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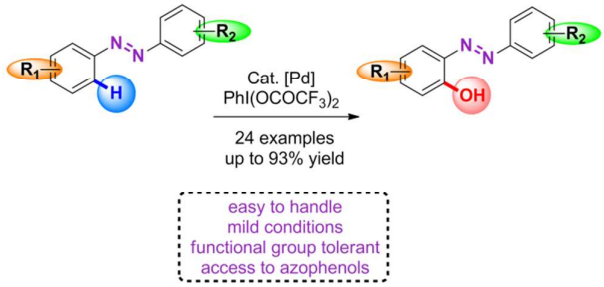
Palladium-Catalyzed Oxidative Synthesis of Unsymmetrical Azophenols

Thi Hong Long Nguyen,‡ Nicolas Gigant,‡ Sandrine Delarue-Cochin, and Delphine Joseph*

BioCIS, Université Paris-Sud, CNRS, Université Paris-Saclay, F-92296 Châtenay-Malabry, France.

*delphine.joseph@u-psud.fr

Abstract Graphic



Abstract

A straightforward palladium-catalyzed oxidative hydroxylation of azobenzenes is reported. The developed methodology tolerates various functional groups and allows the synthesis of diverse unsymmetrical azophenols under mild conditions in good to excellent yields. A complementary procedure was also investigated by in situ generation of PIFA. This study represents the first general method for the synthesis of *ortho*-hydroxy azobenzenes starting from simple azoarenes.

Introduction

Aromatic azo compounds are important scaffolds and find application in many fields due to their unique properties based on light triggered switches.[1] They are mainly involved in protein probes,[2] organic dyes,[3] chemosensors,[4] smart surface materials,[5] polymers[6] and molecular

machines.[7] Given the broad utility of azobenzenes, the development of useful methods for their preparation are keenly pursued.[8] However, no efficient synthesis of *ortho*-azophenol frameworks has been developed. As depicted in Figure 1, these privileged structures possess various useful applications: for example, the azo dye **A** has been approved as a synthesized food colorant by the FDA. The azophenol **B** has been used as an azo-linker for mediating peptide cyclization[9] whereas the fluorescence properties of 2-borylazobenzenes such as **C** have been recently explored.[10] In addition, knowing that the incorporation of an hydroxyl group in arenes can significantly affect their original physical and chemical properties,[11] a general, mild and direct catalytic route to introduce this versatile functional group would be highly attractive.

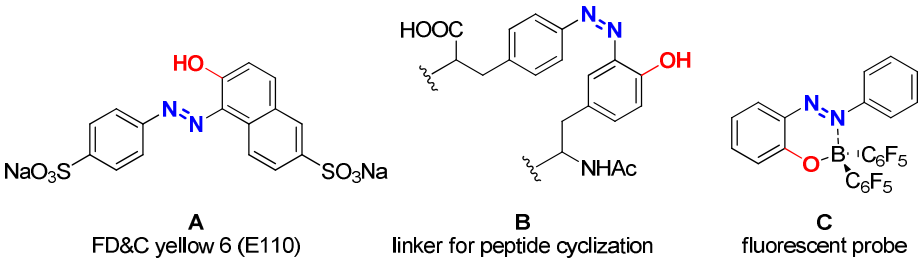


Figure 1. Representative *o*-Azophenol Derivatives

C-H bond transformations have attracted widespread attention as powerful and ideal reactions.[12] Indeed, the ability to directly oxidize carbon hydrogen bonds into carbon heteroatom bonds is very useful for the late-stage functionalization of complex molecules or to rapidly increase the molecular diversity.[13] Over the past decade, there has been significant progress in the development metal-catalyzed C-H oxidation, and recently, several ruthenium- or palladium-catalyzed protocols have been established for hydroxylation in the presence of strong or weak coordinating directing groups.[14] In addition, *ortho*-functionalization of azobenzenes has been investigated toward various coupling partners.[15] During our study, Chakraborti and co-workers have developed a practical palladium-catalyzed aryl

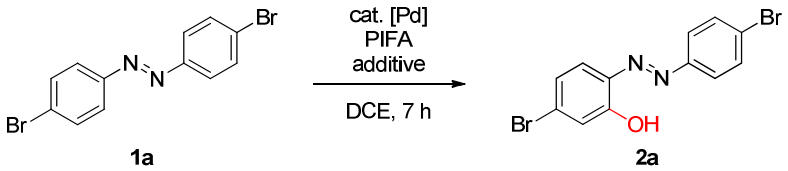
hydroxylation by employing dioxane as a source of hydroxyl radicals.[16] If the protocol was mainly very efficient with a range of benzoxazoles and benzothiazoles as directing groups, this latter was limited and unselective starting from simple azobenzenes due to the generation of the corresponding azoxybenzenes. Therefore, the need for methodology that can address this drawback remains a challenge. Inspired by a seminal work reported by Sanford and co-workers[17] and other previous studies,[18] we reasoned that hypervalent iodine reagents could be highly attractive for the synthesis of *ortho*-azophenols starting from simple azoarenes. We focused a particular attention in developing an operationally simple process involving mild reaction conditions. In this way, we shaped an easy and general route for the oxidative preparation of azophenol compounds. This synthetic method is far more direct and efficient than the rare and narrow previously reported procedures which are mainly based on the Wallach rearrangement.[10,16,19]

Results and Discussion

The present study was initiated starting from the valuable dibromo azobenzene **1a**, which will allow chemical modulations for the introduction of designed molecular anchors.[20] Firstly, **1a** was treated with 5 mol % $Pd(OAc)_2$ and 1.5 equiv of oxidant, the [bis(trifluoroacetoxy)iodo]benzene (PIFA), in 1,2-dichloroethane (DCE) at 70 °C under air atmosphere (Table 1, entry 1). Fruitfully, the targeted azophenol **2a** was isolated in an encouraging 41% yield. A screening of the PIFA loading increases the yield of the reaction up to 67% by using 2 equiv of the hypervalent iodine reagent (Table 1, entries 2-3). The utilization of $K_2S_2O_8$ or oxone as alternative oxidant did not promote the reaction and the starting material **1a** was recovered. Importantly, a control experiment in the absence of metal yielded no product and resulted in the recovery of the starting material. Further optimization indicated that 5 mol% of $Pd(OAc)_2$ is the best loading to fully convert **1a** without significant

degradation (Table 1, entries 4-7 *vs* 2). Surprisingly, albeit pyridine is known to increase the rate of the C–H oxygenation of arenes,[21] this nitrogen-containing ligand totally inhibited the reaction (Table 1, entry 8). Moreover, considering the importance of influencing the electrophilicity of the palladium(II) catalyst,[22] the oxidative reaction was carried out in the presence of 1 equiv of AcOH or TFA, but none of them enhanced the yield of **2a** (Table 1, entries 9-11). Increasing or decreasing the temperature of the reaction did not lead to any additional improvements in the yield (Table 1, entries 12-13). Besides, the nature of solvent is also a critical factor in this reaction type. Although CH_3CN, dioxane or CH_3NO_2 have been commonly employed as efficient solvents in Pd^{II}/Pd^{IV}-catalyzed C-H oxidation, they were absolutely not suitable in our case. Indeed, due to the lack of solubility of **1a** in CH_3CN and CH_3NO_2, and the absence of conversion in the presence of dioxane, the use of DCE was considered of prime importance to reach the reaction.

Table 1. Optimization of the Reaction Conditions[a]



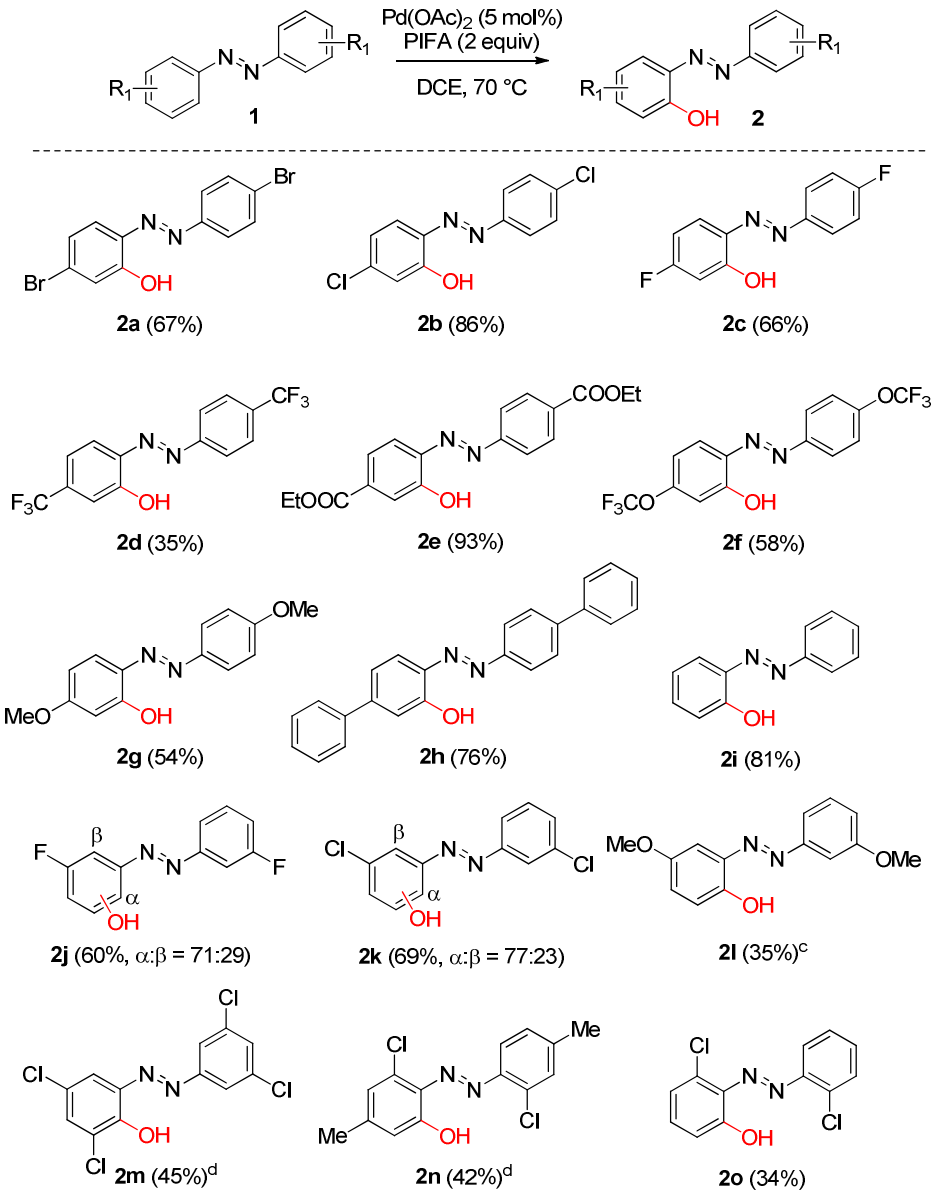
entry	Cat. [Pd] (mol%)	PIFA (equiv)	additive (mol%)	T (°C)	yield[b] (%)
1	$Pd(OAc)_2$ (5)	1.5	-	70	41
2	$Pd(OAc)_2$ (5)	2	-	70	67
3	$Pd(OAc)_2$ (5)	2.5	-	70	56
4	$Pd(OAc)_2$ (2.5)	2	-	70	46
5	$Pd(OAc)_2$ (7.5)	2	-	70	39
6	$PdCl_2(CH_3CN)_2$ (5)	2	-	70	50
7	$Pd(TFA)_2$ (5)	2	-	70	45
8	$Pd(OAc)_2$ (5)	2	pyridine (5)	70	0
9	$Pd(OAc)_2$ (5)	2	AcOH (100)	70	8
10	$Pd(OAc)_2$ (5)	2	TFA (100)	70	46
11	$Pd(TFA)_2$ (5)	2	TFA (100)	70	56
12	$Pd(OAc)_2$ (5)	2	-	60	49
13	$Pd(OAc)_2$ (5)	2	-	80	41

[a]Reaction conditions: **1a** (0.20 mmol) under the appropriate reaction conditions (c = 0.2 $mol.L^{-1}$). [b]Isolated yield.

We next explored the scope and limitations of this system under the optimized reaction conditions (Scheme 1). Gratifyingly, the reaction is tolerant toward a variety of *p,p'*-disubstituted azobenzenes and showed good compatibility with a wide range of valuable

functional groups such as halogen atoms (**2a**-**2c**). Electron-withdrawing groups on the aromatic ring slightly affected the yield of the reaction (**2d**-**2f**). Notably, the moderately deactivating ester substituent proved to be the best functionality, leading to the scaffold **2e** in an excellent 93% yield. Similarly, substrates bearing an electron-donating group such as a *p*-methoxy or a *p*-phenyl moiety underwent hydroxylation to give the corresponding unsymmetrical aromatic azo compounds **2g** and **2h** in good yields. Alternatively, the optimized conditions could be applied to a substituent-exempt azobenzene, providing the desired product **2i** in a 81% yield. We next examined the reactivity of various symmetrical *m,m'*-disubstituted azobenzenes. Starting from halo-substituted scaffolds **1j** and **1k**, the reaction mainly occurred at the sterically less hindered position affording two regioisomers with reasonable selectivities (**2j** and **2k**). Contrariwise, the symmetrical *m*-methoxy azobenzene **1l** led to **2l** with a modest 35% yield but with a complete selectivity. In this particular case, 1.2 equiv of PIFA were employed even if roughly 20% of **1l** was recovered. Indeed, degradation was unexpectedly observed following our previous conditions or attempting sequential additions of PIFA. We first speculated that the low yield might result from the potential formation of highly reactive radical cations. Nevertheless, using degassed DCE under argon in dark conditions did not permit to enhance the reaction yield (30%). The versatility of the reaction was further demonstrated by the fact that more sterically hindered azobenzenes are also compatible (**2m**-**2o**). Although a slight increase of the catalyst loading was sometimes necessary for obtaining good conversions, **2m**, **2n** and **2o** were isolated in moderate yields. However, it's worth mentioning that the synthesis of densely substituted azoarenes is usually not an easy task.

Scheme 1. Substrate Scope of Symmetrical Azobenzenes[a,b]

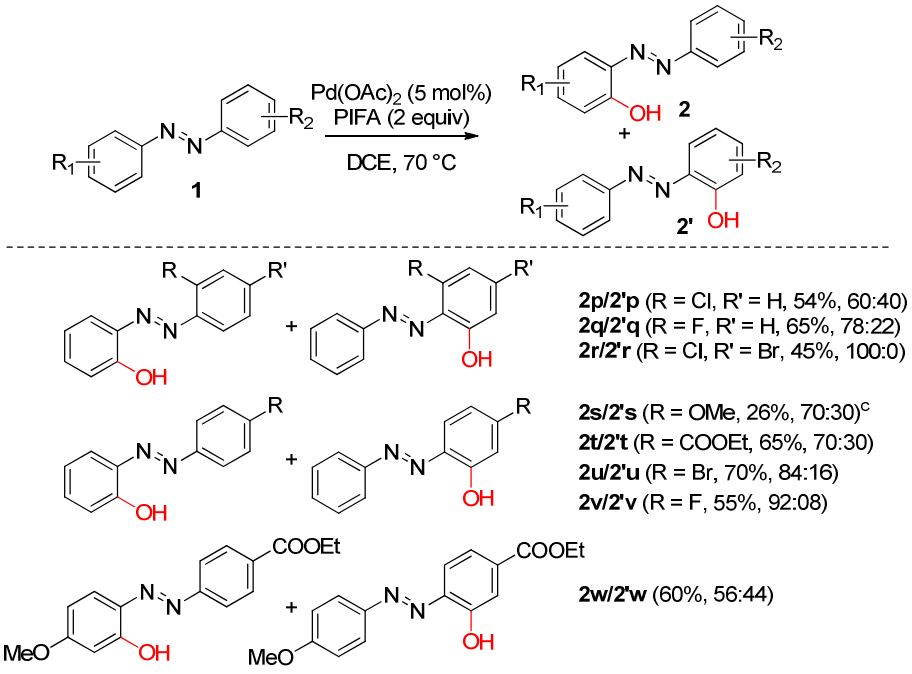


[a]Unless otherwise noted, reaction conditions: **1** (1 equiv), PIFA (2 equiv), $Pd(OAc)_2$ (5 mol%) in DCE (c = 0.2 $mol.L^{-1}$) at 70 °C. [b]Isolated yield. [c]PIFA (1.2 equiv). [d]$Pd(OAc)_2$ (7.5 mol%).

These results encouraged us to further survey the scope of this oxidative reaction with respect to unsymmetrical azobenzene derivatives (Scheme 2). When the reaction was carried out with

o-monosubstituted unsymmetrical azos **1p** and **1q** bearing a weakly deactivating halogen atom, two regioisomers were isolated with satisfying selectivities up to 78:22 (**2p** and **2q**). Each time, the *ortho* position of the unsubstituted aromatic ring was preferentially hydroxylated. Gratifyingly, starting from *o*,*p*-dihalogenated unsymmetrical azo **1r**, the desired azophenol **2r** was formed as a single regioisomer. Other simple *p*-monosubstituted substrates such as **1t** and **1u** reacted efficiently, furnishing respectively **2t** and **2u** as the major products. If the regioselectivity was preserved with the methoxylated compound **1s**, degradation explained once more the low yield observed even in the presence of a reduced amount of PIFA. Interestingly, we were pleased to find that the regioselectivity of the hydroxylation was increased starting from fluorinated scaffold **1v**, leading to **2v** in an excellent 92:08 regioisomers ratio. To gauge the substituent electronic effect on the regioselectivity, the reaction was performed with the push-pull derivative **1w**. A low selectivity was observed, highlighting that the regioselectivity is mainly controlled by the steric hindrance of the starting material.

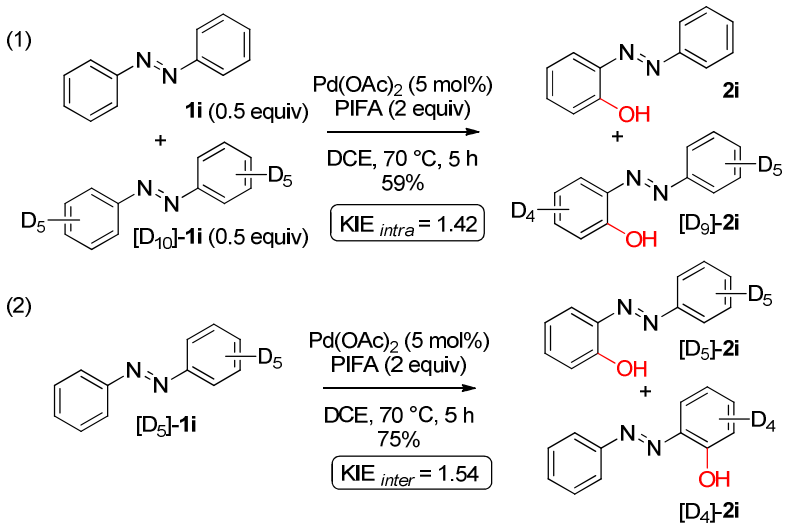
Scheme 2. Substrate Scope of Unsymmetrical Azobenzenes[a,b]



[a]Unless otherwise noted, reaction conditions: **1** (1 equiv), PIFA (2 equiv), $Pd(OAc)_2$ (5 mol%) in DCE (c = 0.2 $mol.L^{-1}$) at 70 °C. [b]Isolated yield. [c]PIFA (1.2 equiv).

Finally, to obtain mechanistic information, we evaluated the intramolecular isotope effect starting from an equimolar mixture of **1i** and [D_{10}]-**1i**. Moderate primary isotope effect (k_H/k_D = 1.42) was measured (Scheme 3, eq 1).

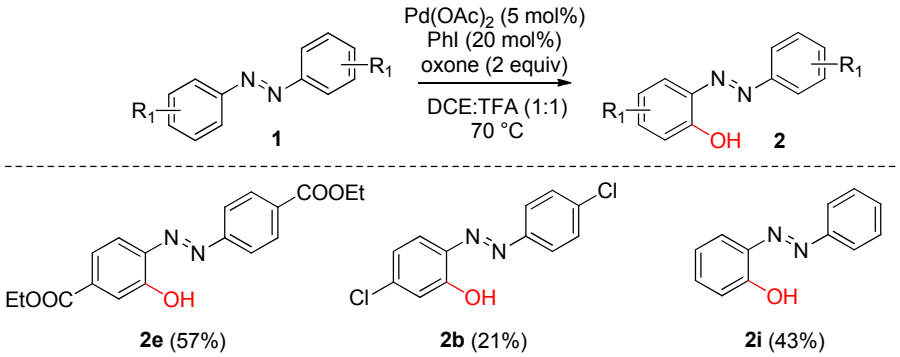
Scheme 3. Evaluation of Deuterium Isotope Effect



A similar magnitude to the product ratio was confirmed with the intermolecular isotope effect starting from [D_5]-**1i** (k_H/k_D = 1.54) (Scheme 3, eq 2), indicating that the aromatic C-H bond cleavage by Pd may be involved in the rate determining step of the reaction.

Aware of the fact that PIFA produces equimolar amounts of iodobenzene as byproducts, we decided to explore the feasibility of a catalytic version of the hydroxylation of azobenzenes by *in situ* generation of PIFA (Scheme 4). A survey of various reaction conditions revealed after optimization that **2e** can be satisfying isolated by using 20 mol% of iodobenzene with oxone (2 equiv) in the presence of TFA as cosolvent.[23] Following this modified oxidative procedure, azophenols **2b** and **2i** were then also obtained in moderate yields.

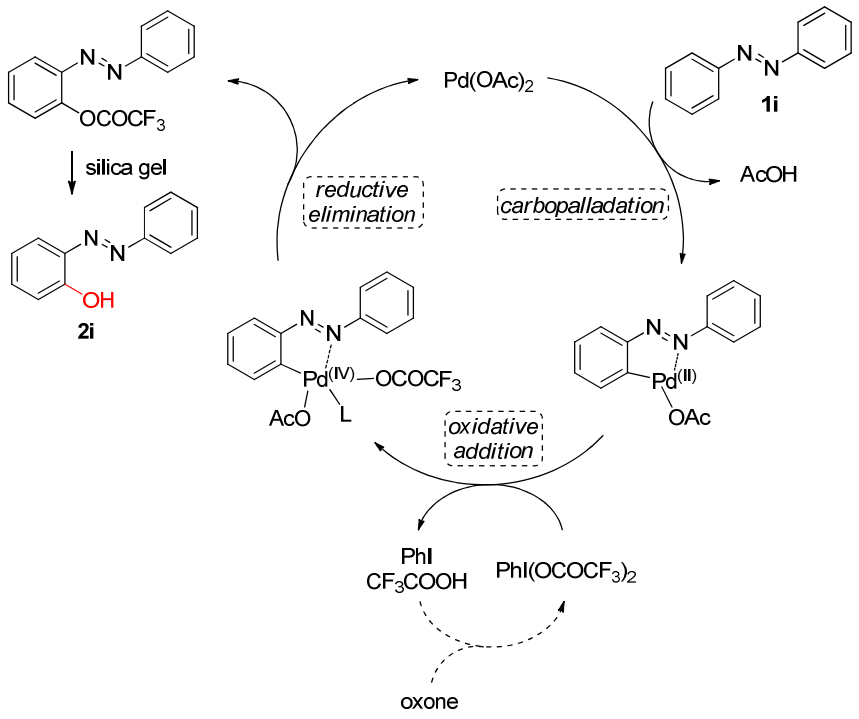
Scheme 4. Synthesis of azophenols by *in situ* generation of PIFA[a,b]



[a]Unless otherwise noted, reaction conditions: **1** (1 equiv), PhI (20 mol%), oxone (2 equiv), $Pd(OAc)_2$ (5 mol%) in DCE (c = 0.2 mol.L^{-1}) at 70 °C. [b]Isolated yield.

The proposed catalytic cycle is depicted in Scheme 5 on the basis of the above observations and the previous literature.[14,15] C-H activation of the arene substrate gives a five-membered palladacycle intermediate with concomitant loss of AcOH. Oxidative addition of PIFA to this arylpalladium(II) intermediate would then generate a Pd(IV) species, releasing iodobenzene and trifluoacetic acid. Although a reaction mechanism involving a Pd^{II}/Pd^{IV} process for this system is proposed, an alternative Pd^{II}/Pd^{III} catalytic cycle through a bimetallic Pd(III) complex could be also envisaged.[24] Subsequent reductive elimination leads the targeted trifluoro-acylated azophenol with concomitant regeneration of the active catalyst. The final product is then obtained after simple hydrolysis on silica gel. In the iodobenzene catalytic version of the reaction, the PIFA is *in situ* generated in the presence of iodobenzene and oxone in trifluoroacetic acid.

Scheme 5. Plausible Mechanism of the Reaction



Conclusion

In summary, we have developed a practical and efficient method for the straightfoward *ortho*-directed hydroxylation of azobenzenes under mild conditions. The reaction showed very good functional groups tolerance, leading to a wide range of original and unsymmetrical azophenols in satisfying to high yields. In addition, our procedure was extended to the *in situ* generation of PIFA in the presence of catalytic amount of iodobenzene. Ongoing efforts are directed toward the application of this methodology to the synthesis of azophenols with potential photoswitching and fluorescence proprieties.

Experimental Section

General Information. Reagents were purchased as reagent grade and were used without further purification other than those above-mentioned. Prior to use, toluene and dichloromethane were dried by means of a solvent purifier system. All anhydrous reactions

were carried out under argon atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on a 300 MHz spectrometer in $CDCl_3$ or C_6D_6 at 25°C. Chemical shifts values are given in ppm downfield from tetramethylsilane (TMS) with the chloroform resonance as the internal standard. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, dq = doublet of quarter. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Mass spectra and high resolution mass spectra were obtained with a Q-TOF micro spectrometer using ESI. Melting points are uncorrected and were recorded on a micromelting point apparatus. Infrared (IR) spectra were recorded as neat films. Analytical thin layer chromatography was performed on 60F-254 precoated silica (0.2 mm) on glass and was revealed by UV light or by spraying with a potassium permanganate solution, followed by charring at 150 °C. Flash chromatography separations were carried out on silica gel (40-63µm).

Preparation of Starting Azobenzenes

Symmetric and asymmetric aromatic azobenzene derivatives were prepared according to the literature procedures.[25,26,27]

General Procedure for Symmetric Azobenzenes[25]

To a solution of amine (0.40 mmol) in toluene (8 mL) was added activated manganese (IV) oxide (348 mg, 4.00 mmol). The mixture was then heated at reflux for 2 h and formed water was removed with a Dean-Stark apparatus. The reaction mixture was filtered through Celite® pad before washing it three times with toluene. After evaporation of the solvent under reduced pressure, products are purified by recrystallization in cyclohexane.

(*E*)-1,2-Bis(3,5-dichlorophenyl)diazene (1m). Yield 88% (112 mg); orange solid, mp 197-198 °C; IR (neat, cm^{-1}) 3083, 1566, 1424, 1235, 1207, 1097, 929, 891, 837, 620; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 1.9 Hz, 4H), 7.52 (t, J = 1.9 Hz, 2H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 153.1 (2×C), 135.8 (4×C), 131.3 (2×CH), 121.8 (4×CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_6N_2Cl_4$ $[M]^-$ 317.9291, found 317.9316.

(*E*)-1,2-Bis(2-chloro-4-methylphenyl)diazene (1n). Yield 70% (78 mg); orange solid, mp 177-178 °C; IR (neat, cm^{-1}) 1595, 1445, 1210, 1056, 889, 835, 686; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.39 (t, J = 1.2 Hz, 2H), 7.15 (dd, J = 8.3 Hz, J = 1.2 Hz, 2H), 2.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8 (2×C), 143.0 (2×C), 135.6 (2×C), 131.0 (2×CH), 128.2 (2×CH), 117.7 (2×CH), 21.3 (2×CH_3); HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{13}N_2Cl_2$ $[M + H]^+$ 279.0450, found 279.0460.

General Procedure for Dissymmetric Azobenzenes [26,27]

Nitrosobenzene derivative (0.80 mmol) was dissolved in glacial acetic acid (2 mL) and the amine (0.80 mmol) in EtOH (0.5 ml) was added to the solution. After stirring for 6 hours at 40 °C, the mixture was poured on ice and filtered. The crude brown product was then purified by column chromatography with silica and cyclohexane/ethyl acetate (98:2 to 80:20).

(*E*)-1-(2-Chlorophenyl)-2-phenyldiazene (1o). 1o was prepared following the general procedure using nitrosobenzene (86 mg, 0.80 mmol) and 2-chloroaniline (100 mg, 0.80 mmol). Yield 45% (78 mg); orange liquid; IR (neat, cm^{-1}) 3071, 1585, 1448, 1256, 1222, 1150, 1057, 926, 769, 753, 716, 684; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.0 Hz, J = 2.1 Hz, 2H), 7.74 (dd, J = 7.6 Hz, J = 2.1 Hz, 1H), 7.61-7.53 (m, 4H), 7.44-7.34 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (C), 148.7 (C), 135.3 (C), 131.7 (CH), 131.6 (CH), 130.7 (CH), 129.2 (2×CH), 127.3 (CH), 123.4 (2×CH), 117.6 (CH).; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{10}N_2Cl$ $[M + H]^+$ 217.0527, found 217.0534.

(*E*)-1-(4-Bromo-2-chlorophenyl)-2-phenyldiazene (1r). 1r was prepared following the general procedure using nitrosobenzene (86 mg, 0.80 mmol) and 2-chloro-4-bromoaniline (165 mg, 0.80 mmol). Yield 40% (94 mg); orange solid, mp 92-93 °C; IR (neat, cm^{-1}) 3077, 3054, 1570, 1484, 1455, 1374, 1220, 1183, 1085, 1053, 865, 824, 766, 711, 615; ^1H NMR

(300 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.76 (d, J = 1.7 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.57-7.54 (m, 3H), 7.49 (dd, J = 8.7 Hz, J = 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6 (C), 147.6 (C), 136.3 (C), 133.3 (CH), 131.8 (CH), 130.6 (CH), 129.2 (2×CH), 125.2 (C), 123.4 (2×CH), 118.6 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_9N_2ClBr$ $[M + H]^+$ 296.9611, found 296.9617.

Ethyl (*E*)-4-[(4-methoxyphenyl)diazenyl]benzoate (1w). 1w was prepared following the general procedure using ethyl 4-nitrosobenzoate (143 mg, 0.80 mmol) and 4-methoxyaniline (99 mg, 0.80 mmol). Yield 75% (170 mg); orange solid, mp 103-104 °C; IR (neat, cm^{-1}) 3006, 2843, 1703, 1601, 1582, 1499, 1401, 1270, 1246, 1184, 1123, 881, 862, 774, 692; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.9 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 3.93 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1 (C), 162.6 (C), 155.3 (C), 147.0 (C), 131.6 (C), 130.5 (2×CH), 125.2 (2×CH), 122.3 (2×CH), 114.3 (2×CH), 61.2 (CH_2), 55.6 (CH), 14.3 (CH_3); HRMS (TOF-ESI) *m/z*: Calcd for $C_{16}H_{17}N_2O_3$ $[M + H]^+$ 285.1234, found 285.1238.

General Procedure for the Direct Palladium-Catalyzed Synthesis of Unsymmetrical Azophenols

A mixture of azobenzene **1** (0.20 mmol), [bis(trifluoroacetoxy)iodo]benzene (0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol%) in dichloroethane (1 mL) was stirred at 70 °C until the disappearance of the starting material followed by TLC. After cooling to room temperature, the solvent was removed under vacuum. The crude product was then purified over a column of silica gel using cyclohexane and ethyl acetate (100:0; 98:2; 95:5; 90:10) as the eluent to afford the desired product **2**.

(*E*)-5-Bromo-2-[(4-bromophenyl)diazenyl]phenol (2a). **2a** was prepared following the general procedure for 7 h. Yield 67% (48 mg); orange solid, mp 182-183 °C; IR (neat, cm^{-1}) 3081, 2959, 2851, 1600, 1571, 1559, 1443, 1410, 1298, 1256, 1175, 1066, 1003, 835, 804; ^{1}H

NMR (300 MHz, $CDCl_3$) δ 12.85 (s, 1H, OH), 7.76 (d, J = 8.8 Hz, 2H), 7.71 (s, 1H), 7.65 (d, J = 8.8 Hz, 2H), 7.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5 (C), 149.3 (C), 136.4 (C), 134.4 (CH), 132.9 (2×CH), 127.9 (C), 126.1 (C), 123.9 (2×CH), 123.8 (CH), 121.7 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_7N_2OBr_2$ $[M - H]^-$ 354.8911, found 354.8905.

(*E*)-5-Chloro-2-[(4-chlorophenyl)diazenyl]phenol (2b). 2b was prepared following the general procedure for 3 h. Yield 86% (46 mg); orange solid, mp 172-173 °C; IR (neat, cm^{-1}) 3085, 2925, 1887, 1750, 1601, 1564, 1475, 1451, 1385, 1301, 1257, 1078, 1005, 944, 895, 839, 808, 776; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.92 (s, 1H, OH), 7.88-7.82 (m, 3H), 7.52 (d, J = 8.7 Hz, 2H), 7.09-7.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5 (C), 148.8 (C), 139.2 (C), 137.4 (C), 136.0 (C), 134.1 (CH), 129.7 (2×CH), 123.5 (2×CH), 120.7 (CH), 118.4 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_7N_2OCl_2$ $[M - H]^-$ 264.9941, found 264.9934.

(*E*)-5-Fluoro-2-[(4-fluorophenyl)diazenyl]phenol (2c). 2c was prepared following the general procedure for 6 h. Yield 66% (31 mg); orange solid, mp 124-125 °C; IR (neat, cm^{-1}) 3083, 2953, 1593, 1501, 1495, 1463, 1428, 1398, 1356, 1310, 1281, 1232, 1142, 1107, 979, 840, 772, 754; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.17 (d, J = 1.4 Hz, 1H, OH), 7.94-7.86 (m, 3H), 7.27-7.20 (m, 2H), 6.80 (td, J = 8.3 Hz, $J_{H\text{-}F}$ = 8.0 Hz, J = 2.4 Hz, 1H), 6.73 (dd, $J_{H\text{-}F}$ = 10.3 Hz, J = 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1 (d, $J_{C\text{-}F}$ = 254.3 Hz, C), 164.3 (d, $J_{C\text{-}F}$ = 251.2 Hz, C), 155.0 (d, $J_{C\text{-}F}$ = 14.3 Hz, C), 146.7 (C), 135.09 (d, $J_{C\text{-}F}$ = 11.3 Hz, CH), 126.9 (C), 124.1 (d, $J_{C\text{-}F}$ = 9.0 Hz, 2×CH), 116.5 (d, $J_{C\text{-}F}$ = 22.5 Hz, 2×CH), 108.0 (d, $J_{C\text{-}F}$ = 23.3 Hz, CH), 104.9 (d, $J_{C\text{-}F}$ = 24.8 Hz, CH); ^{19}F NMR (188 MHz, $CDCl_3$) δ -101.58, -106.58; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_9N_2OF_2$ $[M + H]^+$ 235.0677, found 235.0676.

(*E*)-5-Trifluoromethyl-2-[(4-trifluoromethylphenyl)diazenyl]phenol (2d). 2d was prepared following the general procedure for 48 h. Yield 35% (23 mg); orange solid, mp 121-122 °C; IR (neat, cm^{-1}) 2924, 1593, 1503, 1459, 1425, 1317, 1216, 1172, 1121, 1010, 952, 903, 850, 829, 795, 745, 672; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.60 (s, 1H, OH), 8.12 (d, J =

8.3 Hz, 1H), 8.02 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5 (C), 152.2 (C), 138.4 (C), 135.0 (q, $J_{C\text{-}F}$ = 32.4 Hz, C), 134.1 (CH), 133.3 (q, $J_{C\text{-}F}$ = 32.4 Hz, C), 126.7 (d, $J_{C\text{-}F}$ = 3.5 Hz, 2×CH), 123.6 (q, $J_{C\text{-}F}$ = 271.0 Hz, C), 123.2 (q, $J_{C\text{-}F}$ = 271.4 Hz, C), 122.8 (2×CH), 116.7 (d, $J_{C\text{-}F}$ = 3.3 Hz, CH), 116.1 (d, $J_{C\text{-}F}$ = 3.6 Hz, CH); ^{19}F NMR (188 MHz, $CDCl_3$) δ -60.92, -61.55; HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_7N_2OF_6$ $[M - H]^-$ 333.0468, found 333.0449.

Ethyl (*E*)-4-[(4-ethoxycarbonylphenyl)diazenyl]-3-hydroxybenzoate (2e). **2e** was prepared following the general procedure for 10 h. Yield 93% (64 mg); orange solid, mp 157-159 °C; IR (neat, cm^{-1}) 2962, 1717, 1572, 1491, 1421, 1366, 1307, 1276, 1258, 1222, 1210, 1149, 1084, 1007, 960, 870, 791, 773, 756, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.62 (s, 1H, OH), 8.24 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.76 (m, 2H), 4.49-4.40 (m, 4H), 1.46 (t, J = 7.1 Hz, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6 (CO), 165.4 (CO), 153.2 (C), 152.2 (C), 139.5 (C), 134.7 (C), 133.3 (CH), 132.8 (C), 130.8 (2×CH), 122.3 (2×CH), 120.8 (CH), 120.0 (CH), 61.5 (CH_2), 61.4 (CH_2), 14.3 (2×CH_3); HRMS (TOF-ESI) *m/z*: Calcd for $C_{18}H_{19}N_2O_5$ $[M + H]^+$ 343.1288, found 343.1302.

(*E*)-5-Trifluoromethoxy-2-[(4-trifluoromethoxyphenyl)diazenyl]phenol (2f). **2f** was prepared following the general procedure for 32 h. Yield 58% (42 mg); orange solid, mp 70-71 °C; IR (neat, cm^{-1}) 2958, 1755, 1679, 1589, 1500, 1428, 1400, 1361, 1251, 1150, 990, 924, 848, 820, 701; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.94 (s, 1H, OH), 7.98 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H); 6.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2 (C), 152.3 (C), 151.2 (C), 148.4 (C), 135.6 (C), 134.8 (CH), 123.8 (2×CH), 121.6 (2×CH), 120.4 (q, $J_{C\text{-}F}$ = 256.9 Hz, C), 120.3 (q, $J_{C\text{-}F}$ = 257.6 Hz, C), 112.0 (CH), 109.7 (CH); ^{19}F NMR (188 MHz, $CDCl_3$) δ -55.61, -55.89; HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_7N_2O_3F_6$ $[M - H]^-$ 365.0366, found 365.0363.

(*E*)-5-Methoxy-2-[(4-methoxyphenyl)diazenyl]phenol (2g). 2g was prepared following the general procedure for 24 h. Yield 54% (28 mg); orange solid, mp 137-138 °C; IR (neat, cm^{-1}) 2928, 2837, 1611, 1579, 1503, 1451, 1435, 1397, 1314, 1281, 1251, 1207, 1197, 1147, 1106, 1023, 966, 928, 831, 804, 765, 641; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.73 (br., 1H, OH), 7.81 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 9.0 Hz, 2H), 6.62 (dd, J = 8.8 Hz, J = 2.6 Hz, 1H), 6.51 (d, J = 2.6 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (C), 161.5 (C), 155.7 (C), 144.3 (C), 134.1 (CH), 132.7 (C), 123.3 (2×CH), 114.5 (2×CH), 107.8 (CH), 101.4 (CH), 55.7 (CH_3), 55.6 (CH_3); HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{15}N_2O_3$ $[M + H]^+$ 259.1077, found 259.1081.

(*E*)-4-{[(1,1'-Biphenyl)-4-yl]diazenyl}-(1,1'-biphenyl)-3-ol (2h). 2h was prepared following the general procedure for 10 h. Yield 76% (53 mg); orange solid, mp 228-229 °C; IR (neat, cm^{-1}) 3036, 1618, 1559, 1505, 1479, 1433, 1411, 1383, 1358, 1334, 1253, 1205, 1180, 1159, 1133, 1076, 1038, 1003, 968, 897, 845, 765, 692; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.12 (s, 1H, OH), 8.04-7.98 (m, 3H), 7.80-7.68 (m, 6H), 7.53-7.31 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1 (C), 149.8 (C), 145.9 (C), 143.9 (C), 140.0 (C), 139.7 (C), 136.8 (C), 133.5 (CH), 129.0 (2×CH), 128.9 (2×CH), 128.4 (CH), 128.0 (3×CH), 127.3 (2×CH), 127.2 (2×CH), 122.7 (2×CH), 119.0 (CH), 116.4 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{24}H_{19}N_2O$ $[M + H]^+$ 351.1492, found 351.1471.

(*E*)-2-(Phenyldiazenyl)phenol (2i).[16] **2i** was prepared following the general procedure for 5 h. Yield 81% (32 mg); orange solid, mp 81-82 °C; IR (neat, cm^{-1}) 3057, 2924, 2852, 1617, 1594, 1487, 1454, 1416, 1365, 1321, 1273, 1214, 1182, 1144, 1113, 1069, 1030, 1017, 940, 916, 853, 814, 770, 753, 680; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.94 (s, 1H, OH), 7.96 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.88 (m, 2H), 7.51 (m, 3H), 7.36 (m, 1H), 7.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9 (C), 150.6 (C), 137.5 (C), 133.4 (2×CH), 131.3 (CH), 129.5

(2×CH), 122.4 (2×CH), 120.1 (CH), 118.3 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{11}N_2O$ $[M + H]^+$ 199.0866, found 199.0878.

(*E*)-2-Fluoro-6-[(3-fluorophenyl)diazenyl]phenol and **(*E*)-4-fluoro-2-[(3-fluorophenyl) diazenyl]phenol (2j)**. **2j** was prepared following the general procedure for 4 h. Yield 60% (29 mg); orange solid; IR (neat, cm^{-1}) 3069, 1588, 1494, 1476, 1452, 1443, 1409, 1355, 1301, 1280, 1255, 1231, 1210, 1159, 1136, 1117, 1024, 981, 961, 875, 838, 786, 725, 674; ^1H NMR (300 MHz, $CDCl_3$) δ 12.62 (s, 0.29H, OH), 12.15 (s, 0.71H, OH), 7.65 (d, J = 13.6 Hz, 0.29H), 7.63-7.39 (m, 4.42H), 7.17-7.11 (m, 1.29H), 7.08-7.02 (m, 1H), 6.95-6.90 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ **(*E*)-2-fluoro-6-[(3-fluorophenyl)diazenyl]phenol** 163.4 (d, J_{C-F} = 247.1 Hz, C), 156.0 (d, J_{C-F} = 240.0 Hz, C), 151.9 (d, J_{C-F} = 7.2 Hz, C), 149.0 (C), 136.5 (d, J_{C-F} = 8.8 Hz, C), 130.6 (d, J_{C-F} = 8.3 Hz, CH), 121.0 (d, J_{C-F} = 23.6 Hz, CH), 120.1 (CH), 119.0 (d, J_{C-F} = 7.7 Hz, CH), 118.4 (d, J_{C-F} = 21.9 Hz, CH), 117.8 (d, J_{C-F} = 23.5 Hz, CH), 107.6 (d, J_{C-F} = 23.4 Hz, CH); ^{19}F-decoupling NMR (188 MHz, $CDCl_3$) δ **(*E*)-2-fluoro-6-[(3-fluorophenyl)diazenyl]phenol** -111.41, -124.39, **(*E*)-4-fluoro-2-[(3-fluorophenyl) diazenyl]phenol** -111.33, -137.56; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_7N_2OF_2$ $[M - H]^-$ 233.0532, found 233.0519.

(*E*)-4-Chloro-2-[(3-chlorophenyl)diazenyl]phenol and **(*E*)-2-chloro-6-[(3-chlorophenyl) diazenyl]phenol (2k).**[28] **2k** was prepared following the general procedure for 3 h. Yield 69% (37 mg); orange solid; IR (neat, cm^{-1}) 3063, 2924, 2852, 1606, 1586, 1485, 1401, 1343, 1285, 1267, 1223, 1209, 1164, 1140, 1096, 1084, 1017, 905, 883, 823, 801, 789, 731, 674; ^1H NMR (300 MHz, $CDCl_3$) δ 13.37 (s, 0.23H, OH), 12.42 (s, 0.77H, OH), 7.93 (d, J = 2.1 Hz, 0.77H), 7.86 (m, 1.46H), 7.75 (m, 1.23H), 7.46 (m, 2.54H), 7.31 (dd, J = 9.0 Hz, J = 2.3 Hz, 0.77H), 7.26 (m, 0.23H), 7.05 (m, 0.23H), 6.98 (d, J = 8.9H, 0.77H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4 (2×C), 151.3 (C), 150.9 (C), 149.2 (C), 137.7 (C), 137.3 (C), 135.8 (C), 135.7 (C), 133.9 (CH), 133.7 (CH), 132.3 (CH), 132.2 (CH), 131.6 (CH), 131.6 (CH), 130.6 (CH), 130.6

(CH), 124.8 (C), 122.3 (CH), 120.0 (CH), 121.5 (CH), 121.2 (CH), 120.1 (CH), 119.8 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_9N_2OCl_2$ $[M + H]^+$ 267.0086, found 267.0096.

(*E*)-4-Methoxy-2-[(3-methoxyphenyl)diazenyl]phenol (2l). 2l was prepared following the general procedure using 1.2 eq of PIFA for 5 h. Yield 35% (18 mg); orange solid, mp 75-78 °C; IR (neat, cm^{-1}) 2962, 2833, 1605, 1581, 1481, 1433, 1344, 1317, 1288, 1260, 1194, 1130, 1095, 1079, 1039, 1010, 893, 869, 799, 781, 726, 681; ^1H NMR (300 MHz, C_6D_6) δ 12.73 (s, 1H, OH), 7.49 (d, J = 3.1 Hz, 1H), 7.39 (t, J = 2.0 Hz, 1H), 7.26 (m, 1H), 7.03-6.96 (m, 2H), 6.81-6.77 (m, 2H), 3.31 (s, 3H), 3.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5 (C), 152.9 (C), 151.8 (C), 147.3 (C), 136.9 (C), 130.0 (CH), 121.7 (CH), 118.8 (CH), 117.9 (CH), 116.5 (CH), 114.7 (CH), 105.0 (CH), 55.9 (CH_3), 55.5 (CH_3); HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{15}N_2O_3$ $[M + H]^+$ 259.1077, found 259.1081.

(*E*)-2,4-Dichloro-6-[(3,5-dichlorophenyl)diazenyl]phenol (2m). **2m** was prepared following the general procedure using 7.5 mol% of $Pd(OAc)_2$ for 40 h. Yield 45% (30 mg); orange solid, mp 150-152 °C; IR (neat, cm^{-1}) 3078, 2963, 1759, 1566, 1470, 1434, 1400, 1337, 1281, 1238, 1216, 1166, 1093, 1016, 944, 865, 803, 854, 739, 669; ^1H NMR (300 MHz, $CDCl_3$) δ 12.82 (s, 1H, OH), 7.91 (d, J = 2.0 Hz, 1H), 7.78 (m, 2H), 7.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2 (C), 147.8 (C), 137.1 (C), 136.2 (2×C), 133.7 (CH), 131.5 (CH), 131.0 (CH), 124.8 (C), 123.5 (C), 121.1 (2×CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_5N_2OCl_4$ $[M - H]^-$ 334.9132, found 334.9125.

(*E*)-3-Chloro-2-[(2-chloro-4-methylphenyl)diazenyl]-5-methylphenol (2n). 2n was prepared following the general procedure using 7.5 mol% of $Pd(OAc)_2$ for 48 h. Yield 42% (25 mg); orange solid, mp 184-186 °C; IR (neat, cm^{-1}) 2962, 2921, 1597, 1558, 1451, 1402, 1295, 1259, 1190, 1096, 1053, 1014, 870, 831, 820, 783, 684; ^1H NMR (300 MHz, $CDCl_3$) δ 13.72 (s, 1H, OH), 7.92 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 1.5 Hz, 1H), 7.21 (dd, J = 8.5 Hz, J = 1.5 Hz, 1H), 6.97 (d, J = 1.8 Hz, 1H), 6.78 (d, J = 1.8 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 154.4 (C), 145.7 (C), 144.5 (C), 143.2 (C), 137.5 (C), 133.9 (C), 132.4 (C), 130.7 (CH), 128.6 (CH), 122.4 (CH), 117.7 (CH), 117.6 (CH), 21.9 (CH_3), 21.4 (CH_3); HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{13}N_2OCl_2$ $[M + H]^+$ 295.0399, found 295.0394.

(*E*)-3-Chloro-2-[(2-chlorophenyl)diazenyl]phenol (2o). 2o was prepared following the general procedure for 36 h. Yield 34% (18 mg); orange solid, mp 84-85 °C; IR (neat, cm^{-1}) 3066, 2968, 1699, 1583, 1565, 1464, 1445, 1433, 1406, 1329, 1280, 1258, 1231, 1180, 1154, 1057, 1031, 953, 887, 786, 758, 707, 684; ^1H NMR (300 MHz, $CDCl_3$) δ 13.60 (s, 1H, OH), 8.02 (dd, J = 7.2 Hz, J = 2.5 Hz, 1H), 7.59 (dd, J = 7.2 Hz, J = 2.2 Hz, 1H), 7.46-7.42 (m, 2H), 7.31 (t, J = 8.2 Hz, 1H), 7.15 (dd, J = 7.9 Hz, J = 1.1 Hz, 1H), 7.00 (dd, J = 8.4 Hz, J = 1.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (2×C), 146.5 (C), 138.2 (C), 134.4 (C), 134.2 (CH), 132.4 (CH), 130.5 (CH), 127.7 (CH), 121.3 (CH), 118.0 (CH), 117.7 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_9N_2OCl_2$ $[M + H]^+$ 267.0086, found 267.0096.

(*E*)-2-[(2-Chlorophenyl)diazenyl]phenol (2p) and **(*E*)-3-chloro-2-(phenyldiazenyl)phenol (2'p)**. **2p** and **2'p** were prepared following the general procedure for 48 h. Yield 54% (25 mg); orange solid; IR (neat, cm^{-1}) 3072, 2963, 2925, 1611, 1585, 1564, 1484, 1463, 1445, 1409, 1352, 1278, 1259, 1180, 1145, 1113, 1056, 1030, 950, 887, 785, 761, 684; ^1H NMR (300 MHz, $CDCl_3$) δ 13.63 (s, 0.40H, OH), 13.00 (s, 0.60H, OH), 7.99 (dd, J = 8.2 Hz, J = 1.6 Hz, 0.8H), 7.96-7.93 (m, 1.20H), 7.61-7.53 (m, 2H), 7.44-7.38 (m, 1.60H), 7.28 (m, J = 7.9 Hz, 0.4H), 7.15-7.08 (m, 1.60H), 6.96 (dd, J = 8.3 Hz, J = 1.2 Hz, 0.40H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5 (2×C), 152.7 (2×C), 150.5 (C), 146.4 (C), 138.0 (C), 137.9 (C), 133.9 (CH), 133.7 (CH), 133.6 (CH), 131.9 (CH), 131.7 (CH), 130.5 (CH), 129.5 (2×CH), 127.6 (CH), 122.7 (2×CH), 121.3 (CH), 120.0 (CH), 118.5 (CH), 117.4 (CH), 117.3 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{10}N_2OCl$ $[M + H]^+$ 233.0476, found 233.0488.

(*E*)-2-[(2-Fluorophenyl)diazenyl]phenol (2q) and **(*E*)-3-fluoro-2-(phenyldiazenyl)phenol (2'q)**. **2q** and **2'q** were prepared following the general procedure for

20 h. Yield 65% (28 mg); orange solid; IR (neat, cm^{-1}) 3068, 2959, 2926, 1729, 1625, 1612, 1586, 1483, 1412, 1358, 1282, 1239, 1206, 1178, 1146, 1100, 1041, 1026, 816, 761, 741, 686; ^1H NMR (300 MHz, $CDCl_3$) δ 13.31 (s, 0.22H, OH), 12.84 (s, 0.78H, OH), 7.98 (dd, J = 7.9 Hz, J = 1.4 Hz, 0.78H), 7.92 (d, J = 7.7 Hz, 0.78H), 7.89 (d, J = 1.4 Hz, 0.22H), 7.54 (d, J = 7.3 Hz, 0.78H), 7.49-7.46 (m, 0.78H), 7.43 (dd, J = 7.7 Hz, J = 1.6 Hz, 0.22H), 7.39-7.37 (m, 0.78H), 7.32-7.26 (m, 1.56H), 7.26-7.24 (m, 0.44H), 7.13-7.09 (m, 0.78H), 7.07 (m, 0.44H), 6.84-6.81 (m, 0.22H), 6.79-6.76 (m, 0.22H); ^{13}C NMR (75 MHz, $CDCl_3$) δ **(*E*)-2-[(2-Fluorophenyl)diazenyl]phenol** 159.2 (d, $J_{C\text{-}F}$ = 255.8 Hz, C), 154.1(C), 152.8 (C), 138.0 (C), 133.7 (CH), 133.8 (CH), 132.6 (d, $J_{C\text{-}F}$ = 8.2 Hz, CH), 124.6 (d, $J_{C\text{-}F}$ = 3.5 Hz, CH), 119.9 (CH), 118.5 (CH), 117.2 (CH), 117.0 (d, $J_{C\text{-}F}$ = 19.3 Hz, CH), **(*E*)-3-fluoro-2-(phenyldiazenyl)phenol** 161.6 (d, $J_{C\text{-}F}$ = 258.2 Hz, C), 152.8 (C), 150.4 (C), 138.4 (d, $J_{C\text{-}F}$ = 6.9 Hz, C), 134.1 (d, $J_{C\text{-}F}$ = 11.0 Hz, CH), 131.6 (CH), 129.4 (2×CH), 122.5 (2×CH), 113.8 (d, $J_{C\text{-}F}$ = 3.4 Hz, CH), 106.5 (d, $J_{C\text{-}F}$ = 19.8 Hz, CH); ^{19}F NMR (188 MHz, $CDCl_3$) δ **(*E*)-2-[(2-fluorophenyl)diazenyl]phenol (2q)** -122.65; **(*E*)-3-fluoro-2-(phenyldiazenyl)phenol (2'q)** -118.95; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{10}N_2OF$ $[M + H]^+$ 217.0772, found 217.0780.

(*E*)-2-[(4-Bromo-2-chlorophenyl)diazenyl]phenol (2r). 2r was prepared following the general procedure for 48 h. Yield 45% (28 mg); orange solid, mp 114-116 °C; IR (neat, cm^{-1}) 3082, 2962, 2924, 1612, 1582, 1476, 1454, 1409, 1343, 1274, 1226, 1208, 1179, 1143, 1081, 1054, 1028, 945, 867, 818, 793, 737, 702, 660; ^1H NMR (300 MHz, $CDCl_3$) δ 12.81 (s, 1H, OH), 7.96 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 2.0 Hz, 1H), 7.52 (dd, J = 8.7 Hz, J = 2.0 Hz, 1H), 7.44-7.39 (m, 1H), 7.13-7.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7 (C), 145.5 (C), 137.9 (C), 134.8 (C), 134.3 (CH), 133.8 (CH), 133.1 (CH), 131.0 (CH), 125.4 (C), 120.1 (CH), 118.6 (CH), 118.3 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_9N_2OClBr$ $[M + H]^+$ 312.9575, found 312.9580.

(*E*)-2-[(4-Methoxyphenyl)diazenyl]phenol (2s) and **(*E*)-5-methoxy-2-(phenyldiazenyl) phenol (2's)** . **2s** and **2's** were prepared following the general procedure for 4 h. Yield 26% (12 mg); orange solid; IR (neat, cm^{-1}) 3079, 2967, 2838, 1601, 1580, 1502, 1455, 1434, 1392, 1371, 1315, 1277, 1205, 1185, 1150, 1102, 1028, 965, 832, 796, 756, 719, 683; ^1H NMR (300 MHz, $CDCl_3$) δ 13.89 (s, 0.30H, OH), 12.92 (s, 0.70H, OH), 7.96-7.93 (m, 0.60H), 7.88 (d, J = 9.0 Hz, 1.40H), 7.84-7.78 (m, 1H), 7.54-7.49 (m, 1.30H), 7.46 (d, J = 7.1 Hz, 0.30H), 7.33 (td, J = 8.1 Hz, J = 1.7 Hz, 0.70H), 7.10-7.07 (m, 0.70H), 7.04 (d, J = 9.0 Hz, 1.40H), 6.63 (dd, J = 8.9 Hz, J = 2.6 Hz, 0.30H), 6.48 (d, J = 2.6 Hz, 0.30H), 3.91 (s, 2.10H, CH_3), 3.89 (s, 0.90H, CH_3) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (C), 162.2 (C), 156.9 (C), 152.7 (C), 150.0 (C), 144.7 (C), 137.3 (C), 134.7 (CH), 132.9 (C), 132.6 (CH), 132.4 (2×CH), 130.0 (CH), 129.3 (2×CH), 124.0 (2×CH), 121.5 (CH), 119.8 (CH), 118.0 (CH), 114.6 (2×CH), 108.4 (CH), 101.4 (CH), 55.7 (CH_3), 55.6 (CH_3); (HRMS (TOF-ESI) *m/z*: Calcd for $C_{13}H_{13}N_2O_2$ $[M + H]^+$ 229.0972, found 229.0970.

Ethyl (*E*)-4-[(2-hydroxyphenyl)diazenyl]benzoate (2t) and **ethyl (*E*)-3-hydroxy-4-phenyl diazenyl benzoate (2't)**. **2t** and **2't** were prepared following the general procedure for 10 h. Yield 65% (35 mg); orange solid; IR (neat, cm^{-1}) 2962, 1720, 1589, 1486, 1467, 1449, 1426, 1405, 1361, 1316, 1283, 1259, 1146, 1123, 1022, 964, 842, 798, 771, 753, 685; ^1H NMR (300 MHz, $CDCl_3$) δ 12.79 (s, 1H, OH), 8.21 (d, J = 8.5 Hz, 1.33H), 8.02 (m, 0.33H), 7.99 (d, J = 7.9 Hz, 0.67H), 7.92 (d, J = 8.5 Hz, 1.33H), 7.74 (m, 0.67H), 7.55 (m, 1H), 7.40 (m, 1H), 7.09 (m, 1.67H), 4.41 (m, 2H, CH_2), 1.45 (t, J = 7.2 Hz, 2.01H), 1.44 (t, J = 6.8 Hz, 0.99H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8 (C), 165.6 (C), 153.1 (C), 152.9 (C), 152.2 (C), 150.5 (C), 147.2 (C), 139.2 (C), 137.6 (C), 134.1 (CH), 133.7 (CH), 132.9 (CH), 132.3 (C), 131.9 (CH), 130.8 (2×CH), 129.5 (2×CH), 122.6 (2×CH), 122.0 (2×CH), 120.7 (CH), 120.1 (CH), 119.8 (CH), 118.4 (CH), 61.4 (CH_2), 61.3 (CH_2), 14.6 (2×CH_3); HRMS (TOF-ESI) *m/z*: Calcd for $C_{15}H_{15}N_2O_3$ $[M + H]^+$ 271.1077, found 271.1072.

(*E*)-2-[(4-Bromophenyl)diazenyl]phenol (2u) and **(*E*)-5-bromo-2-(phenyldiazenyl)phenol (2'u). 2u** and **2'u** were prepared following the general procedure for 4 h. Yield 70% (38 mg); orange solid; IR (neat, cm^{-1}) 3081, 2965, 1608, 1584, 1478, 1419, 1395, 1342, 1269, 1174, 1142, 1065, 1028, 1004, 939, 917, 882, 853, 751, 684; ^1H NMR (300 MHz, $CDCl_3$) δ 13.11 (s, 0.16H, OH), 12.70 (s, 0.84H, OH), 7.95 (dd, J = 7.9 Hz, J = 1.5 Hz, 0.84H), 7.87 (dd, J = 8.0 Hz, J = 2.5 Hz, 0.32H), 7.77 (d, J = 8.6 Hz, 1.68H), 7.67 (d, J = 8.6 Hz, 1.68H), 7.55-7.24 (m, 0.48H), 7.42-7.36 (m, 0.84H), 7.28 (s, 0.16H), 7.24 (m, 0.32H), 7.12-7.04 (m, 1.68H); ^{13}C NMR (75 MHz, $CDCl_3$) δ **(*E*)-2-[(4-bromophenyl)diazenyl] phenol** 152.8 (C), 149.4 (C), 137.4 (C), 133.7 (CH), 133.3 (CH), 132.6 (2×CH), 125.5 (C), 123.6 (2×CH), 120.1 (CH), 118.3 (CH); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{10}N_2OBr$ $[M + H]^+$ 276.9971, found 276.9986.

(*E*)-2-[(4-Fluorophenyl)diazenyl]phenol (2v) and **(*E*)-5-fluoro-2-(phenyldiazenyl)phenol (2'v)**. **2v** and **2'v** were prepared following the general procedure for 4 h. Yield 55% (24 mg); orange solid; IR (neat, cm^{-1}) 3061, 2961, 2853, 1611, 1594, 1580, 1499, 1481, 1430, 1403, 1345, 1319, 1260, 1234, 1176, 1093, 1028, 980, 862, 805, 753, 684; ^1H NMR (300 MHz, $CDCl_3$) δ **(*E*)-2-[(4-Fluorophenyl)diazenyl]phenol** 12.70 (s, 1H, OH), 7.96-7.88 (m, 3H), 7.40-7.35 (m, 1H), 7.27-7.22 (m, 2H), 7.12-7.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4 (d, $J_{C\text{-}F}$ = 251.1 Hz, C), 152.7 (C), 147.1 (C), 137.2 (C), 133.3 (CH), 133.1 (CH), 124.2 (d, $J_{C\text{-}F}$ = 8.8 Hz, 2×CH), 120.0 (CH), 118.2 (CH), 116.3 (d, $J_{C\text{-}F}$ = 22.9 Hz, 2×CH); ^{19}F NMR (188 MHz, $CDCl_3$) δ **(*E*)-2-[(4-fluorophenyl)diazenyl]phenol (2v)** -106.75, **(*E*)-5-fluoro-2-(phenyldiazenyl)phenol (2'v)** -101.95, HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{10}N_2OF$ $[M + H]^+$ 217.0772, found 217.0777.

Ethyl (*E*)-3-hydroxy-4-[(4-methoxyphenyl)diazenyl]benzoate (2w) and **ethyl (*E*)-4-[(2-hydroxy-4-methoxyphenyl)diazenyl]benzoate (2'w)**. **2w** and **2'w** were prepared following the general procedure for 24 h. Yield 60% (36 mg); orange solid; IR (neat, cm^{-1}) 2926, 2852,

1704, 1627, 1600, 1501, 1466, 1418, 1365, 1271, 1249, 1104, 1094, 1024, 862, 837, 800, 691; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.03 (s, 0.44H, OH), 12.76 (s, 0.56H, OH), 8.17 (d, J = 8.5 Hz, 1.12H), 7.96 (dd, J = 8.3 Hz, J = 2.5 Hz, 0.56H), 7.90 (d, J = 9.0 Hz, 0.88H), 7.83 (d, J = 9.0 Hz, 0.88H), 7.78-7.70 (m, 1.56H), 7.04 (d, J = 9.0 Hz, 1.12 Hz), 6.63 (d, J = 9.2 Hz, 0.44H), 6.45 (s, 0.44H), 4.42 (m, 2H), 3.92 (s, 1.68H), 3.89 (s, 1.32H), 1.44 (t, J = 7.1 Hz, 1.68H), 1.44 (t, J = 7.1 Hz, 1.32H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 (C), 165.7 (C), 165.1 (C), 162.9 (C), 158.8 (C), 152.3 (C), 152.1 (C), 144.6 (C), 139.2 (C), (135.1 (CH), 133.6 (C), 133.1 (C), 132.2 (CH), 130.9 (C), 130.7 (2×CH), 124.5 (2×CH), 120.9 (2×CH), 120.6 (CH), 119.6 (CH), 114.7 (2×CH), 109.6 (CH), 101.4 (CH), 61.3 (CH_2), 61.2 (CH_2), 55.7 (CH_3), 55.6 (CH_3), 14.3 (2×CH_3) ; HRMS (TOF-ESI) *m/z*: Calcd for $C_{16}H_{17}N_2O_4$ $[M + H]^+$ 301.1183, found 301.1196.

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Supporting Information

Full characterization details including ^{1}H, ^{13}C and ^{19}F NMR spectra. Reaction optimization via *in situ* generation of PIFA. This material is available free of charge via the Internet at http://pubs.acs.org.

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