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Palladium-Catalyzed Direct Ortho C–O bond construction of Azobenzenes with Iodobenzene diacetate via C–H Activation

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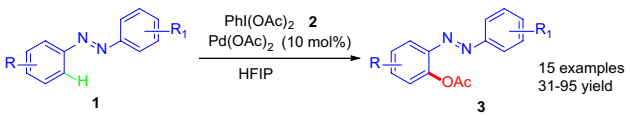
Abstract
Abstract A method of direct synthesis of ortho-acyloxylated azoarenes via palladium-catalyzed C–H bond activation was developed. The reaction proceeded was smoothly at room temprature and have better yield in shorter times. The obtained ortho-acyloxylated azoarenes could be efficiently converted into 2-hydroxyazobenzenes in good yields through a hydrolysis process.

Graphical Abstract Many various ortho-acyloxylated azoarenes were obtained in moderate to high yields by palladium-catalyzed direct C(sp^2)-H acyloxylation of aromatic azo compounds with $PhI(OAc)_2$



Keywords C–O bond construction · C–H Activation · Room temprature

1 Introduction

The azobenzenes have been proven to be a valuable structural motifs in pharmaceutical [1, 2], liquid crystals [3], molecular switches [4, 5], a femtosecond fluorescence [6]. Among them, the hydroxyazobenzenes play an important role in the field of functional materials such as photo-switchable [7] and spectral probe [8], because an ether bond can be formation between the hydroxyl group with phenol, α-cyclodextrin and β-cyclodextrin and many other supramolecular are shown in (Fig. 1). Especially, 2-hydroxyazobenzenes have many excellent features and has attracted a great deal of attention. For example, it can be work as acidity indicators [9, 10] or synthesis of neutral dyeing metal–complex dyes [11, 12] which having no ionic groups in early. Hereafter, 2-hydroxyazobenzenes have been reported to synthesis of 2-aryl-2*H*-benzotriazoles that are important intermediate [13]. It was said that the hybrid metal–organic compounds with 2-hydroxyazobenzene (HAB) rings have are high industrial and economic potential as thin films, transfer for sensor, optical-storage and detectors [14–23]. Also, the role of H-bonded chelate rings of 2-hydroxyazobenzenes is most important in the organization of liquid crystalline such as modification of mesophases [24–29]. Similarly, this H-bonded is better for have excellent spectroscopic and electrochemical properties [27–29]. So, several methods for synthesis of 2-hydroxyazobenzenes have been developed. The common approaches for preparing ortho-hydroxyazobenzenes include the Hydroxylated of 1,2-diphenyldiazene oxide [30–33] or diazotization of diazonium salt [34–36]. It is disappointing that these methods are tedious and have a low conversion. In 2010, Yoshino et al. [37] reported a methord to produce of 2-hydroxyazobenzenes by hydrolysis of the (2-(phenyldiazenyl)phenyl)boronic acid at a high

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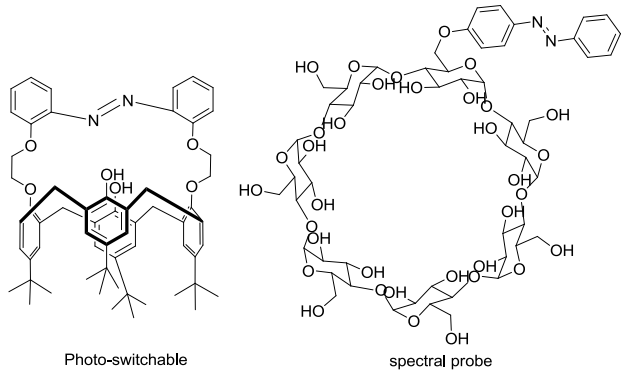


Fig. 1 Many functional materials of hydroxyazobenzenes

yield but these arylboronic acids are difficult to obtain. In recent years, many more efficient routes such as directed C–H hydroxylation of arenes have been developed although they have low yields [38, 39].

Similar to 2-aryloxypyridines [40, 41], quinoline *N*-Oxide [42], arylpyrazoles [43], triazene azoxybenzenes [44], quinoline [45–47], and 2-aryl-1,2,3-triazoles group [48], the azoxybenzenes work as the directing groups in this strategy have attracted more and more attention. For example, Satoh's [49] group reported a method of rhodium-catalyzed regioselective arylation of phenylazoles and related compounds with arylboron reagents via C–H bond cleavage. In addition, Wang's group have done excellent work on the formate C–C bonds through ortho-selective C–H activation with alkenes [50, 51] and heteroarenes [52]. Tang [53] and co-workers have developed a highly efficient method by palladium-catalyzed cascade oxidative C–H cross-coupling of azoarenes with alcohols to synthesis ortho-acylazoarenes. Similarly, Cui's group [54] also reported a practical procedure to synthesize mono and diacylazobenzene via Pd-catalyzed oxidative C–H bond activation from toluene. In addition, Li et al. [55–57] has made a remarkable progress that a palladium-catalyzed decarboxylative ortho acylation of azobenzenes with α-oxocarboxylic acids. Recently, Jia's [58] group independently reported a rhodium(III)-catalyzed direct ortho-amidation of azobenzenes with sulfonyl azides as the amino source is disclosed. More recently, Wu [59] and Zhang [60] disclosed a method to formation sulfonylazobenzenes from azobenzene and arylsulfonyl chlorides. Also, cinnolinium salts [61, 62] and indolo[2,1-α]isoquinolines [63] have been produced from azobenzenes and alkynes catalyzed by Rhodium. Additionally, Ellman's and wang's groups [64, 65] independently reported a new Co- catalyst or Pd-Catalyzed for the synthesis of 2-aryl indazoles and furans use aldehyde and azobenzenes. However, methods for direct conversion of a C–H bond into a C–O bond by metal-catalyzed remains a tremendous challenge. In 2004, Sanford's [66] group first reported a methord oxidative functionalization of C–H bonds and product 2-(phenyldiazenyl)phenyl acetate in 62% yield at 100 °C about 12H. After these, Tato [67] discover a palladium-catalyzed acetoxylation of arenes by novel sulfinyl *N*-heterocyclic carbene ligand complexes, and reaction was carried out with azobenzene and PIDA in MeCN at 80 °C for 72H at 66% yield. Simultaneously, sun's group [68] released a palladium-catalyzed direct ortho alkoxylation of aromatic azo compounds with alcohols. More recently, Qian et al. [69] find a good methord to synthesis of various ortho-acyloxylated azoarenes by palladium-catalyzed ortho-functionalization of azoarenes with aryl acylperoxides. But it no desired product was observed under same reaction conditions when use acetyl peroxide as an acyloxyl source. As part of our continuing efforts in C–X bonds formation [70, 71], herein we describe a palladium-catalyzed direct C–O bond formation of azobenzenes with iodobenzene diacetate via C–H activation to synthesize 2-alkoxy aromatic azo compounds at room temprature and have better yield in shorter times. Also, it is important method to synthesis of 2-hydroxyazobenzene by hydrolysis reaction of the above product.

2 Results and Discussion

We initiated our investigation on the model reaction of azobenzene (**1a**) with $PhI(OAc)_2$ (**2**) to optimize the reaction parameters (Table 1). To our delight, the C_2- esterification took place in the presence of $Pd(OAc)_2$ (10 mol%) in hexafluoroisopropanol (HFIP) under air for 30 min, the desired product was acquired in 93% yield (entry 1, Table 1).

Thus, $Pd(CH_3CN)_2Cl_2$, $Pd(Ph_3P)_2$, $Pd(CF_3COO)_2$, $PdCl_2$, $PtCl_2$, $Cu(OAc)_2$, $Co(OAc)_2$ $4H_2O$ and $LaCl_2$ were tested to catalyze this reaction, in which $Pd(OAc)_2$ gave the best result (entries 1–9, Table 1). Without catalyst, the reaction could not take place at all (entry 10, Table 1). The solvent also played an important role in the reaction. Solvents such as HOAc, CH_3CN, DMF, DMSO, and EtOH were screened, but the yield is poor (entries 11–15, Table 1). Subsequently, the yield decreased to 72% when the catalyst loading was reduced to 5 mol% from 10 mol% (entry 16, Table 1). When the temperature was increased to 60 °C or reduced to 20 °C, the yield decreased to 80 and 73%, respectively (entries 17–18, Table 1). And the reaction time on 30 min has a highest yield (entries 1 and 19–20, Table 1). Based on the results obtained above, the optimized reaction conditions were identified as follows: 10 mol% of $Pd(OAc)_2$ as the catalyst, and HFIP as the solvent, at 40 °C under an air atmosphere for 30 min.

Table 1 Optimization of reaction conditions

Entry	Catalyst	Solvent	Yield(%)[a]
1	$Pd(OAc)_2$	HFIP	93
2	$Pd(CH_3CN)_2Cl_2$	HFIP	73
3	$Pd(Ph_3P)_2$	HFIP	41
4	$Pd(CF_3COO)_2$	HFIP	17
5	$PdCl_2$	HFIP	Trace
6	$PtCl_2$	HFIP	Trace
7	$Cu(OAc)_2$	HFIP	Trace
8	$Co(OAc)_2\ 4H_2O$	HFIP	Trace
9	La Cl_2	HFIP	Trace
10	–	HFIP	Trace
11	$Pd(OAc)_2$	HOAc	Trace
12	$Pd(OAc)_2$	CH_3CN	4
13	$Pd(OAc)_2$	DMF	Trace
14	$Pd(OAc)_2$	DMSO	Trace
15	$Pd(OAc)_2$	EtOH	Trace
16	$Pd(OAc)_2$	HFIP	72[b]
17	$Pd(OAc)_2$	HFIP	80[c]
18	$Pd(OAc)_2$	HFIP	73[d]
19	$Pd(OAc)_2$	HFIP	87[e]
20	$Pd(OAc)_2$	HFIP	82[f]

Reaction conditions:**1a** (0.5 mmol), **2** (0.5 equiv), catalyst (10 mol%) and solvent (2.0 mL) under air atmosphere at 40°Cfor 30 min, unless otherwise noted

[a]Isolated yields

[b]$Pd(OAc)_2$ (5 mol%)

[c]60 °C

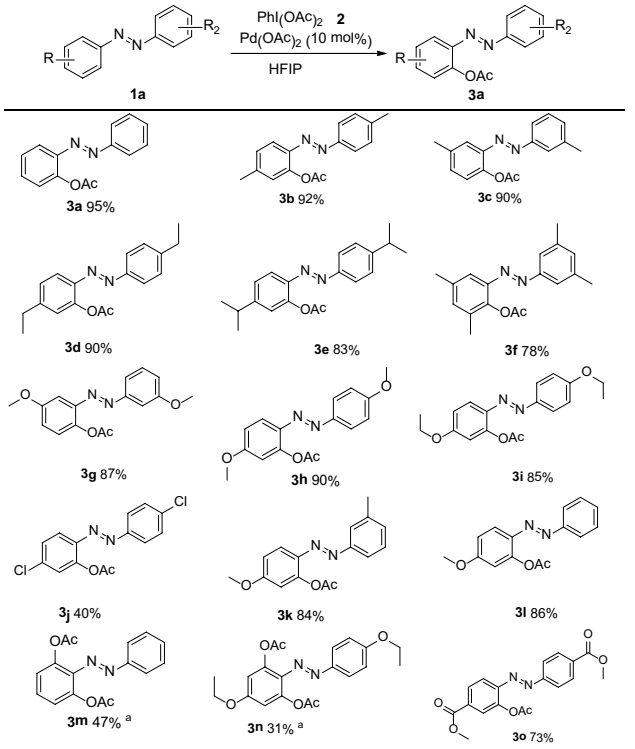
[d]20 °C

[e]1 h

[f]4 h

With the optimized reaction conditions in hand, we then investigated the substrate scope of this transformation (Scheme 1, 2)

A series of azobenzenes were allowed to react with iodobenzene diacetate (**2**), affording the corresponding 2-alkoxy aromatic azo compounds in moderate to good yields. It was found that azobenzenes containing an electron-donating groups such as 1,2-diphenyldiazene, 1,2-di-*p*-tolyldiazene, 1,2-di-*m*-tolyldiazene, 1,2-bis(4-ethylphenyl)diazene, 1,2-bis(4-isopropylphenyl)diazene, 2-bis(3-methoxyphenyl) diazene, 1,2-bis(4-methoxyphenyl)-diazene, 1,2-bis(4-ethoxyphenyl)diazene, 1-(4-methoxyphenyl)-2-(*m*-tolyl) diazene, 1-(4-methoxyphenyl)-2-phenyldiazene, gave good yields (Scheme 1, see compounds **3a–i, 3k, l**). However, the 1,2-bis(4-chlorophenyl)diazene, dimethyl 4,4'-(diazene-1,2-diyl)dibenzoate substituted with electron-withdrawing group afforded a lower yield (Scheme 1, see compounds **3j, o**). Meanwhile, the bulkier group at the phenyl ring of azobenzenes impede the reaction, as exemplified by **3e, f**.

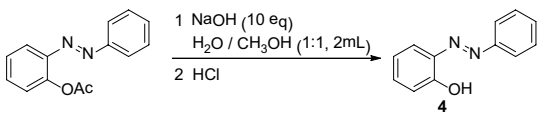


Scheme 1 Substrate scope of the palladium-catalyzed direct ortho C–O bond construction of an azobenzenes. Conditions: **1** (0.5 mmol), **2** (0.5 equiv), $Pd(OAc)_2$ (10 mol%) and solvent (2.0 mL) under air atmosphere at 40 °C for 30 min. The yields are of the isolated products. [a] **1** (0.5 mmol), **2** (1.0 equiv), $Pd(OAc)_2$ (10 mol%) and solvent (2.0 mL) under air atmosphere at 40 °C for 1h. The yields are of the isolated products

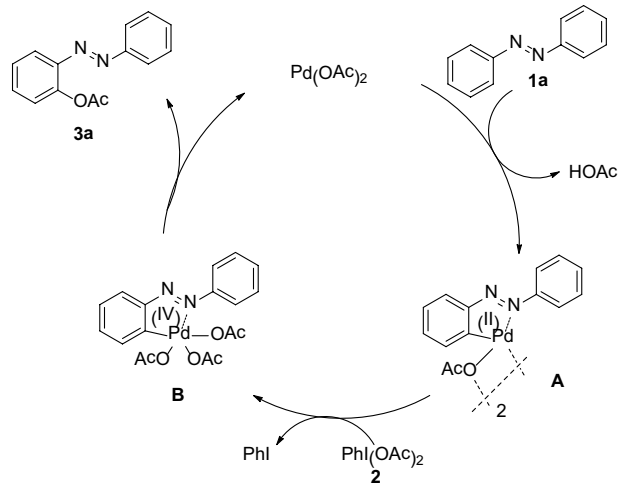
Furthermore, the reactions of unsymmetrical azobenzenes also proceeded smoothly and gave the products which could be determined by ^1H NMR, were obtained in good yields (84% for **3k**; 86% for **3l**, respectively). Next, we were interested in examining the 2 equivalent of iodobenzene diacetate (**2**) and extend the duration to 1 hours, the reactions only delivered corresponding products of **3m** and 3**n** in lower yields (47 and 31%) (Scheme 3).

Furthermore, we find an important method to synthesis of2-hydroxyazobenzene by hydrolysis reaction of the above-product at room temperature.

On the basis of previous related studies [55–60] and these results we obtained, a plausible reaction mechanism of this direct ortho C–O bond construction of an azobenzenes with iodobenzene diacetate via C–H activation is proposed, as



Scheme 2 Hydrolysis reaction



Scheme 3 Plausible reaction mechanism

shown in Scheme 1. Step (i), coordination of the nitrogen atom in azobenzene (**1a**) with palladium(II) species triggers cyclopalladation to form a five-membered cyclopalladated(II) intermediate **A**. In step (ii), the cyclopalladated(II) intermediate **A** would then be oxidized to Pd (IV) species **B** by $PhI(OAc)_2$(**2**). In step (iii), the final product **3a** would be obtained via reductive elimination of **B**. Meanwhile, the Pd(II) was regenerated for the next catalytic cycle.

3 Conclusions

In conclusion, we have developed a palladium-catalyzed direct $C(sp^2)$–H acyloxylation of aromatic azo compounds with $PhI(OAc)_2$. This novel method provides a convenient method for the syntheses of various ortho-acyloxylated azoarenes from commercially available materials under mild reaction conditions. And also we can get 2-hydroxyazobenzenes or o-aminophenol through hydrolysis reaction of the ortho-acyloxylated azoarenes.

4 Experimental Section

4.1 General Information

All reactions were run under argon in Schlenk tubes using vacuum lines. HOAc, CH_3CN, DMF, DMSO, and EtOH, analytical grade were not distilled before use. Commercial $PhI(OAc)_2$ and azobenzenes were used without purification. ^1H NMR, ^{13}C NMR spectra were recorded using a 500 MHz spectrometer in $CDCl_3$ and DMSO with shifts referenced to $SiMe_4$ (δ=0). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a CHN analyzer. Mass spectra were recorded using LC–MS and HRMS (ESI-TOF analyzer) equipment.

4.2 General procedure for Palladium-Catalyzed Direct Ortho C–O bond construction of an Azobenzenes with Iodobenzene diacetate via C–H Activation

Mix azoic compound (0.5equiv), $PhI(OAc)_2$ (0.5equiv), $Pd(OAc)_2$ (10 mol%) in HFIP (2 ml) under atmosphere. The reaction mixture was vigorously stirred at 40 °C for 30 min. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford corresponding product.

4.2.1 (E)-2-(phenyldiazenyl)phenyl acetate (3a)

Obtained as an orange liquid in 95% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.73 (dd, J=8.1, 1.6 Hz, 1H), 7.44–7.38 (m, 4H), 7.28–7.23 (m, 1H), 7.17–7.14 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.61, 152.84, 148.98, 143.97, 132.09, 131.38, 129.12, 126.59, 123.35, 123.01, 117.67, 20.78. HRMS (ESI+): Calculated for $C_{14}H_{13}N_2O_2$: $[M+H]^+$ 241.0977, Found 241.0952.

4.2.2 (E)-5-methyl-2-(p-tolyldiazenyl)phenyl acetate(3b)

Obtained as an orange liquid in 92% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.64 (dd, J=11.7, 8.3Hz, 3H), 7.19 (d, J=8.2Hz, 2H), 7.03 (dd, J=8.2, 1.1 Hz, 1H), 6.94 (s, 1H), 2.32 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.67, 149.99, 147.68, 141.77, 140.83, 140.59, 128.66, 126.33, 122.60, 121.82, 116.38, 20.45, 20.40, 19.71. HRMS (ESI+): Calculated for $C_{16}H_{16}N_2O_2$: $[M+H]^+$ 269.1290, Found 269.1267.

4.2.3 (E)-4-methyl-2-(m-tolyldiazenyl)phenyl acetate(3c)

Obtained as an orange liquid in 90% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.68–7.63 (m, 2H), 7.60 (d, J=1.4 Hz, 1H), 7.38 (dd, J=13.0, 5.4 Hz, 1H), 7.30–7.26 (m, 2H), 7.13–7.09 (m, 1H), 2.43 (d, J=3.7 Hz, 3H), 2.40 (s, 3H), 2.37 (d, J=3.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.83, 152.98, 146.76, 143.55, 138.95, 136.51, 132.66, 132.06, 128.91, 123.63, 122.96, 120.11, 117.86, 21.40, 21.04, 20.77. HRMS (ESI+): Calculated for $C_{16}H_{16}N_2O_2$: $[M+H]^+$ 269.1290, Found 269.1253.

4.2.4 (E)-5-ethyl-2-((4-ethylphenyl)diazenyl)phenyl acetate(3d)

Obtained as an orange liquid in 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92–7.82 (m, 2H), 7.79–7.72 (m, 3H), 7.31 (d, J = 8.4 Hz, 2H), 2.72 (d, J = 7.6 Hz, 4 H), 2.39 (s, 3H), 1.28 (dd, J = 2.5, 1.1 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.72, 151.15, 149.01, 148.85, 128.57, 128.52, 126.76, 126.17, 122.96, 122.36, 117.51, 20.80, 15.42, 14.99. HRMS (ESI+): Calculated for $C_{18}H_{20}N_2O_2$: $[M+H]^+$ 297.1603, Found 297.1583.

4.2.5 (E)-5-isopropyl-2-((4-isopropylphenyl)diazenyl) phenyl acetate(3e)

Obtained as an orange liquid in 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3Hz, 2H), 7.66 (d, J = 8.3Hz, 1 H), 7.26 (d, J = 8.3Hz, 2H), 7.11 (dd, J = 8.3, 1.7 Hz, 1 H), 7.00 (d, J = 1.5 Hz, 1 H), 2.94–2.85 (m, 2H), 2.31 (s, 3H), 1.21 (dd, J = 6.9, 2.1 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.64, 152.58, 151.39, 150.31, 147.83, 141.06, 126.04, 123.75, 121.92, 119.90, 116.48, 33.12, 33.01, 22.82, 22.63, 19.76. HRMS (ESI+): Calculated for $C_{20}H_{24}N_2O_2$: $[M+H]^+$ 325.1916, Found 325.1871.

4.2.6 (E)-2-((3,5-dimethylphenyl) diazenyl)-4,6-dimethylphenyl acetate(3 f)

Obtained as an orange liquid in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.40 (d, J = 0.8 Hz, 1 H), 7.17 (dd, J = 1.3, 0.6 Hz, 1 H), 7.11 (s, 1 H), 2.40 (d, J = 2.4 Hz, 9 H), 2.36 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.54, 153.14, 145.49, 143.70, 138.66, 135.86, 134.11, 132.83, 131.34, 120.76, 115.32, 21.29, 21.00, 20.55, 15.89. HRMS (ESI+): Calculated for $C_{18}H_{20}N_2O_2$: $[M+H]^+$ 297.1603, Found 297.1578.

4.2.7 (E)-4-methoxy-2-((3-methoxyphenyl)diazenyl)phenyl acetate(3 g)

Obtained as an orange liquid in 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, J = 7.8, 1.4, 1.0 Hz, 1H), 7.43–7.37 (m, 2H), 7.34 (d, J = 3.0 Hz, 1H), 7.15 (d, J = 8.9 Hz, 1H), 7.08–7.02 (m, 2H), 3.87 (d, J = 6.6 Hz, 6H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.95, 160.27, 157.90, 153.97, 144.06, 143.12, 129.81, 123.93, 119.15, 118.03, 117.14, 106.21, 100.77, 55.83, 55.39, 20.70. HRMS (ESI+): Calculated for $C_{16}H_{16}N_2O_4$: $[M+H]^+$ 301.1188, Found 301.1158.

4.2.8 (E)-5-methoxy-2-((4-methoxyphenyl)diazenyl)phenyl acetate(3h)

Obtained as an orange liquid in 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.85 (m, 2H), 7.83 (dd, J = 8.7, 2.3Hz, 1 H), 7.65 (d, J = 2.3Hz, 1H), 7.09–7.05 (m, 1H), 7.02–6.97 (m, 2H), 3.89 (d, J = 14.7 Hz, 6H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.88, 161.81, 153.07, 146.90, 146.78, 140.24, 124.52, 124.31, 115.04, 114.21, 111.79, 56.16, 55.58, 20.68. HRMS (ESI+): Calculated for $C_{16}H_{16}N_2O_4$: $[M+H]^+$ 301.1188, Found 301.1163.

4.2.9 (E)-5-ethoxy-2-((4-ethoxyphenyl)diazenyl)phenyl acetate(3i)

Obtained as an orange liquid in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.83 (m, 2H), 7.80 (dt, J = 5.2, 2.6 Hz, 1H), 7.65 (t, J = 2.4 Hz, 1H), 7.06–7.03 (m, 1 H), 6.99–6.96 (m, 2H), 4.12 (dd, J = 13.8, 6.9 Hz, 4H), 2.34 (d, J = 4.5 Hz, 3H), 1.44 (dd, J = 7.0, 3.8 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.24, 152.46, 146.74, 146.61, 146.56, 140.48, 124.54, 124.18, 115.02, 114.68, 112.66, 64.61, 63.81, 20.60, 14.78, 14.67. HRMS (ESI+): Calculated for $C_{18}H_{20}N_2O_4$: $[M+H]^+$ 329.1501, Found 329.1461.

4.2.10 (E)-5-chloro-2-((4-chlorophenyl)diazenyl)phenyl acetate(3j)

Obtained as an orange liquid in 40% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.68 (m, 3H), 7.44–7.39 (m, 3H), 7.25 (dd, J = 8.7, 2.2Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.99, 158.08, 153.76, 149.80, 141.24, 137.65, 128.44, 125.98, 123.21, 122.86, 117.47, 19.63. HRMS (ESI+): Calculated for $C_{14}H_{10}Cl_2N_2O_2$: $[M+H]^+$ 309.0198, Found 309.0154.

4.2.11 (E)-5-methoxy-2-(m-tolyldiazenyl)phenyl acetate(3k)

Obtained as an orange liquid in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.47 (m, 2H), 7.42–7.31 (m, 2H), 7.31–7.26 (m, 1H), 7.13 (dd, J = 11.0, 8.5 Hz, 1H), 7.06–7.00 (m, 1H), 3.85 (d, J = 7.7 Hz, 3H), 2.39 (dd, J = 23.3, 11.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.54, 157.85, 146.72, 137.18, 131.97, 129.18, 123.33, 120.27, 117.81, 116.87, 106.08, 55.01, 21.13, 20.49. HRMS (ESI+): Calculated for $C_{16}H_{16}N_2O_3$: $[M+H]^+$ 285.1239, Found 285.1203.

4.2.12 (E)-5-methoxy-2-(phenyldiazenyl)phenyl acetate(3l)

Obtained as an orange liquid in 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.84 (m, 1H), 7.52–7.49 (m,

2H), 7.44–7.37 (m, 1 H), 7.37–7.32 (m, 1H), 7.26–7.14 (m, 2H), 7.08–7.03 (m, 1 H), 3.87 (d, J = 6.3Hz, 3H), 2.39 (d, J = 5.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.02, 160.26, 157.88, 132.14, 131.40, 129.11, 123.94, 123.33, 123.04, 119.07, 100.77, 55.83, 20.73. HRMS (ESI+): Calculated for $C_{15}H_{14}N_2O_3$: $[M+H]^+$ 271.1083, Found 271.1044.

4.2.13 (E)-2-(phenyldiazenyl)-1,3-phenylene diacetate(3 m)

Obtained as an orange solid in 47% yield; M.p. 40–41 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.74 (m, 2H), 7.51–7.48 (m, 3H), 7.42 (dd, J = 10.6, 5.8 Hz, 1H), 7.12 (d, J = 8.2Hz, 2H), 2.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.07, 153.20, 144.77, 136.62, 131.74, 130.53, 129.21, 122.62, 121.68, 20.80. HRMS (ESI+): Calculated for $C_{16}H_{14}N_2O_4$: $[M+H]^+$ 299.1032, Found 299.1003.

4.2.14 (E)-5-ethoxy-2-((4-ethoxyphenyl) diazenyl)-1,3-phenylene diacetate(3n)

Obtained as an orange solid in 31% yield; M.p. 50–51 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.71 (m, 2H), 7.50 (s, 1H), 7.18 (s, 1H), 6.93–6.87 (m, 2H), 4.06–4.00 (m, 4H), 2.27 (d, J = 10.6 Hz, 6H), 1.37 (dd, J = 9.2, 4.7 Hz, 3H), 1.27 (dd, J = 9.0, 5.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.55, 160.70, 146.80, 145.50, 143.88, 143.57, 123.87, 114.36, 113.69, 111.37, 68.88, 62.82, 28.68, 19.74. HRMS (ESI+): Calculated for $C_{20}H_{22}N_2O_6$: $[M+H]^+$ 387.1556, Found 387.1527.

4.2.15 (E)-methyl 3-acetoxy-4-((4-(methoxycarbonyl) phenyl) diazenyl)benzoate(3o)

Obtained as a light-red solid in 73% yield; M.p. 143–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4, 2H), 8.03 (d, J = 8.4, 1H), 7.89–7.94 (m, 3H), 7.84 (d, J = 8.4, 1 H), 3.96 (s, 6H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.27, 166.32, 165.57, 155.10, 148.90, 146.53, 133.77, 132.71, 130.70, 127.83, 125.98, 125.05, 124.11, 122.98, 125.05, 124.11, 122.98, 117.59, 52.59, 52.44, 20.66. HRMS (ESI+): Calculated for $C_{18}H_{16}N_2O_6$: $[M+H]^+$ 357.1087, Found 357.1085.

4.2.16 (E)-2-(phenyldiazenyl)phenol (4)

Obtained as an orange solid in 91% yield; M.p. 82–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.94 (s, 1H), 7.95 (d, J = 10 Hz, 1H), 7.88 (d, J = 5 Hz, 2H), 7.48–7.54 (m, 3H), 7.35 (t, J = 10 Hz, 1H), 7.02–7.09 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.80, 150.54, 137.38, 133.30, 133.27, 131.20, 129.38, 122.27, 119.95, 118.22.

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