* Yield: 65% (83 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 2.8 Hz, 2H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.56–7.41 (m, 4H), 7.11 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.06–7.01 (m, 1H), 3.97 (d, J = 6.4 Hz, 2H), 2.29–2.22 (m, 1H), 1.12 (d, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.8, 153.2, 142.7, 132.3, 130.6, 129.0, 123.0, 120.7, 117.0, 114.7, 76.1, 28.5, 19.3. HRMS-ESI (m/z): calcd for $C_{16}H_{19}N_2O$ [M + H]$^+$ 255.1497, found 255.1501.

*(E)-1-(2-(Cyclopentyloxy)phenyl)-2-phenyldiazene (**3ag**).* Yield: 52% (69 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96–7.94 (m, 2H), 7.69 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.57–7.40 (m, 4H), 7.14–7.01 (m, 2H), 5.00 (t, J = 2.4 Hz, 1H), 2.08–1.87 (m, 6H), 1.69–1.62 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.9, 153.2, 143.5, 132.1, 130.6, 129.1, 123.0, 120.8, 117.0, 116.8, 81.8, 33.0, 24.0. HRMS-ESI (m/z): calcd for $C_{17}H_{19}N_2O$ [M + H]$^+$ 267.1497, found 267.1492.

*(E)-1-(2-Methoxy-5-methylphenyl)-2-m-tolyldiazene (**3ba**).* Yield: 69% (83 mg). Reddish-orange solid, mp 71–73 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76–7.73 (m, 2H), 7.49 (d, J = 1.6 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.30–7.26 (m, 2H), 7.01 (d, J = 8.0 Hz, 1H), 4.03 (s, 3H), 2.47 (s, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.0, 153.3, 142.0, 138.9, 132.9, 131.5, 130.3, 128.8, 122.6, 121.0, 117.2, 112.7, 56.5, 21.3, 20.5. HRMS-ESI (m/z): calcd for $C_{15}H_{17}N_2O$ [M + H]$^+$ 241.1341, found 241.1352.

*(E)-1-(2-Ethoxy-5-methylphenyl)-2-m-tolyldiazene (**3bb**).* Yield: 57% (72 mg). Orange solid, mp 57–59 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, J = 6.4 Hz, 2H), 7.48 (d, J = 1.6 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.24 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 4.26 (q, J = 6.8 Hz, 2H), 2.47 (s, 3H), 2.36 (s, 3H), 1.53 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 153.2, 142.4, 138.9, 132.8, 131.5, 130.4, 128.8, 123.1, 120.6, 117.2, 114.8, 65.6, 21.4, 20.5, 14.9. HRMS-ESI (m/z): calcd for $C_{16}H_{18}N_2ONa$ [M + Na]$^+$ 277.1317, found 277.1333.

*(E)-1-(5-Methyl-2-propoxyphenyl)-2-m-tolyldiazene (**3bc**).* Yield: 70% (94 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76–7.75 (m, 2H), 7.49 (d, J = 1.6 Hz, 1H), 7.43–7.39 (m, 1H), 7.30–7.23 (m, 2H), 7.02 (d, J = 8.4 Hz, 1H), 4.15 (t, J = 6.4 Hz, 2H), 2.48 (s, 3H), 2.36 (s, 3H), 1.96–1.91 (m, 2H), 1.11 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.7, 153.3, 142.5, 138.8, 132.8, 131.4, 130.4, 128.8, 123.2, 120.5, 117.2, 115.0, 71.7, 22.7, 21.4, 20.5, 10.5. HRMS-ESI (m/z): calcd for $C_{17}H_{21}N_2O$ [M + H]$^+$ 269.1648, found 269.1642.

*(E)-1-(2-Isopropoxy-5-methylphenyl)-2-m-tolyldiazene (**3bd**).* Yield: 51% (68 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78–7.76 (m, 2H), 7.50 (d, J = 1.6 Hz, 1H), 7.45–7.40 (m, 1H), 7.31–7.29 (m, 1H), 7.25–7.22 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 4.65 (m, 1H), 2.49 (s, 3H), 2.38 (s, 3H), 1.44 (d, J = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.0, 153.2, 144.0, 138.9, 132.7, 131.5, 131.4,

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128.8, 123.5, 120.3, 119.2, 117.2, 74.4, 22.3, 21.4, 20.6. HRMS-ESI (m/z): calcd for $C_{17}H_{21}N_2O$ $[M + H]^+$ 269.1648, found 269.1653.

*(E)-1-(2-Isobutoxy-5-methylphenyl)-2-m-tolyldiazene (**3bf**).* Yield: 67% (95 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78−7.76 (m, 2H), 7.49 (d, J = 1.6 Hz, 1H), 7.44−7.40 (m, 1H), 7.30−7.29 (m, 1H), 7.25−7.23 (m, 1H), 7.01 (d, J = 8.4 Hz, 1H), 3.95 (d, J = 6.4 Hz, 2H), 2.48 (s, 3H), 2.37 (s, 3H), 2.29−2.19 (m, 1H), 1.11 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.9, 153.3, 142.5, 138.8, 132.8, 131.4, 130.3, 128.8, 123.4, 120.3, 117.1, 115.1, 76.6, 28.5, 21.4, 20.5, 19.3. HRMS-ESI (m/z): calcd for $C_{18}H_{23}N_2O$ $[M + H]^+$ 283.1805, found 283.1803.

*(E)-1-(2-(Cyclopentyloxy)-5-methylphenyl)-2-m-tolyldiazene (**3bg**).* Yield: 47% (69 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76−7.74 (m, 2H), 7.48−7.47 (m, 1H), 7.41 (t, J = 8.2 Hz, 1H), 7.30 (t, J = 0.4 Hz, 1H), 7.24−7.21 (m, 1H), 7.02 (d, J = 8.4 Hz, 1H), 4.95 (m, 1H), 2.48 (s, 3H), 2.36 (s, 3H), 2.04−2.02 (m, 2H), 1.95−1.89 (m, 4H), 1.66 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.8, 153.2, 143.4, 138.8, 132.7, 131.4, 130.5, 128.8, 123.4, 120.3, 117.3, 117.2, 82.3, 32.9, 23.9, 21.4, 20.5. HRMS-ESI (m/z): calcd for $C_{19}H_{23}N_2O$ $[M + H]^+$ 295.1810, found 295.1823.

*(E)-1-(5-Chloro-2-methoxyphenyl)-2-(3-chlorophenyl)diazene (**3ca**).* Yield: 62% (87 mg). Orange solid, mp 77−79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91−7.89 (m, 1H), 7.86−7.81 (m, 1H), 7.69 (d, J = 2.8 Hz, 1H), 7.49−7.42 (m, 3H), 7.05 (d, J = 8.8 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.0, 153.6, 142.1, 135.2, 132.3, 130.9, 130.1, 126.5, 122.8, 121.8, 117.0, 114.1, 56.7. HRMS-ESI (m/z): calcd for $C_{13}H_{11}Cl_2N_2O$ $[M + H]^+$ 281.0248, found 281.0272.

*(E)-1-(5-Chloro-2-ethoxyphenyl)-2-(3-chlorophenyl)diazene (**3cb**).* Yield: 43% (63 mg). Orange solid, mp 54−55 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91−7.90 (m, 1H), 7.87−7.84 (m, 1H), 7.69 (d, J = 2.8 Hz, 1H), 7.48−7.45 (m, 2H), 7.40 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.05 (d, J = 9.2 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.55 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.5, 153.6, 142.4, 135.1, 132.2, 130.9, 130.1, 126.5, 122.6, 122.0, 117.0, 115.8, 65.7, 14.8. HRMS-ESI (m/z): calcd for $C_{14}H_{13}Cl_2N_2O$ $[M + H]^+$ 295.0405, found 295.0418.

*(E)-1-(5-Chloro-2-propoxyphenyl)-2-(3-chlorophenyl)diazene (**3cc**).* Yield: 59% (91 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, J = 1.2 Hz, 1H), 7.86−7.83 (m, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.48−7.46 (m, 2H), 7.40 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 4.16 (t, J = 6.4 Hz, 2H), 1.94 (m, 2H), 1.12 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.7, 153.6, 142.5, 135.1, 132.0, 130.9, 130.1, 126.5, 122.5, 122.1, 117.0, 115.9, 71.6, 22.6, 10.5. HRMS-ESI (m/z): calcd for $C_{15}H_{15}Cl_2N_2O$ $[M + H]^+$ 309.0561, found 309.0567.

*(E)-1-(5-Chloro-2-isopropoxyphenyl)-2-(3-chlorophenyl)diazene (**3cd**).* Yield: 35% (54 mg). Orange solid, mp 50−52 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91−7.90 (m, 1H), 7.86−7.83 (m, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.50−7.45 (m, 2H), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.06 (d, J = 5.6 Hz, 1H), 4.70 (m, 1H), 1.45 (d, J = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.9, 153.6, 143.8, 135.1, 132.1, 130.9, 130.1, 127.1, 122.6, 122.2, 119.4, 117.1, 74.1, 22.2. HRMS-ESI (m/z): calcd for $C_{15}H_{15}Cl_2N_2O$ $[M + H]^+$ 309.0561, found 309.0566.

*(E)-1-(5-Bromo-2-methoxyphenyl)-2-(3-bromophenyl)diazene (**3da**).* Yield: 66% (122 mg). Orange solid, mp 140−142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (t, J = 2.0 Hz, 1H), 7.91−7.88 (m, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.63−7.56 (m, 2H), 7.42 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 8.8 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.4, 153.7, 142.4, 135.2, 133.9, 130.5, 124.6, 123.4, 123.2, 120.0, 114.6, 113.8, 56.6. HRMS-ESI (m/z): calcd for $C_{13}H_{11}Br_2N_2O$ $[M + H]^+$ 370.9218, found 370.9240.

*(E)-1-(5-Bromo-2-ethoxyphenyl)-2-(3-bromophenyl)diazene (**3db**).* Yield: 47% (90 mg). Orange solid, mp 77−79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (t, J = 2.0 Hz, 1H), 7.91−7.88 (m, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.63−7.60 (m, 1H), 7.56−7.53 (m, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 4.27 (q, J = 6.8 Hz, 2H), 1.55 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.9, 153.7, 142.7, 135.1, 133.8, 130.4, 125.0, 123.2, 123.1, 120.0, 116.2, 113.8, 65.6, 14.8. HRMS-ESI (m/z): calcd for $C_{14}H_{13}Br_2N_2O$ $[M + H]^+$ 384.9374, found 384.9377.

*(E)-1-(5-Bromo-2-propoxyphenyl)-2-(3-bromophenyl)diazene (**3dc**).* Yield: 65% (129 mg). Orange solid, mp 55−57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (t, J = 2.0 Hz, 1H), 7.90−7.88 (m, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.63−7.60 (m, 1H), 7.53 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 4.15 (t, J = 6.4 Hz, 2H), 1.94 (m, 2H), 1.12 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.1, 153.7, 142.8, 135.1, 133.8, 130.4, 125.1, 123.1, 123.0, 120.0, 116.3, 113.7, 71.6, 22.6, 10.4. HRMS-ESI (m/z): calcd for $C_{15}H_{15}Br_2N_2O$ $[M + H]^+$ 398.9531, found 398.9515.

*(E)-1-(5-Bromo-2-isopropoxyphenyl)-2-(3-bromophenyl)diazene (**3dd**).* Yield: 40% (79 mg). Orange solid, mp 62−64 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (t, J = 2.0 Hz, 1H), 7.90−7.88 (m, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.63−7.60 (m, 1H), 7.53 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 8.8 Hz, 1H), 4.69 (m, 1H), 1.45 (d, J = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.4, 153.7, 144.0, 135.0, 133.8, 130.4, 125.1, 123.1, 123.0, 120.1, 119.7, 114.3, 74.0, 22.6, 22.2. HRMS-ESI (m/z): calcd for $C_{15}H_{15}Br_2N_2O$ $[M + H]^+$ 398.9531, found 398.9542.

*(E)-1-(2-Ethoxy-5-methoxyphenyl)-2-(3-methoxyphenyl)diazene (**3eb**).* Yield: 55% (79 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61−7.58 (m, 1H), 7.49 (t, J = 2.4 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.29 (t, J = 2.8 Hz, 1H), 7.08−7.03 (m, 3H), 4.25 (q, J = 6.8 Hz, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 1.51 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3, 154.3, 151.5, 142.9, 129.7, 119.6, 117.6, 117.3, 117.1, 106.2, 100.4, 66.9, 55.8, 55.4, 15.1. HRMS-ESI (m/z): calcd for $C_{16}H_{19}N_2O_3$ $[M + H]^+$ 287.1396, found 287.1401.

*(E)-1-(5-Methoxy-2-propoxyphenyl)-2-(3-methoxyphenyl)-diazene (**3ec**).* Yield: 51% (76 mg). Red thick oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61−7.58 (m, 1H), 7.50 (t, J = 2.4 Hz, 1H), 7.47−7.42 (m, 1H), 7.29 (t, J = 2.8 Hz, 1H), 7.09−7.00 (m, 3H), 4.14 (t, J = 6.4 Hz, 2H), 3.91 (s, 3H), 3.86 (s, 3H), 1.91−1.90 (m, 2H), 1.11 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3, 154.3, 154.2, 151.8, 142.9, 129.7, 119.6, 117.7, 117.4, 117.3, 105.7, 100.3, 72.9, 55.8, 55.4, 22.9, 10.6. HRMS-ESI (m/z): calcd for $C_{17}H_{21}N_2O_3$ $[M + H]^+$ 301.1552, found 301.1556.

*(E)-1-(5-Acetyl-2-methoxyphenyl)-2-(3-acetylphenyl)diazene (**3fa**).* Yield: 42% (62 mg). Orange solid, mp 129−131 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (t, J = 2.0 Hz, 1H), 8.27 (d, J = 2.0 Hz, 1H), 8.17−8.09 (m, 3H), 7.64 (t, J = 8.0 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 4.13 (s, 3H), 2.72 (s, 3H), 2.65 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.5, 196.7, 160.5, 153.0, 141.4, 138.2, 132.8, 130.5, 130.1, 129.5, 126.8, 123.6, 117.6, 112.5, 56.6, 26.8, 26.5. HRMS-ESI (m/z): calcd for $C_{17}H_{17}N_2O_3$ $[M + H]^+$ 297.1239, found 297.1243.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra for all products. 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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