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Palladium-catalyzed *ortho*-functionalization of azoarenes with aryl acylperoxides†

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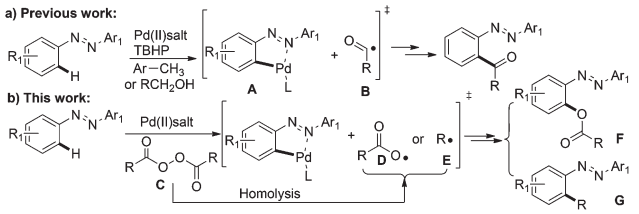
With the aid of an azo directing group, Pd-catalyzed *ortho*-sp^2 C–H bond activation/functionalization of azoarenes with aryl acyl peroxides has been explored. This transformation provides easy access to regioselectively introducing acyloxyl and aryl groups into azoarenes by simply changing the reaction temperature and solvent.

Introduction

Regioselective installation of special functional groups into aromatic molecules is one of the most attractive and challenging hot topics in organic chemistry. Recently, much effort has been made to develop transition metal-catalyzed C–H functionalization with the chelation assistance of a directing group.[1] Among them, aromatic sp^2 C–H activation/oxygenation has attracted increasing attention due to that hydroxylated arenes have been widely employed as fundamental building blocks of many pharmaceuticals and biologically natural compounds.[2]

Recently, several elegant studies have demonstrated that pyridine,[3] amide,[4] oxime ether,[5] pyrimidine[6] group, *etc.* could be used as an anchor to form cyclopalladated intermediates, which could further react with coupling partners including $PhI(OAc)_2$,[3a–h,k–m] carboxylic acids,[4–6] alcohols,[3j,5a] and acid anhydrides[7] to realize the C–H activation/oxygenation reactions *via* C–O bond forming reductive elimination. However, although significant attention has been focused on the above-mentioned directing groups, there are rare reported cases of using the azo group as a directing group to accelerate the C–H activation/functionalization process.[3a,8] More recently, we found that the $Pd(OAc)_2$/TBHP system could efficiently catalyze a cascade oxidation/sp^2 C–H bond acylation of azoarenes with aryl methanes or alcohols, and its mechanism was proposed to be involved in an oxidative addition process between palladacyclic intermediate (**A**) and acyl radical (**B**) (Scheme 1a).[9] Based on this work and considering that acyl peroxides (**C**) could easily produce acyloxyl radical (**D**) or aryl radical (**E**) *via* homolysis under heating conditions,[10] herein we reported, for the first time, that Pd-catalyzed sp^2 C–H acyloxylation and arylation of azoarenes with aryl acylperoxides could concisely construct *ortho*-acyloxylated azoarenes (**E**) (Scheme 1b).



Scheme 1 Pd-catalyzed *ortho*-functionalization of azoarenes.

Results and discussion

The acyloxylation of azobezene (**1a**) (0.15 mmol) with benzoyl peroxide (**2a**) (0.30 mmol) was initially chosen as a model reaction to optimize the reaction parameters. At first, this transformation was carried out at 60 °C in the presence of $PdCl_2$ (10 mol%) for 24 h to screen the various solvents (Table 1, entries 1–7), and we quickly found that CH_3CN could provide us the desired *ortho*-acyloxylated product (**3a**) in 43% yield (entry 7). Subsequently, a further screening of Pd salts indicated that $Pd(OAc)_2$ was the best catalyst which could lead to the formation of **3a** in 82% yield (compare entries 7–9 with 10). To our surprise, when we investigated the effect of the reaction temperature on this transformation, we accidentally found that higher reaction temperature (80 °C) could also lead to the formation of 16% yield of arylated product (**4a**) besides **3a** (59%) (compare entries 10 and 11 with 12). So, we continued to further optimize the reaction solvent and the reaction temperature (entries 12–17), and finally the Pd-catalyzed *ortho*-functionalization of azobenzene with benzoyl peroxide could

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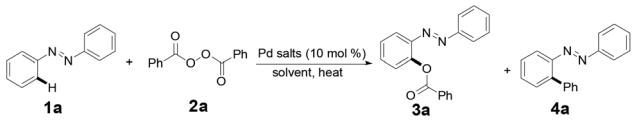
†Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization of products. See DOI: 10.1039/c4ob00993b

Table 1 Optimization of the Pd-catalyzed *ortho*-functionalization of azobenzene with benzoyl peroxide[a]



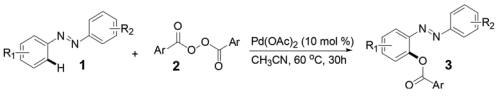
Entry	PdX_2	Solvent	Temp. (°C)	**3a**/**4a** yield[b] (%)
1	$PdCl_2$	DMSO	60	Trace/0
2	$PdCl_2$	CH_2Cl_2	60	26/0
3	$PdCl_2$	THF	60	14/0
4	$PdCl_2$	Toluene	60	34/0
5	$PdCl_2$	$PhCF_3$	60	37/0
6	$PdCl_2$	PhCl	60	31/0
7	$PdCl_2$	CH_3CN	60	43/0
8	$Pd(TFA)_2$	CH_3CN	60	60/0
9	$Pd(MeCN)_2Cl_2$	CH_3CN	60	33/0
10	$Pd(OAc)_2$	CH_3CN	60	82/0
11	$Pd(OAc)_2$	CH_3CN	40	67/0
12	$Pd(OAc)_2$	CH_3CN	80	59/16
13	$Pd(OAc)_2$	$PhCF_3$	80	54/21
14	$Pd(OAc)_2$	PhCl	80	48/26
15	$Pd(OAc)_2$	PhCl	120	0/70
16	$Pd(OAc)_2$	PhCl	130	0/76
17	$Pd(OAc)_2$	PhCl	135	0/74

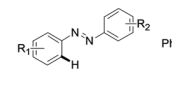
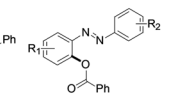
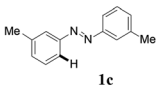
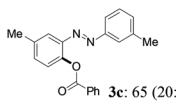
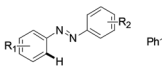
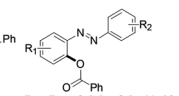
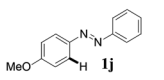
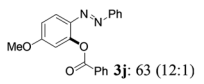
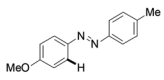
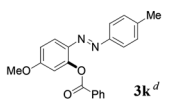
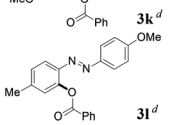
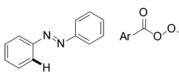
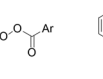
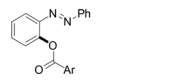
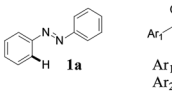
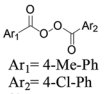
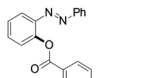
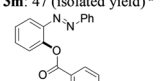
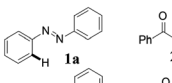
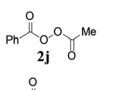
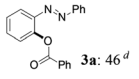
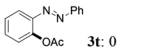
[a] All the reactions were carried out using azobenzene (**1a**) (0.15 mmol) and benzoylperoxide (**2a**) (0.30 mmol) with Pd catalyst (10 mol%) in solvent (2.0 mL) for 24 h under air conditions in a sealed tube, followed by flash chromatography on SiO_2. [b] Isolated yield.

afford another sole *ortho*-aryl product **4a** in 76% yield using chlorobenzene as a solvent at 130 °C for 24 h (entry 16).

After we established an efficient reaction protocol that enables the *ortho*-acyloxylation of azobenzene with benzoyl peroxide, the scope of this transformation with regard to azoarenes and aryl acylperoxides was first explored. As shown in Table 2, although the C–H acyloxylation of substituted azoarenes with peroxides could proceed smoothly and furnish the corresponding acyloxylated products, the substitution on the benzene ring of azoarenes and acyl peroxides showed significant electronic effects. The substrates with a *para*-electron donating group (4-H, 4-MeO and 4-Me) on the azophenyl and acylphenyl rings afforded the desired products in moderate to good yields (**3a**, **3b**, **3e** and **3p**). It is noteworthy that the *ortho*-substituted azobenzene (**1d**) and *meta*- or *ortho*-substituted aryl acyl peroxide (**2c** and **2d**) gave poorer yield of product (**3d**, **3n**, **3o**) because of higher steric hindrance (compare **3b**, **3m** and **3c** with **3d**, **3n** and **3o**). In contrast, the electron-poor azoarenes or aryl acylperoxides with 4-Cl, 4-Br, 4-F and 4-NO_2 groups on the phenyl ring afforded the desired products in moderate to poor yields (**3f**–**3h** and **3q**–**3s**). Unfortunately, the substrate **1i** with the 4-CO_2Et group did not produce the corresponding acyloxylated product (**3i**), possibly due to its low reactivity. Moreover, we also investigated the electronic effect of various substituents on the regioselectivity of *ortho*-acyloxylation of unsymmetric azoarenes, and found that *ortho*-acyloxylation reactions took place mainly on the electron-rich azo aromatic rings, possibly due to the fact that the electron-rich phenyl ring easily nucleophilically attacks the Pd(II) and leads

Table 2 Pd-catalyzed ortho-acyloxylation of azoarenes with aryl acylperoxides[a]



Azorenes (**1**)	Peroxides (**2**)	Product (%)[b], (*trans*:*cis*)[c]
		
R_1=R_2= 4-H, **1a** R_1=R_2= 4-Me, **1b**	**2a**	R_1=R_2= 4-H, **3a**: 82 (30:1) R_1=R_2= 4-Me, **3b**: 68 (30:1)
	**2a**	
1c		**3c**: 65 (20:1)
		
R_1=R_2= 2-Me, **1d** R_1=R_2= 4-MeO, **1e** R_1=R_2= 4-Cl, **1f** R_1=R_2= 4-Br, **1g** R_1=R_2= 4-F, **1h** R_1=R_2= 4-CO_2Et, **1i**	**2a**	R_1=R_2= 2-Me, **3d**: 41 (6:1) R_1=R_2= 4-MeO, **3e**:75 (13:1) R_1=R_2= 4-Cl, **3f**: 41 (14:1) R_1=R_2= 4-Br, **3g**: 42 (9:1) R_1=R_2= 4-F, **3h**: 35 (25:1) R_1=R_2= 4-CO_2Et, **3i**: 0
	**2a**	
1j		**3j**: 63 (12:1)
	**2a**	
1k		**3k** [d]
		
		3l [d]
		3k + **3l** (mixture) : 56 [d] **3k** : **3l** = 1 : 1
		
1a	Ar=4-Me-Ph: **2b** Ar=3-Me-Ph: **2c** Ar=2-Me-Ph: **2d** Ar=4-MeO-Ph: **2e** Ar=4-F-Ph: **2f** Ar=4-Cl-Ph: **2g** Ar=4-NO_2-Ph: **2h**	Ar=4-Me-Ph: **3m**: 56 (5:1) Ar=3-Me-Ph: **3n**: 42 (4:1) Ar=2-Me-Ph: **3o**: 0 Ar=4-MeO-Ph: **3p**: 55 (15:1) Ar=4-F-Ph: **3q**: 42 (10:1) Ar=4-Cl-Ph: **3r**: 48 (12:1) Ar=4-NO_2-Ph: **3s**: 23 (12:1)
		
1a	Ar_1= 4-Me-Ph Ar_2= 4-Cl-Ph **2i**	**3m**: 47 (isolated yield) [d]
		
		3r: 26 (isolated yield) [d]
		
1a	**2j**	**3a**: 46 [d]
		
1a	**2k**	**3t**: 0

[a] The mixture of azoarenes (**1**) (0.15 mmol) and peroxides (**2**) (2.0 equiv.) was stirred in the presence of $Pd(OAc)_2$ (10 mol%) in CH_3CN (2.0 mL) at 60 °C for 24 h under air conditions in a sealed tube, followed by flash chromatography on SiO_2. [b] Isolated yield. [c] The ratio of *trans* to *cis* diastereomers was determined by ^1H NMR spectroscopy. [d] The ratio of *trans* to *cis* diastereomers was not provided.

to the formation of cyclopalladium intermediate *via* C–H activation (compare **3j** with **3k** and **3l**). Similarly, for the unsymmetric aryl acylperoxide **2i**, the electron-rich (4-Me-phenyl)-acyloxy group is also more reactive than the electron-poor (4-Cl-phenyl)-acyloxy group. It is worth noting that unsymmetric acylperoxide **2j** only produced phenylacyloxylated azobenzene **3a** in 67% yield. At last, we tried to use acetyl peroxide **2k** as an acyloxyl source, but no desired product (**3t**) was observed under our reaction conditions.

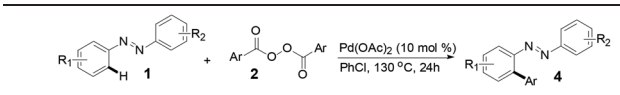
Subsequently, the above-mentioned substrates were continuously employed in the Pd-catalyzed *ortho*-arylation of azoarenes using chlorobenzene as a solvent at 130 °C. As shown in Table 3, the reaction properties including the substituent electronic effects, the "*ortho*-substituent" effect and regioselectivity of unsymmetric azoarenes and acylperoxides are similar to the *ortho*-acyloxylation of azoarenes with aryl acylperoxides.[11]

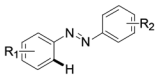
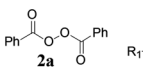
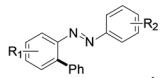
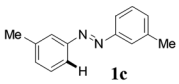
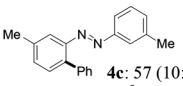
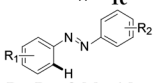
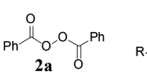
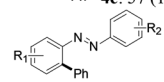
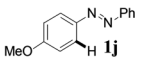
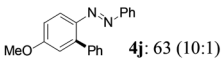
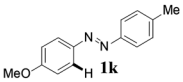
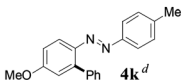
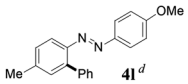
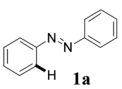
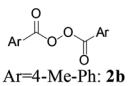
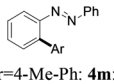
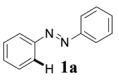
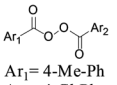
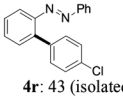
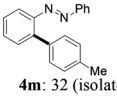
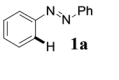
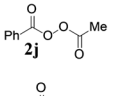
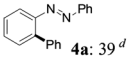
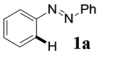
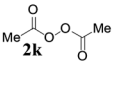
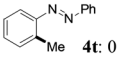
ortho-Hydroxy azoarene and *ortho*-hydroxy hydrazoarene derivatives belong to useful intermediates in pharmaceutical and dye industries.[12] *ortho*-Acyloxylated arene **3a** could be easily hydrolyzed and reduced to produce the corresponding *ortho*-hydroxyl azobenzene **5** (91% yield) and *ortho*-phenyl-acyloxyl hydrazobenzene **6** (82% yield), respectively (Scheme 2a). Moreover, we further found *ortho*-acyoxlylated azobenzene **3a** could also be converted to *N*-phenyl-benzamide **7** (71% yield) and 2-amino-phenol **8** (64% yield) under Zn/NH_4Cl conditions at 80 °C *via* a cascade reduction/nucleophilic substitution (Scheme 2b).

To further probe the reaction mechanism, we ran the Pd-catalyzed C–H acyloxyation of azobenzene with benzoyl peroxide in the presence of TEMPO under our reaction conditions. Unfortunately, no acyloxylated **3a** was observed possibly due to the fact that TEMPO suppressed the formation of phenyl acyloxy radical (Scheme 3a). And also, when acyloxylated product **3a** was employed as the starting material and stirred at 130 °C for 24 h in the presence of $Pd(OAc)_2$, we did not observe the formation of **4a** by the GC-MS method; these controlled experiments indicated that a radical process was involved in this reaction system, and the possibility that **3a** could be directly converted to **4a** *via* a decarboxylation process was also ruled out (Scheme 3b).

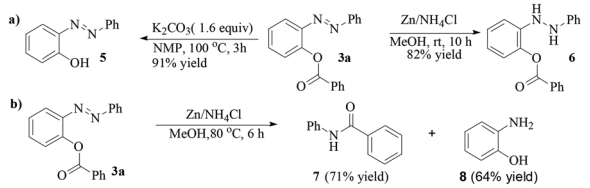
Taking previous reports on Pd-catalyzed sp^2 C–H acylation into account,[13] and in combination with the results from the above-mentioned controlled reactions, we proposed a plausible reaction mechanism for this transformation (see Fig. 1), in which $Pd(OAc)_2$ reacted with azobenzene (**1a**) by sp^2 C–H activation to form a palladacyclic intermediate **A**.[13b] Then **A** reacted with acyloxyl **B** or phenyl radical **C** which was *in situ*-homolysed from benzoyl peroxide under heating conditions to produce either Pd(IV)[14] or Pd(III)[15] species **D**. Finally, the species **D** underwent reductive elimination to afford the acyloxyated or arylated product **D** with the release of the Pd(II) species. In addition to the above-mentioned radical mechanism, an alternative reaction pathway involving the oxidation of Pd(II) to Pd(IV) by aryl acyl peroxide *via* a two-electron process cannot be ruled out.

Table 3 Pd-catalyzed *ortho*-arylation of azoarenes with aryl acylperoxides[a]

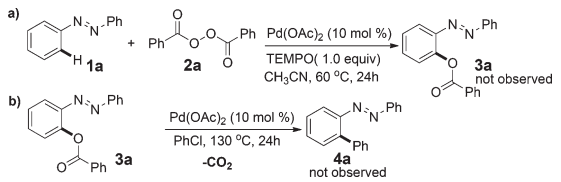


Azorenes (**1**)	Peroxides (**2**)	Product (%)[b], (*trans*:*cis*)[c]
 R_1=R_2= 4-H, **1a** R_1=R_2= 4-Me, **1b**	 **2a**	 R_1=R_2= 4-H, **4a**: 76[d] R_1=R_2= 4-Me, **4b**: 70 (7:1)
 **1c**	**2a**	 **4c**: 57 (10:1)
 R_1=R_2= 2-Me, **1d** R_1=R_2= 4-MeO, **1e** R_1=R_2= 4-Cl, **1f** R_1=R_2= 4-Br, **1g** R_1=R_2= 4-F, **1h** R_1=R_2= 4-CO_2Et, **1i**	 **2a**	 R_1=R_2= 2-Me, **4d**: 40 (14:1) R_1=R_2= 4-MeO, **4e**:75 (20:1) R_1=R_2= 4-Cl, **4f**: 47 (4:1) R_1=R_2= 4-Br, **4g**: 38[d] R_1=R_2= 4-F, **4h**: 34[d] R_1=R_2= 4-CO_2Et, **4i**: 29[d]
 **1j**	**2a**	 **4j**: 63 (10:1)
 **1k**	**2a**	 **4k**[d]  **4l**[d] **4k** + **4l** : 70 (mixture)[d] **4k** : **4l** = 3 : 2
 **1a**	 Ar=4-Me-Ph: **2b** Ar=3-Me-Ph: **2c** Ar=2-Me-Ph: **2d** Ar=4-MeO-Ph: **2e** Ar=4-F-Ph: **2f** Ar=4-Cl-Ph: **2g** Ar=4-NO_2-Ph: **2h**	 Ar=4-Me-Ph: **4m**: 70 (6:1) Ar=3-Me-Ph: **4n**: 43 (10:1) Ar=2-Me-Ph: **4o**: 0 Ar=4-MeO-Ph: **4p**: 0 Ar=4-F-Ph: **4q**: 53 (6:1) Ar=4-Cl-Ph: **4r**: 56 (2:1) Ar=4-NO_2-Ph: **4s**: 0
 **1a**	 Ar_1= 4-Me-Ph Ar_2= 4-Cl-Ph **2i**	 **4r**: 43 (isolated yield)[d]  **4m**: 32 (isolated yield)[d]
 **1a**	 **2j**	 **4a**: 39[d]
 **1a**	 **2k**	 **4t**: 0

[a] The mixture of azoarenes (**1**) (0.15 mmol) and peroxides (**2**) (2.0 equiv.) was stirred at 130 °C in the presence of $Pd(OAc)_2$ (10 mol %) in PhCl (2.0 mL) for 24 h under air conditions in a sealed tube, followed by flash chromatography on SiO_2. [b] Isolated yield. [c] The ratio of *trans* to *cis* diastereomers was determined by ^1H NMR spectroscopy. [d] The ratio of *trans* to *cis* diastereomers was not provided.



Scheme 2 Synthetic application of this transformation.



Scheme 3 Control reactions.

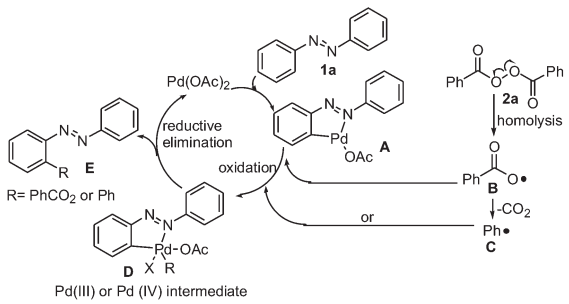


Fig. 1 The proposed reaction mechanism.

Conclusion

In summary, we have developed a Pd(II)-catalyzed sp^2 C–H functionalization of azoarenes with aryl acylperoxides under mild conditions. This protocol provided easy access to the synthesis of various *ortho*-acyloxylated azoarenes and *ortho*-aryl azoarene derivatives by simply changing the reaction solvent and the reaction temperature.

Experimental section

General information

Unless otherwise noted, reactions were conducted in dry solvents. Purifications of reaction products were carried out by flash chromatography using silica gel (40–63 mm). Infrared spectra (IR) were recorded on a 400 MHz spectrometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ^1H and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as an internal standard at ambient temperature unless otherwise indicated on 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), and triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a mass spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatography mass spectra were obtained with a model spectrometer.

General procedure for the synthesis of 1b–1i

A mixture containing aniline derivatives (5 mmol), CuBr (0.3 mmol), pyridine (0.9 mmol), and 10 mL of toluene was stirred vigorously at 60 °C under air for 24 h. After cooling down to room temperature and concentrating under vacuum, the residue was purified by flash chromatography (hexanes) to get the products.

(*E*)-1,2-Di-*p*-tolyldiazene (1b).[16] Yellow solid; mp 142–143 °C; 456 mg, 87% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 4H), 7.30 (d, J = 8.1 Hz, 4H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 141.2, 129.7, 122.7, 21.5; MS (EI, 70 eV) m/z: 210.01 (M^+).

(*E*)-1,2-Di-*m*-tolyldiazene (1c).[16] Yellow solid; mp 55–56 °C; 451 mg, 86% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 4H), 7.40 (t, J = 7.9 Hz, 2H), 7.28 (d, J = 7.4 Hz, 2H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 138.9, 131.6, 128.9, 122.9, 120.4, 21.3; MS (EI, 70 eV) m/z: 210.10 (M^+).

(*E*)-1,2-Di-*o*-tolyldiazene (1d).[16] Yellow solid; mp 56–57 °C; 288 mg, 55% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 2.8 Hz, 4H), 7.26–7.23 (m, 2H), 2.73 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 138.0, 131.3, 130.7, 126.4, 115.9, 17.6; MS (EI, 70 eV) m/z: 209.99 (M^+).

(*E*)-1,2-Bis(4-methoxyphenyl)diazene (1e).[16] Yellow solid; mp 142–143 °C; 338 mg, 56% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.9 Hz, 4H), 7.00 (d, J = 8.9 Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 147.0, 124.3, 114.1, 55.5; MS (EI, 70 eV) m/z: 242.06 (M^+).

(*E*)-1,2-Bis(4-chlorophenyl)diazene (1f).[16] Yellow solid; mp 166–168 °C; 518 mg, 83% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 4H), 7.49 (d, J = 8.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 137.2, 129.4, 124.2; MS (EI, 70 eV) m/z: 250.03 (M^+).

(*E*)-1,2-Bis(4-bromophenyl)diazene (1g).[16] Yellow solid; mp 132–134 °C; 480 mg, 54% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82–7.77 (m, 4H), 7.66 (dd, J = 6.5, 4.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 132.4, 125.7, 124.4; MS (EI, 70 eV) m/z: 337.45 (M^+).

(*E*)-1,2-Bis(4-fluorophenyl)diazene (1h).[16] Yellow solid; mp 102–104 °C; 476 mg, 87% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.91 (m, 4H), 7.22 (t, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 163.1, 149.0, 124.8, 124.7, 116.1, 115.9; MS (EI, 70 eV) m/z: 218.95 (M^+).

(*E*)-Diethyl 4,4′-(diazene-1,2-diyl)dibenzoate (1i).[16] Yellow solid; mp 128–130 °C; 417 mg, 51% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 4H), 7.98 (d, J = 8.4 Hz, 4H), 4.43 (q, J = 7.1 Hz, 4H), 1.43 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 154.8, 132.7, 130.6, 122.8, 61.3, 14.3; MS (EI, 70 eV) m/z: 326.95 (M^+).

Procedure for the synthesis of 1j. The mixture of CuBr (2.9 mg, 0.02 mmol), pyridine (4.8 mg, 0.06 mmol), aniline (93 mg, 1 mmol) and 4-methoxybenzenamine (25 mg, 0.2 mmol) in toluene (4 mL) was vigorously stirred at 60 °C under O_2 (1 atm) for 24 h. Then cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography (hexanes) on silica gel to afford **1j**.

(*E*)-1-(4-Methoxyphenyl)-2-phenyldiazene (1j).[16] Yellow solid; mp 56–58 °C; 19 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.90 (m, 2H), 7.88 (dd, J = 5.2, 3.4 Hz, 2H), 7.49 (dd, J = 10.1, 4.7 Hz, 2H), 7.45–7.39 (m, 1H), 7.01–6.98 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 152.8, 147.0, 130.4, 129.0, 124.8, 122.6, 114.2, 55.6; MS (EI, 70 eV) m/z: 212.3 (M^+).

Procedure for the synthesis of 1k. The mixture of CuBr (2.9 mg, 0.02 mmol), pyridine (4.8 mg, 0.06 mmol), *p*-toluidine (93 mg, 1 mmol) and 4-methoxybenzenamine (25 mg, 0.2 mmol) in toluene (4 mL) was vigorously stirred at 60 °C under O_2 (1 atm) for 24 h. Then cooling down to room temperature and concentrating in a vacuum, the residue was purified by flash chromatography (hexanes) on silica gel to afford **1k**.

(*E*)-1-(4-Methoxyphenyl)-2-(*p*-tolyl)diazene (1k).[16] Yellow solid; mp 109–111 °C; 20 mg, 44% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 150.8, 147.1, 140.8, 129.6, 124.5, 122.7, 122.5, 114.1, 55.5, 21.4; MS (EI, 70 eV) m/z: 226.2 (M^+).

Procedure for the synthesis of 2i. Hydrogen peroxide (250 mg, 10 mmol) was added dropwise over 10 min to a cold (ice bath) solution of *p*-toluoylchloride (750 mg, 5 mmol) and *para*-chlorobenzoylchloride (850 mg, 5 mol) in diethyl ether (10 mL). This was followed by the dropwise addition of an aqueous solution of NaOH (200 mg, 10 mmol) over 10 min. The resulting white precipitate was collected by filtration, and then purified by flash chromatography (hexanes–ethyl acetate 30 : 1) to get the desired products.[10c]

4-Chlorobenzoic 4-methylbenzoic peroxyanhydride (2i). White solid; mp 119–121 °C; 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.99 (m, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.53–7.47 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 162.3, 145.4, 140.9, 131.1, 129.8, 129.6, 129.3, 124.1, 122.5, 21.8; HR-MS (EI) calcd for $[M]^+$: $C_{15}H_{11}ClO_4$ 290.0346, found 290.0341; IR (KBr): 3852, 3739, 3618, 2922, 2862, 2360, 1754, 1231, 996, 740, 475 cm^{-1}.

Procedure for the synthesis of 2j. Acetyl chloride (780 mg, 10 mmol) and perbenzoic acid (1520 mg, 11 mmol) were added to 15 mL diethyl ether, the mixture was cooled with an ice–water bath and pyridine (880 mg, 11 mmol) was added dropwise. After the addition, the reaction mixture was stirred for an additional 45 min, washed twice with 5% HCl, twice with 5% $NaHCO_3$, and twice with distilled water, respectively, to get the desired product.[17]

Aceticbenzoic peroxyanhydride (2j).[18] White oil; 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.19, 162.96, 134.26, 129.73, 128.83, 125.58, 16.69; MS (EI, 70 eV) m/z: 180.1 (M^+); IR (KBr): 2974, 1770, 1591, 1448, 1371, 1231, 1169, 1011, 890, 838, 700 cm^{-1}.

Procedure for the synthesis of 2k. Hydrogen peroxide (510 mg, 5 mmol) was added dropwise over 10 min to a cold (ice bath) solution of acetyl chloride (780 mg, 10 mmol) in diethyl ether (10 mL). This was followed by the dropwise addition of an aqueous solution of NaOH (400 mg, 10 mmol) over 10 min. The resulting white precipitate was collected by filtration and then was purified by flash chromatography (hexanes–ethyl acetate 40 : 1).[10c]

Acetic peroxyanhydride (2k).[19] White oil; 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.66, 20.71; MS (EI, 70 eV) m/z: 118.2 (M^+); IR (KBr): 2907, 1812, 1754, 1375, 1352, 1415 cm^{-1}.

General procedure for the synthesis of 3a–3r

A 10 mL reaction tube was charged with aromatic azo compound (**1**) (0.15 mmol), aryl acylperoxide (**2**) (0.30 mmol), $Pd(OAc)_2$ (10 mol%), and CH_3CN (2.0 mL). After the reaction was carried out at 60 °C for 24 h, it was cooled to room temperature and concentrated in vacuum. The residue was purified by flash chromatography (hexanes–ethyl acetate 100 : 1) to afford the desired products.

(*E*)-2-(Phenyldiazenyl)phenyl benzoate (3a). Yellow solid; mp 91–93 °C; 36 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 7.6 Hz, 2H), 7.90–7.84 (m, 1H), 7.71–7.67 (m, 2H), 7.65 (d, J = 7.5 Hz, 1H), 7.58–7.49 (m, 3H), 7.38 (q, J = 6.5 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 152.7, 149.2, 143.9, 133.6, 132.0, 131.2, 130.3, 128.9, 128.6, 126.5, 123.5, 123.0, 117.8; HR-MS (EI) calcd for $[M + Na]^+$: $C_{19}H_{14}N_2O_2Na$ 325.0947, found 325.0939; IR (KBr): 3063, 2924, 2853, 2361, 1521, 1418, 1258, 1150, 1077, 1022, 999, 842, 752, 521 cm^{-1}.

(*E*)-5-Methyl-2-(*p*-tolyldiazenyl)phenyl benzoate (3b). Yellow solid; mp 90–92 °C; 34 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 8.7 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.53 (t, J = 7.7 Hz, 2H), 7.16 (dd, J = 13.5, 7.5 Hz, 4H), 2.45 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 151.0, 149.0, 142.7, 141.9, 141.4, 133.4, 130.3, 129.6, 129.5, 128.5, 127.3, 123.8, 122.8, 117.6; HR-MS (EI) calcd for $[M + Na]^+$: $C_{21}H_{18}N_2O_2Na$ 353.1260, found 353.1272; IR (KBr): 3689, 3031, 2852, 1868, 1831, 1600, 1492, 1339, 1176, 1144, 1058, 818, 766, 545 cm^{-1}.

(*E*)-4-Methyl-2-(*m*-tolyldiazenyl)phenyl benzoate (3c). Yellow solid; mp 78–79 °C; 33 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (t, J = 8.0 Hz, 2H), 7.69–7.61 (m, 2H), 7.51 (dd, J = 13.2, 5.8 Hz, 3H), 7.44 (s, 1H), 7.37–7.32 (m, 1H), 7.30–7.21 (m, 2H), 7.18 (d, J = 7.4 Hz, 1H), 2.44 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.7, 152.9, 147.2, 143.4, 138.7, 136.4, 133.4, 132.6, 131.8, 130.3, 128.5, 122.9, 120.8, 117.9, 21.1, 21.0; HR-MS (EI) calcd for $[M + Na]^+$: $C_{21}H_{18}N_2O_2Na$ 353.1260, found 353.1274; IR (KBr): 3060, 2992, 2853, 2359, 1784, 1711, 1692, 1659, 1484, 1457, 1380, 1131, 1108, 914, 740, 687, 588 cm^{-1}.

(*E*)-3-Methyl-2-(*o*-tolyldiazenyl)phenyl benzoate (3d). Yellow solid; mp 71–73 °C; 21 mg, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.10 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.48–7.41 (m, 2H), 7.39 (d, J = 8.1 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.24 (s, 1H), 7.17 (dd, J = 13.2, 7.7 Hz, 3H), 7.08 (dd, J = 15.1, 7.1 Hz, 1H), 2.55 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 151.3, 143.7, 142.8, 138.30, 134.7, 133.3, 131.0, 130.2, 129.4, 129.2, 128.4, 126.1, 121.5, 115.1, 19.3, 17.4; HR-MS (EI) calcd for $[M + Na]^+$: $C_{21}H_{18}N_2O_2Na$ 353.1260, found 353.1277; IR (KBr): 3704, 2359, 2339, 1785, 1663, 1552, 1483, 1002, 749, 670, 653, 510 cm^{-1}.

(*E*)-5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl benzoate (3e). Yellow solid; mp 125–127 °C; 41 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 7.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.71–7.60 (m, 3H), 7.53 (dd, J = 15.6, 7.8 Hz, 2H), 6.90 (dd, J = 11.7, 2.5 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.90 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 162.3, 161.7, 150.3, 147.3, 138.2, 133.5, 130.3, 128.4, 124.5, 118.9, 114.0, 112.8, 108.1, 55.8, 55.4; HR-MS (EI) calcd for $[M + Na]^+$: $C_{21}H_{18}N_2O_4Na$ 385.1159, found 385.1131; IR (KBr): 3433, 2921, 2851, 2361, 1795, 1558, 1345, 1257, 1173, 1069, 685, 550 cm^{-1}.

(*E*)-5-Chloro-2-((4-chlorophenyl)diazenyl)phenyl benzoate (3f). Red oil; 23 mg, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (t, J = 8.4 Hz, 2H), 7.82 (d, J = 8.7 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.63–7.58 (m, 1H), 7.52 (dt, J = 13.6, 7.7 Hz, 2H), 7.42 (dd, J = 5.0, 2.7 Hz, 2H), 7.33 (dd, J = 9.9, 5.4 Hz, 2H), 7.24 (dd, J = 16.1, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 150.9, 149.7, 142.4, 137.5, 133.9, 133.5, 130.4, 129.5, 128.7, 127.0, 125.8, 124.2, 121.7, 118.7; HR-MS (EI) calcd for $[M + Na]^+$: $C_{19}H_{12}Cl_2N_2O_2Na$ 393.0168, found 393.0183; IR (KBr): 3736, 3673, 3446, 2852, 1699, 1541, 1477, 1402, 1199, 1110, 890, 766, 652, 526 cm^{-1}.

(*E*)-5-Bromo-2-((4-bromophenyl)diazenyl)phenyl benzoate (3g). Yellow solid; mp 143–145 °C; 28 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (t, J = 7.2 Hz, 2H), 7.75 (d, J = 8.6 Hz, 1H), 7.71–7.61 (m, 2H), 7.58–7.48 (m, 5H), 7.43 (t, J = 7.0 Hz, 1H), 7.25–7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 151.3, 151.0, 149.7, 142.8, 133.5, 132.3, 130.1, 129.5, 128.5, 127.0, 125.8, 124.4, 121.7, 118.9; HR-MS (EI) calcd for $[M]^+$: $C_{19}H_{12}Br_2N_2O_2$ 457.9260, found 457.9261; IR (KBr): 3652, 3315, 2913, 2894, 1632, 1526, 1436, 1418, 846, 768, 459 cm^{-1}.

(*E*)-5-Fluoro-2-((4-fluorophenyl)diazenyl)phenyl benzoate (3h). Yellow solid; mp 78–79 °C; 18 mg, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dt, J = 5.9, 2.8 Hz, 2H), 7.96–7.88 (m, 1H), 7.76–7.67 (m, 3H), 7.58 (t, J = 7.7 Hz, 2H), 7.21–7.11 (m, 2H), 7.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, $^2J_{(C,F)}$ = 8.9 Hz), 165.1 (d, $^2J_{(C,F)}$ = 9.1 Hz), 163.2, 150.4, 140.6, 133.9, 130.4, 128.7, 124.9, 119.2, 116.1, 115.8, 113.9, 113.7, 111.4, 111.1; HR-MS (EI) calcd for $[M + Na]^+$: $C_{19}H_{12}F_2N_2O_2Na$ 361.0759, found 361.0769; IR (KBr): 2919, 2851, 2589, 2283, 1592, 1530, 1513, 1497, 1451, 1093, 1052, 750, 702, 531, 413 cm^{-1}.

(*E*)-2-((4-Methoxyphenyl)diazenyl)phenyl benzoate (3j). Yellow solid; mp 114–115 °C; 31 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 7.3 Hz, 2H), 7.91 (d, J = 8.8 Hz, 1H), 7.71–7.60 (m, 3H), 7.53 (dd, J = 15.8, 8.1 Hz, 2H), 7.38–7.32 (m, 3H), 6.92 (dd, J = 13.0, 2.5 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 152.8, 150.9, 133.6, 130.5, 130.4, 128.8, 128.6, 122.7, 119.0, 112.8, 108.2, 55.8; HR-MS (EI) calcd for $[M + Na]^+$: $C_{20}H_{16}N_2O_3Na$ 355.1053, found 355.1065; IR (KBr): 2864, 2812, 2354, 1864, 1832, 1542, 1479, 1097, 983, 681, 453, 398 cm^{-1}.

(*E*)-2-((4-Methoxyphenyl)diazenyl)-5-methylphenyl benzoate (3l) and (*E*)-5-methoxy-2-(*p*-tolyldiazenyl)phenyl benzoate (3k). Red oil; 29 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 7.6 Hz, 4H), 7.89 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.66 (dd, J = 5.7, 3.1 Hz, 4H), 7.52 (dd, J = 19.4, 12.3 Hz, 6H), 7.17 (d, J = 4.0 Hz, 2H), 7.11 (t, J = 10.1 Hz, 2H), 6.96–6.89 (m, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 3.82 (s, 3H), 2.45 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 162.0, 150.7, 148.7, 147.2, 142.3, 141.0, 138.1, 133.5, 133.4, 130.4, 130.3, 129.5, 128.6, 127.3, 124.7, 123.8, 122.7, 118.9, 117.6, 114.0, 112.8, 108.1, 55.8, 55.5; HR-MS (EI) calcd for $[M + Na]^+$: $C_{21}H_{18}N_2O_3Na$ 369.1210, found 369.1189; IR (KBr): 3740, 3696, 3630, 2923, 2360, 1900, 1860, 1530, 1500, 1462, 1295, 1179, 1104, 710, 540 cm^{-1}.

(*E*)-2-(Phenyldiazenyl)phenyl 4-methylbenzoate (3m). Yellow solid; mp 101–103 °C; 26 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.2 Hz, 2H), 7.89–7.84 (m, 1H), 7.74–7.68 (m, 2H), 7.57–7.50 (m, 1H), 7.38 (td, J = 5.8, 2.5 Hz, 5H), 7.33 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 152.7, 149.3, 144.4, 144.0, 132.0, 130.6, 130.4, 129.3, 128.9, 126.4, 123.6, 123.0, 117.7, 21.8; HR-MS (EI) calcd for $[M + Na]^+$: $C_{20}H_{16}N_2O_2Na$ 339.1104, found 339.1106; IR (KBr): 3445, 2027, 1832, 1736, 1648, 1260, 1130, 992, 750, 638, 616 cm^{-1}.

(*E*)-2-(Phenyldiazenyl)phenyl 3-methylbenzoate (3n). Oil; 27 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 7.0 Hz, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 7.4 Hz, 1H), 7.34–7.29 (m, 6H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.64, 152.77, 149.33, 144.05, 138.44, 134.37, 132.03, 131.21, 130.88, 128.52, 127.55, 126.51, 123.57, 117.80, 21.30; HR-MS (EI) calcd for $[M + H]^+$: $C_{20}H_{17}N_2O_2$ 317.1284, found 317.1287; IR (KBr): 3357, 2017, 1798, 1725, 1643, 1317, 1287, 1230, 1109, 746, 639, 620 cm^{-1}.

(*E*)-2-(Phenyldiazenyl)phenyl 4-methoxybenzoate (3p). Yellow solid; mp 99–101 °C; 28 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 6.6 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.39 (s, 5H), 7.01 (d, J = 8.5 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.20, 163.93, 152.73, 149.39, 144.10, 132.51, 132.02, 131.17, 128.98, 126.41, 123.67, 123.05, 117.71, 113.89, 55.54; HR-MS (EI) calcd for $[M + Na]^+$: $C_{20}H_{16}N_2O_3Na$ 355.1053, found 355.0871; IR (KBr): 2922, 2360, 2339, 1739, 1610, 1484, 1452, 1208, 1192, 1056, 835, 741, 544 cm^{-1}.

(*E*)-2-(Phenyldiazenyl)phenyl 4-fluorobenzoate (3q). Yellow oil; 20 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.24 (m, 2H), 7.88 (dd, J = 8.0, 1.4 Hz, 1H), 7.71–7.67 (m, 2H), 7.58–7.51 (m, 1H), 7.43–7.35 (m, 5H), 7.23–7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.5, 152.6, 149.0, 143.9, 133.0, 132.9, 132.0, 131.3, 129.0, 126.6, 123.4, 123.0, 117.9,

115.9, 115.7; HR-MS (EI) calcd for $[M + Na]^+$: $C_{19}H_{13}FN_2O_2Na$ 343.0853, found 343.0862; IR (KBr): 2921, 2851, 2360, 2338, 1741, 1504, 1478, 1412, 1195, 1060, 819, 716, 684, 622, 507 cm^{-1}.

(*E*)-2-(Phenyldiazenyl)phenyl 4-chlorobenzoate (3r). Yellow solid; mp 74–76 °C; 24 mg, 48% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22–8.17 (m, 2H), 7.88 (dd, J = 8.0, 1.5 Hz, 1H), 7.72–7.66 (m, 2H), 7.56–7.49 (m, 3H), 7.43–7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 152.6, 149.0, 143.8, 140.1, 132.0, 131.7, 131.3, 129.0, 127.8, 126.7, 123.4, 123.0, 117.9; HR-MS (EI) calcd for $[M + Na]^+$: $C_{19}H_{12}ClN_2O_2Na$ 359.0558, found 359.0567; IR (KBr): 3105, 2956, 1612, 1500, 1209, 615, 593, 495 cm^{-1}.

(*E*)-2-(Phenyldiazenyl)phenyl 4-nitrobenzoate (3s). Yellow solid; mp 154–156 °C; 12 mg, 23% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 8.6 Hz, 2H), 8.37 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.7 Hz, 1H), 7.45–7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 152.6, 150.9, 148.6, 143.6, 134.8, 132.1, 131.5, 131.4, 129.0, 127.1, 123.8, 123.1, 122.9, 118.2; HR-MS (EI) calcd for $[M]^+$: $C_{19}H_{13}N_3O_4$ 347.0901, found 347.0902; IR (KBr): 3435, 2920, 1744, 1641, 1613, 1348, 1258, 837, 686, 500 cm^{-1}.

General procedure for the synthesis of 4a–4r

A 10 mL reaction tube was charged with aromatic azo compound (**1**) (0.15 mmol), aryl acylperoxide (**2**) (0.30 mmol), $Pd(OAc)_2$ (10 mol%), and PhCl (1.0 mL). After the reaction was carried out at 130 °C for 24 h, it was cooled to room temperature and concentrated in vacuum. The residue was purified by flash chromatography (hexanes) to afford the desired products.

(*E*)-1-([1,1′-Biphenyl]-2-yl)-2-phenyldiazene (4a).[20] Yellow solid; mp 78–80 °C; 30 mg, 76% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (dt, J = 21.8, 10.1 Hz, 3H), 7.59 (d, J = 7.5 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.48–7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 149.7, 141.1, 138.8, 130.9, 130.8, 130.8, 129.0, 128.0, 127.6, 127.2, 123.2, 115.9; MS (EI, 70 eV) m/z: 258.1 (M^+); IR (KBr): 3687, 3498, 2879, 1792, 1834, 1823, 1532, 1512, 982, 534 cm^{-1}.

(*E*)-1-(5-Methyl-[1,1′-biphenyl]-2-yl)-2-(*p*-tolyl)diazene (4b). Yellow solid; mp 76–78 °C; 30 mg, 70% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.0, 5.1 Hz, 3H), 7.47 (d, J = 7.6 Hz, 2H), 7.44–7.36 (m, 4H), 7.30 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 12.8 Hz, 2H), 2.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 147.8, 141.1, 140.9, 139.0, 131.3, 130.9, 129.6, 128.8, 127.5, 127.1, 123.1, 122.7, 115.7, 21.4, 21.4; HR-MS (EI) calcd for $[M + H]^+$: $C_{20}H_{19}N_2$ 287.1543, found 287.1548; IR (KBr): 3711, 3546, 2921, 1828, 1600, 1457, 1103, 766, 580, 540 cm^{-1}.

(*E*)-1-(4-Methyl-[1,1′-biphenyl]-2-yl)-2-(*m*-tolyl)diazene (4c). Yellow solid; mp 70–72 °C; 24 mg, 57% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.56 (m, 2H), 7.54 (s, 1H), 7.50–7.44 (m, 3H), 7.41 (t, J = 7.2 Hz, 2H), 7.39–7.32 (m, 3H), 7.24 (d, J = 4.9 Hz, 1H), 2.46 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 149.6, 138.9, 138.8, 138.3, 138.0, 131.6, 130.9, 130.6, 128.8, 127.5, 127.0, 124.0, 120.2, 116.1, 21.3, 21.1; HR-MS (EI) calcd for $[M + H]^+$: $C_{20}H_{19}N_2$ 287.1543, found 287.1541; IR (KBr): 3434, 2920, 2851, 1636, 1475, 1275, 1219, 765, 697, 476 cm^{-1}.

(*E*)-1-(3-Methyl-[1,1′-biphenyl]-2-yl)-2-(*o*-tolyl)diazene (4d). Red oil; 19 mg, 40% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 7H), 7.25–7.22 (m, 3H), 7.21–7.12 (m, 2H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 140.2, 138.2, 135.9, 131.2, 130.9, 130.7, 130.3, 129.0, 127.9, 127.8, 126.5, 126.2, 115.2, 19.2, 17.1; HR-MS (EI) calcd for $[M + H]^+$: $C_{20}H_{19}N_2$ 287.1543, found 287.1543; IR (KBr): 3433, 3056, 2853, 1943, 1734, 1540, 1443, 766, 699, 577, 454 cm^{-1}.

(*E*)-5-Methoxy-2-((5-methoxy-[1,1′-biphenyl]-2-yl)diazenyl)-phenol (4e). Yellow solid; mp 132–134 °C; 37 mg, 75% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 14.55 (s, 1H), 7.57 (d, J = 9.0 Hz, 3H), 7.50 (d, J = 6.5 Hz, 2H), 7.47–7.39 (m, 4H), 6.93 (t, J = 8.9 Hz, 2H), 6.62 (d, J = 2.7 Hz, 1H), 6.49 (d, J = 2.6 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 161.1, 156.9, 146.0, 144.5, 139.2, 130.7, 127.4, 123.4, 114.4, 109.4, 100.8, 55.6, 55.5; HR-MS (EI) calcd for $[M - H]^-$: $C_{20}H_{17}N_2O_3$ 333.1245, found 333.1252; IR (KBr): 3852, 3739, 2925, 2360, 1605, 1485, 1203, 1030, 835, 831, 757, 670, 526 cm^{-1}.

(*E*)-1-(5-Chloro-[1,1′-biphenyl]-2-yl)-2-(4-chloro phenyl)-diazene (4f). Yellow solid; mp 91–93 °C; 23 mg, 47% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, J = 7.7 Hz, 1H), 7.72 (dd, J = 13.7, 8.7 Hz, 2H), 7.58 (d, J = 2.2 Hz, 1H), 7.51–7.39 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.8, 147.7, 142.9, 137.4, 137.1, 136.9, 130.7, 129.4, 129.3, 128.2, 127.8, 127.8, 124.5, 124.2, 117.3; HR-MS (EI) calcd for $[M]^+$: $C_{18}H_{12}Cl_2N_2$ 326.0372, found 326.0371; IR (KBr): 3694, 3683, 3472, 2921, 2850, 1725, 1710, 1690, 1403, 1383, 1257, 1171, 960, 883, 656, 572, 482, 414 cm^{-1}.

(*E*)-1-(5-Bromo-[1,1′-biphenyl]-2-yl)-2-(4-bromo phenyl)-diazene (4g). Yellow solid; mp 143–142 °C; 22 mg, 38% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 1H), 7.58 (dd, J = 20.6, 12.0 Hz, 4H), 7.53–7.49 (m, 2H), 7.37 (d, J = 8.8 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 148.1, 143.1, 137.3, 133.7, 132.4, 131.1, 130.7, 127.8, 127.8, 124.7, 124.4, 117.5; HR-MS (EI) calcd for $[M + H]^+$: $C_{18}H_{13}Br_2N_2$ 414.2811, found 414.2802; IR (KBr): 3682, 3637, 2340, 1765, 1725, 1493, 1479, 1414, 1270, 1147, 749, 688, 484 cm^{-1}.

(*E*)-1-(5-Fluoro-[1,1′-biphenyl]-2-yl)-2-(4-fluoro phenyl)-diazene (4h). Yellow solid; mp 77–78 °C; 15 mg, 34% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (ddd, J = 19.2, 8.8, 5.5 Hz, 3H), 7.47 (dd, J = 7.7, 2.4 Hz, 4H), 7.32 (ddd, J = 12.7, 5.9, 3.5 Hz, 2H), 7.17 (dt, J = 14.9, 5.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (d, $^2J_{(C,F)}$ = 17.9 Hz), 163.0 (d, $^2J_{(C,F)}$ = 17.4 Hz), 149.3, 145.9, 143.7, 137.8, 130.7, 127.7, 125.2, 125.1, 118.0, 117.9, 117.3, 117.0, 116.1, 115.9, 115.3, 115.0; HR-MS (EI) calcd for $[M + H]^+$: $C_{18}H_{13}F_2N_2$ 295.1041, found 295.1039; IR (KBr): 3673, 3446, 1649, 1541, 1222, 1199, 1101, 1081, 995, 893, 765, 700, 578, 524 cm^{-1}.

(*E*)-Ethyl 6-((4-(ethoxycarbonyl)phenyl)diazenyl)-[1,1′-biphenyl]-3-carboxylate (4i). Yellow solid; mp 115–117 °C; 18 mg, 29% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.6 Hz, 1H), 8.13 (dd, J = 13.8, 5.2 Hz, 3H), 7.83 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.51–7.42 (m, 5H), 4.42 (dq, J = 14.4,

7.1 Hz, 4H), 1.42 (dt, J = 9.5, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 155.0, 152.0, 141.3, 137.8, 132.6, 132.3, 130.8, 130.6, 129.2, 127.8, 123.1, 116.0, 61.4, 61.3, 14.3, 14.3; HR-MS (EI) calcd for $[M + Na]^+$: $C_{24}H_{22}N_2O_4Na$ 425.1472, found 425.1487; IR (KBr): 3125, 2989, 1735, 1634, 1468, 1246, 1106, 1056, 846, 526 cm^{-1}.

(*E*)-1-(5-Methoxy-[1,1′-biphenyl]-2-yl)-2-phenyl diazene (4j). Red oil; 27 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (t, J = 10.4 Hz, 1H), 7.92 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 7.5 Hz, 2H), 7.51 (dd, J = 13.8, 6.9 Hz, 3H), 7.42 (d, J = 7.2 Hz, 2H), 7.24–7.17 (m, 1H), 7.02 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 147.0, 130.3, 129.0, 124.7, 122.5, 114.2, 55.5; HR-MS (EI) calcd for $[M + H]^+$: $C_{19}H_{17}ON_2$ 289.1335, found 289.1330; IR (KBr): 3433, 3007, 2838, 2360, 1741, 1601, 1501, 1255, 1143, 1028, 837, 806, 751, 548 cm^{-1}.

(*E*)-1-(4-Methoxyphenyl)-2-(5-methyl-[1,1′-biphenyl]-2-yl)diazene (4l) and (*E*)-1-(5-methoxy-[1,1′-biphenyl]-2-yl)-2-(*p*-tolyl)-diazene (4k). Yellow solid; mp 76–78 °C; 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 7.7 Hz, 3H), 7.89 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.66 (d, J = 8.7 Hz, 3H), 7.52 (dd, J = 15.5, 8.4 Hz, 5H), 7.17 (s, 2H), 7.12 (s, 1H), 6.91 (d, J = 9.3 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 3.90 (s, 1.5H), 3.82 (s, 3H), 2.45 (s, 3H), 2.34 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.5, 162.6, 162.0, 150.9, 148.7, 147.2, 142.3, 141.9, 141.0, 133.5, 133.4, 130.3, 130.3, 129.6, 129.5, 128.5, 127.3, 124.7, 123.8, 122.7, 118.9, 117.6, 114.0, 112.8, 108.1, 55.8, 55.5, 21.4, 21.3; HR-MS (EI) calcd for $[M]^+$: $C_{20}H_{18}N_2O$ 302.1419, found 302.1413; IR (KBr): 3687, 3541, 2913, 1815, 1584, 1435, 1128, 754, 579, 526 cm^{-1}.

(*E*)-1-(4′-Methyl-[1,1′-biphenyl]-2-yl)-2-phenyl diazene (4m). Yellow solid; mp 78–79 °C; 29 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.4 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.52 (dd, J = 13.6, 5.9 Hz, 1H), 7.49–7.40 (m, 5H), 7.37 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 149.8, 141.0, 137.0, 135.8, 130.8, 129.0, 128.4, 127.8, 127.5, 123.2, 120.4, 115.9, 21.2; HR-MS (EI) calcd for $[M + H]^+$: $C_{19}H_{17}N_2$ 273.1386, found 273.1381; IR (KBr): 3738, 3615, 2921, 2850, 1785, 1764, 1450, 1410, 1382, 1216, 961, 926, 513, 503 cm^{-1}.

(*E*)-1-(3′-methyl-[1,1′-biphenyl]-2-yl)-2-phenyl diazene (4n). Oil; 23 mg, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 7.5 Hz, 4H), 7.25–7.22 (m, 2H), 7.18 (d, J = 9.5 Hz, 1H), 7.13 (d, J = 7.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.92, 149.79, 141.20, 138.73, 137.17, 131.63, 130.83, 130.76, 129.06, 128.25, 128.01, 127.98, 127.48, 123.25, 115.92, 21.51; HR-MS (EI) calcd for $[M + H]^+$: $C_{19}H_{17}N_2$ 273.1386, found 273.1386; IR (KBr): 3687, 3642, 3605, 2931, 2819, 1797, 1748, 1449, 1435, 1368, 1209, 943, 916, 498, 476 cm^{-1}.

(*E*)-1-(4′-Fluoro-[1,1′-biphenyl]-2-yl)-2-phenyl diazene (4q). Red oil; 22 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.2 Hz, 1H), 7.82–7.70 (m, 2H), 7.58–7.52 (m, 3H), 7.45 (dt, J = 8.5, 5.5 Hz, 5H), 7.12 (t, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.2, 152.8 (d, $^2J_{(C,F)}$ = 11.7 Hz), 149.6, 140.1, 132.4, 132.3, 131.3, 130.8, 130.7, 129.1, 128.1, 123.2, 122.8, 120.4, 115.9, 114.6, 114.4; HR-MS (EI) calcd for $[M + H]^+$: $C_{18}H_{14}FN_2$ 277.1136, found 277.1135; IR (KBr): 2935, 2910, 2835, 1503, 1489, 1439, 1021, 998, 676, 654, 531, 493 cm^{-1}.

(*E*)-1-(4′-Chloro-[1,1′-biphenyl]-2-yl)-2-phenyl diazene (4r). Red oil; 25 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.1 Hz, 1H), 7.77 (t, J = 7.3 Hz, 3H), 7.54 (d, J = 3.7 Hz, 2H), 7.47 (dd, J = 13.1, 6.1 Hz, 4H), 7.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 149.5, 140.0, 137.3, 132.1, 131.1, 130.9, 130.6, 129.3, 129.1, 128.4, 127.8, 123.2, 122.2, 116.0; HR-MS (EI) calcd for $[M + H]^+$: $C_{18}H_{14}ClN_2$ 293.0840, found 293.0849; IR (KBr): 3433, 2924, 2360, 2340, 1744, 1589, 1260, 1176, 1056, 749, 655, 524 cm^{-1}.

Synthetic application for this transformation

(a) A mixture of **3a** (0.15 mmol, 1 equiv.) and K_2CO_3 (0.24 mmol, 1.6 equiv.) in NMP (2.0 mL) was heated at 100 °C for 3 h under N_2. It was cooled to room temperature and then purified by flash chromatography (hexanes) to get the desired products.[21]

(*E*)-2-(Phenyldiazenyl)phenol (5).[22] Solid; mp 121–123 °C; 27 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.92 (s, 1H), 7.95 (dd, J = 7.9, 1.6 Hz, 1H), 7.88 (dd, J = 8.2, 1.2 Hz, 2H), 7.56–7.47 (m, 3H), 7.39–7.33 (m, 1H), 7.10–7.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 137.3, 133.2, 133.2, 131.1, 129.3, 122.2, 119.9, 118.2; MS (EI, 70 eV) m/z: 198.1 (M^+); IR (KBr): 3411, 2977, 2898, 1649, 1449, 1057, 882, 770, 685, 434 cm^{-1}.

(b) A suspension of the azo compound **3a** (0.2 mmol, 1 equiv.) and zinc dust (0.2 mmol, 1 equiv.) in methanol (3 mL) and ammonium chloride (0.4 mmol, 2 equiv.) was stirred under a nitrogen atmosphere at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered through a celite pad and washed with solvent. The combined filtrate and washings were concentrated, and the residue was dissolved in chloroform (5 mL) or diethyl ether and was washed with saturated brine solution (5 mL) and water. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate 10 : 1).[23]

2-(2-Phenylhydrazinyl)phenyl benzoate (6). Solid; mp 86–88 °C; 50 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.08 (m, 2H), 7.55 (dd, J = 10.6, 4.3 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.12 (dd, J = 13.3, 5.5 Hz, 2H), 7.04 (m, 3H), 6.80–6.72 (m, 4H), 5.71 (s, 1H), 5.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 148.5, 140.5, 137.0, 133.9, 130.2, 129.4, 128.7, 127.0, 122.4, 120.1, 119.6, 113.6, 112.4; HR-MS (EI) calcd for $[M + Na]^+$: $C_{19}H_{16}O_2N_2Na$ 327.1109, found 327.1075; IR (KBr): 3338, 2974, 2895, 2269, 1923, 1657, 1387, 1050, 881, 695 cm^{-1}.

(c) A suspension of the azo compound **3a** (0.2 mmol, 1 equiv.) and zinc dust (0.2 mmol, 1 equiv.) in methanol (3 mL) and ammonium chloride (0.4 mmol, 2 equiv.) was stirred under a nitrogen atmosphere at 80 °C. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered through a celite pad and washed with

solvent. The combined filtrate and washings were concentrated, and the residue was dissolved in chloroform (5 mL) or diethyl ether and was washed with saturated brine solution (5 mL) and water. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate 10 : 1).[23]

***N*-Phenyl-benzamide (7).**[24] Solid; mp 163–165 °C; 28 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.8–7.82 (m, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.53 (m, 1H), 7.50–7.43 (m, 2H), 7.36 (dd, J = 10.8, 5.1 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 137.9, 135.0, 131.8, 129.0, 128.7, 127.0, 124.5, 120.2; MS (EI, 70 eV) m/z: 197.13 (M^+); IR (KBr): 3342, 2991, 2374, 1762, 1654, 1440, 1243, 924, 639, 498 cm^{-1}.

2-Aminophenol (8).[25] Solid; mp 172–173 °C; 14 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 6.65 (dd, J = 7.7, 1.1 Hz, 1H), 6.59 (dd, J = 7.7, 1.7 Hz, 1H), 6.54 (td, J = 7.5, 1.2 Hz, 1H), 6.40 (td, J = 7.5, 1.7 Hz, 1H), 4.45 (s, 2H); MS (ESI): m/z = 109 [M^+].

The mechanism studies about this transformation

(a) A 10 mL reaction tube was charged with azobenzene (**1a**) (0.15 mmol), benzoylperoxide (**2a**) (0.30 mmol), TEMPO (0.15 mmol), $Pd(OAc)_2$ (10 mol%), and CH_3CN (2.0 mL). After the reaction was carried out at 60 °C for 24 h, it was cooled to room temperature. The reaction was monitored by GC-MS, and no acyloxylated **3a** was observed.

(b) A 10 mL reaction tube was charged with acyloxylated product (**3a**) (0.15 mmol), $Pd(OAc)_2$ (10 mol%), and PhCl (1.0 mL). After the reaction was carried out at 130 °C for 24 h, it was cooled to room temperature. The reaction was monitored by GC-MS, and no **4a** was observed.

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