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Palladium(II)-Catalyzed Direct Regioselectively Oxidative Acylation of Azobenzenes with Toluene Derivatives

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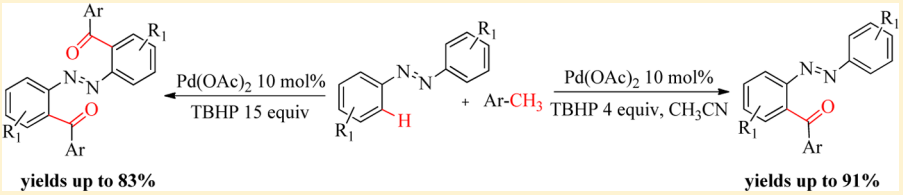
Supporting Information



ABSTRACT: A highly efficient and practical procedure to acylazobenzene via Pd-catalyzed oxidative C−H bond activation from toluene has been developed. Various mono- and diacylazobenzene were afforded simultaneously in moderate to excellent yields for 33 examples. Toluene and its derivatives were served as potential and ideal acylation reagents. The mono- and diacylated products could be controlled by the oxidant loading.

INTRODUCTION

Acylazobenzene and its derivatives are ubiquitous motifs and have been widely applied in the fields of functional advanced materials, chemical sensors, pharmaceuticals, food additives, and industrial dyes.[1] However, the process of building such a structure has lagged behind. Only several impressive examples have emerged in the recent two years. For instance, the research group of Wang developed the acylation of azobenzene by Pd-catalyzed oxidative coupling of azobenzenes with aldehydes using *tert*-butyl hydroperoxide (TBHP) as an oxidant via chelation-assisted ortho C−H bond activation.[2] Then, they further disclosed the palladium-catalyzed decarboxylative ortho-acylation of azobenzenes with α-oxocarboxylic acids.[3]

Remarkable progress has made on aldehydes, α-oxocarboxylic acids, or alcohol as a reactant for the acylation of aromatic compounds based on transition metal-catalyzed C−H activation.[4,5] Recently, great attention has been paid to the use of toluene and its derivatives as acylation reagents, due to its stability, low toxicity, and ample availability compared to those of aldehydes and α-oxocarboxylic acids. Patel,[6] Kwong,[7] Sun,[8] and Zhang[9] independently realized the regioselective acylation of 2-phenylpyridine and acetanilide with toluene derivatives to afford *o*-acyl-2-phenylpyridines and *o*-acylacetanilides. Recently, the Lu[10] group reported the acylation of azobenzene with toluene to afford acylated products. Herein, we present a highly efficient and regioselective acylation of azobenzenes with toluene and its derivatives catalyzed by palladium in the presence of TBHP, leading to a variety of acylazobenzenes. Both mono- and diacylazobenzene were obtained simultaneously. Further investigation revealed that TBHP loading contributed to the distribution of mono- and dibenzoylated products. To the best of our knowledge, this is the first case to access dibenzoylated azobenzenes via transition metal-catalyzed C−H bond activation.

RESULTS AND DISCUSSION

The condensation of azobenzene **1a** and toluene **2a** was initially chosen as a model reaction to screen the reaction parameters. The results are summarized in Table 1. The reaction was carried out in toluene at 80 °C with 10 mol % $Pd(OAc)_2$ as a catalyst and TBHP (4 equiv, 70% solution in water) as an oxidant. As expected, this protocol was feasible and the desired *o*-benzoylazobenzene **3a** was afforded in 49% yield (entry 1). When the reaction temperature was reduced, the yield was decreased to 38% (entry 2). Screening solvents revealed that CH_3CN and DCE were effective solvents (entries 3−4), while other solvents, such as DMSO, DMF, and dioxane turned out to be inferior in the model reaction (entries 5−7). When the mole ratio of toluene and CH_3CN was changed from 1/1 (v/v) to 3/1 (v/v), the yield was increased obviously and reached 80% (entry 8−9). It could be concluded that solvent played a crucial role, and CH_3CN proved to be the best solvent for this transformation. Furthermore, different Pd catalysts were also investigated, in which $Pd(OAc)_2$ exhibited the highest activity. Other Pd sources including $Pd(TFA)_2$ and $PdCl_2$ did not enhance the yield of product **3a** (entries 11 and 12). Further exploration on TBHP loading was also examined and indicated that 4 equiv of TBHP could bring the highest yield of 80%. Increasing the TBHP loading to 6 equiv or decreasing to 3

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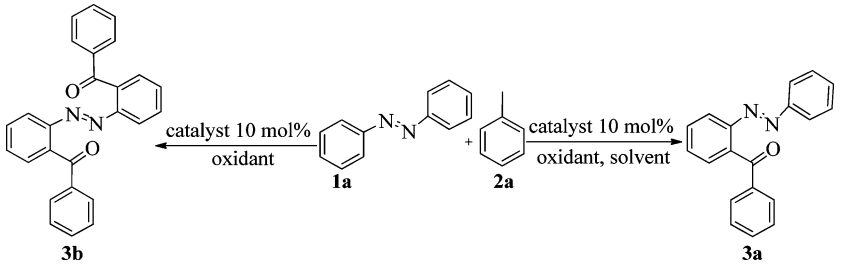
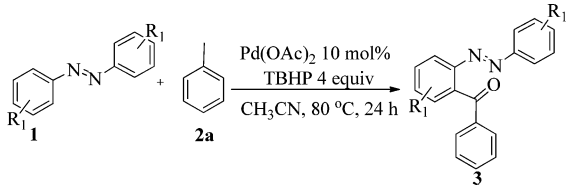
Table 1. Optimization of the reaction conditions for the condensation of azobenzene 1a with toluene 2a[a]

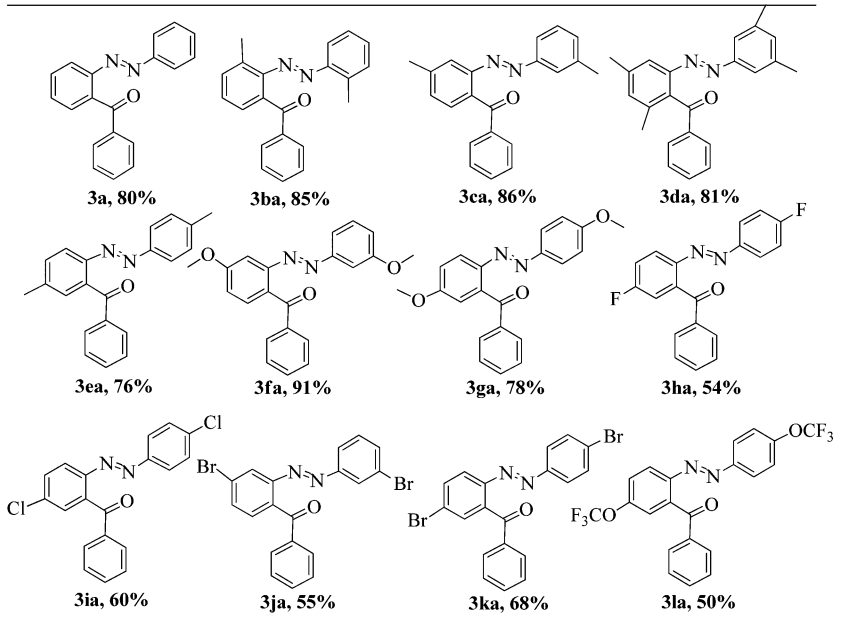


entry	catalyst	oxidant (equiv)	solvent (v/v)	T (°C)	yield (%)[b]
1	$Pd(OAc)_2$	TBHP (4)	$PhCH_3$	80	49
2	$Pd(OAc)_2$	TBHP (4)	$PhCH_3$	70	38
3	$Pd(OAc)_2$	TBHP (4)	$PhCH_3/CH_3CN$ (1:1)	80	70
4	$Pd(OAc)_2$	TBHP (4)	$PhCH_3$/DCE (1:1)	80	59
5	$Pd(OAc)_2$	TBHP (4)	$PhCH_3$/DMSO (1:1)	80	trace
6	$Pd(OAc)_2$	TBHP (4)	$PhCH_3$/DMF (1:1)	80	trace
7	$Pd(OAc)_2$	TBHP (4)	$PhCH_3$/dioxane (1:1)	80	trace
8	$Pd(OAc)_2$	TBHP (4)	$PhCH_3/CH_3CN$ (2:1)	80	65
9	**$Pd(OAc)_2$**	**TBHP (4)**	**$PhCH_3/CH_3CN$ (3:1)**	**80**	**80**
10	$Pd(OAc)_2$	TBHP (3)	$PhCH_3/CH_3CN$ (3:1)	80	57
11	$Pd(TFA)_2$	TBHP (4)	$PhCH_3/CH_3CN$ (3:1)	80	68
12	$PdCl_2$	TBHP (4)	$PhCH_3/CH_3CN$ (3:1)	80	55
13	$Pd(OAc)_2$	TBHP (5)	$PhCH_3/CH_3CN$ (3:1)	80	75
14	$Pd(OAc)_2$	TBHP (6)	$PhCH_3/CH_3CN$ (3:1)	80	67
15	**$Pd(OAc)_2$**	**TBHP (15)**	**$PhCH_3$**	**80**	**83**

[a]Reaction conditions: azobenzene **1a** (0.2 mmol), catalyst (10 mol %), TBHP (4 equiv), solvent (2 mL), 80 °C under air atmosphere for 24 h. [b]Isolated yields.

Table 2. Ortho-acylation of azobenzenes with toluene[a]





[a]Reaction conditions: azobenzene derivatives (0.2 mmol), toluene (1.5 mL), $Pd(OAc)_2$ (10 mol %), TBHP (4 equiv), CH_3CN (0.5 mL) at 80 °C under air atmosphere for 24 h.

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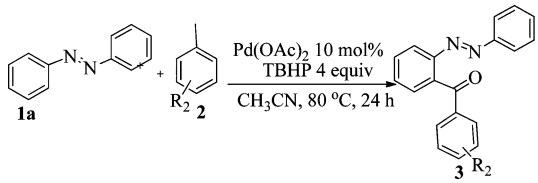
equiv could not improve the yield evidently (entries 10, 13, 14). Only monoacylated product **3a** was afforded under the above-mentioned reaction conditions. To our surprise, when the TBHP loading was increased to 15 equiv, a diacylated product **3b** was afforded in 83% yield (entry 15). Monoacylated product **3a** was not observed, while a trace amount of triacylated product was detected. These results indicated that the loading of TBHP contributed to the distribution of mono- and dibenzoylated products.

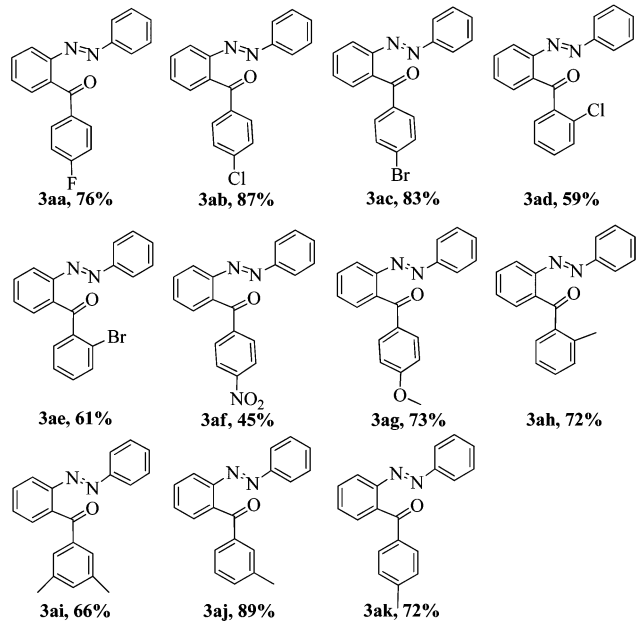
With the optimized reaction conditions in hand, the ortho-acylation of various azobenzenes with toluene was investigated and the results were summarized in Table 2. Moderate to excellent yields were obtained for most cases. In general, the azobenzenes with electron-donating groups gave higher yields than those with electron-withdrawing groups. Electron-rich azobenzenes, such as azobenzene, 2,2′-dimethylazobenzene, 3,3′-dimethylazobenzene, bis(3,5-dimethyl)-azobenzene, 4,4′-dimethylazobenzene, 3,3′-dimethoxyazobenzene, 4,4′-dimethoxyazobenzene provided the corresponding products in 76−91% yields (**3a**, **3ba**−**3ga**). Azobenzenes with electron-withdrawing groups, for example, 4,4′-difluoroazobenzene, 4,4′-dichloroazobenzene, 3,3′-dibromoazobenzene, and 4,4′-di-(trifluoromethoxy)azobenzene gave the desired products in 50−68% yields (**3ha**−**3la**). The strong electron-withdrawing group, such as NO_2, obviously restrained the reaction and could not afford the desired product under the standard reaction conditions. These results further demonstrated that the electron density of substrates played a more important role than the steric hindrance. No significant steric effect of the ortho- or meta-substituted azobenzene was found in the acylation reaction. 2,2′-Dimethylazobenzene, 3,3′-dimethylazobenzene, bis(3,5-dimethyl)azobenzene could give similar yields (**3a** vs **3ba**, **3ca**, **3da**). An excellent regioselectivity was found for the meta-substituted azobenzenes (**3ca**, **3fa**, **3ja**), in which the acylation reaction only occurred at the para-position of the substituent group, largely due to the steric hindrance.

Next, we tested the scope of the toluene derivatives as the acylation reagents (Table 3). Both electron-deficient (such as F, Cl, Br; **3aa**−**3af**) and electron-rich (such as CH_3O, CH_3; **3ag**−**3ak**) toluene derivatives could proceed smoothly and afford the corresponding acylated products in moderate to good yields. This transformation was slightly affected by the steric hindrance. Toluene substituted at the para-position gave higher yields than those with ortho-substituted groups. For examples, 4-chlorotoluene and 4-bromotoluene gave 87% and 83% yields respectively, while 2-chlorotoluene, 2-bromotoluene only gave 59% and 61% yields (**3ab** vs **3ad** and **3ac** vs **3ae**). To our delight, halo groups (F, Cl, Br) on the aromatic ring remained intact in the products, which provided the possibility for the further useful transformations (**3aa**−**3ae**). It is worth noting that the reaction only took place on one methyl group and the other one still remained (such as mesitylene, xylene; **3aj**, **3ak**) because the oxidation of one methyl to the carbonyl group slows down the oxidation of the second methyl group.

Then, we investigated the diacylation reaction of azobenzene (**1a**) with toluene (**2a**). The substrate scope was also tested, and the results are shown in Table 4. When the loading of TBHP was increased to 15 equiv, a diacylazobenzene was formed. Azobenzene derivatives substituted with weakly electron-withdrawing or electron-donating groups could give moderate to good yields. An amazing phenomenon was discovered wherein azobenzenes substituted with electron-withdrawing groups mainly afforded diacylazobenzenes (such as

Table 3. Ortho-acylation of azobenzene with toluene derivatives[a]





[a]Reaction conditions: azobenzene (**1a**, 0.2 mmol), toluene derivatives (1.5 mL), $Pd(OAc)_2$ (10 mol %), TBHP (4 equiv), CH_3CN (0.5 mL) at 80 °C under air atmosphere for 24 h.

F, Cl; **3m**, **3n**) and triacylazobenzenes were obtained as main products for those with electron-donating groups (such as CH_3, CH_3O; **3r**, **3s**, **3t**, **3u**). The molecular structure of the diacylated product (**3o**) was further confirmed by single-crystal X-ray diffraction analysis,[11] and the configuration is shown in Figure 1 in the Supporting Information.

To clarify the reaction mechanism, some controlled experiments were carried out under the optimized conditions as follows: (1) By adding a radical scavenger (ascorbic acid) to the reaction,[12] this reaction was inhibited, and the rate of reactions was greatly suppressed. Only a trace amount of the desired product was detected (Scheme 1a). (2) Benzaldehyde was obtained in 7% yield from the oxidization of toluene under the standard reaction condition in the absence of palladium catalyst and azobenzene (Scheme 1b). 3) With the use of benzaldehyde as an acylation reagent instead of toluene under the standard reaction conditions, the desired product **3a** was obtained in 45% yield, and benzoic acid was detected (Scheme 1c). Part of benzaldehyde **2b** was oxidated into benzoic acid, whereas toluene gave higher yield, and an unwanted side reaction was prevented under the same reaction conditions. Moreover, toluene and its derivatives are less toxic and more easily available compared to benzaldehyde. In view of the above merits, toluene was used as an ideal and efficient acylation reagent. The results obtained demonstrated that a radical process was involved in the catalytic system and that the azobenzene reacted with the benzoyl radical rather than the benzyl radical.

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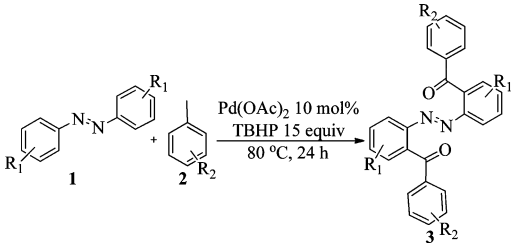
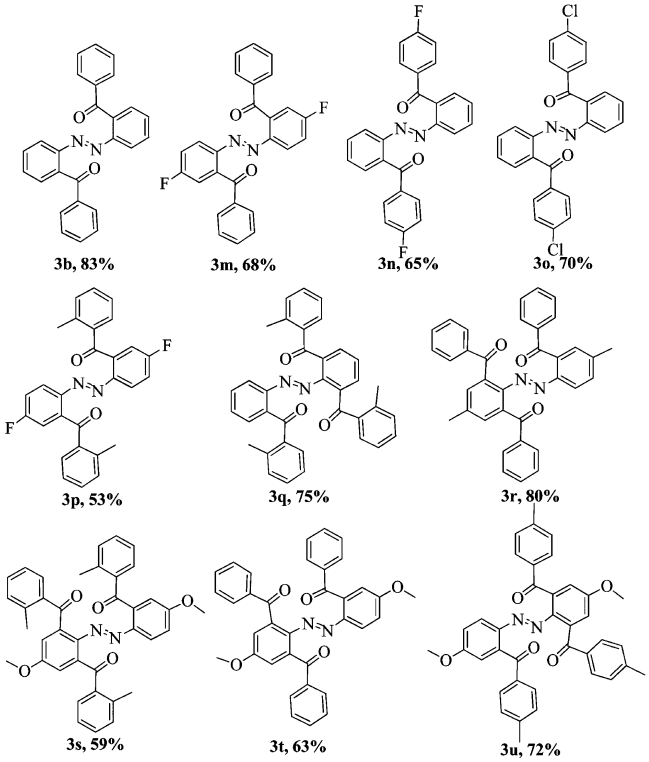
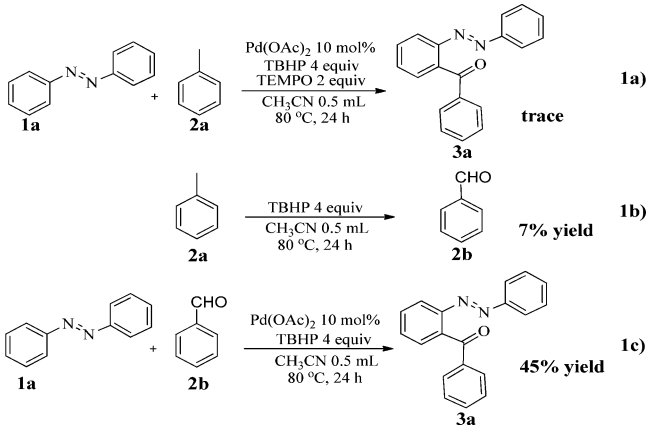
Table 4. Multi-acylation of azobenzenes with toluene derivatives[a]





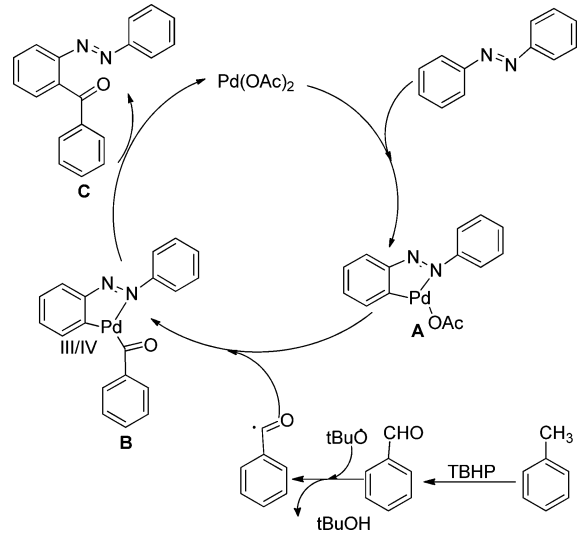
[a]Reaction conditions: azobenzene derivatives (**1a**, 0.2 mmol), toluene derivatives (**2a**, 2 mL), $Pd(OAc)_2$ (10 mol %), TBHP (3 mmol) at 80 °C under air atmosphere for 24 h.

Scheme 1. Controlled experiments



On the basis of these results we obtained and found in the literature[3,13] a plausible reaction mechanism that was proposed and is shown in Scheme 2. First, $Pd(OAc)_2$ reacted with azobenzene by chelation-directed C−H bond activation to form

Scheme 2. Proposed reaction mechanism for Pd(II)-catalyzed acylation of azobenzene



a five-membered cyclopalladated intermediate **A**,[9,14] which has been confirmed by previous research.[7f] Then the palladacycle **A** reacted with the benzoyl radical,[15] which was formed *in situ* from the oxidation of toluene, and produced the dimeric Pd(III)[16] or reactive Pd(IV)[17] species **B**. Finally, the intermediate **B** underwent reductive elimination and provided the acylazobenzene **C**. Meanwhile, the Pd(II) was regenerated for the next catalytic cycle.

CONCLUSIONS

In summary, we have developed a highly efficient protocol to synthesize *o*-acylazobenzenes through the Pd(II)-catalyzed C−H bond activation of azobenzenes with toluene derivatives. Toluene could be used as an ideal acylation reagent in this transformation. Meanwhile, diacylazobenzenes were obtained when TBHP loading was increased. Moreover, the mild reaction conditions together with operational simplicity would provide an unprecedented capacity in the installation of various versatile functional groups at various positions of the azobenzene. It could be applied to the synthesis of natural products and other available compounds.

EXPERIMENTAL SECTION

General Procedure for Preparation of Azobenzenes. Arylamine (1.0 mmol), CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), and toluene (4 mL) were added together. The mixture was stirred at 60 °C under air (1 atm) for 20 h, then cooled down to room temperature. The volatiles were removed under reduced pressure. The residue was purified by flash chromatography on a short silica gel using petroleum ether/ethyl acetate (v/v = 50:1) to afford the azobenzene and its derivatives.

Typical Procedure for the Acylation of Azobenzenes. The mixture of azobenzene (**1a**, 36.4 mg, 0.20 mmol), toluene (**2a**, 1.5 mL). $Pd(OAc)_2$ (4.6 mg, 0.02 mmol), TBHP (4 equiv, 0.8 mmol), and anhydrous CH_3CN (0.5 mL) was stirred at 80 °C for 24 h and then cooled down to room temperature. The volatiles were removed under reduced pressure, and the residue was purified by a flash column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 20:1) to give the corresponding monoacylated product.

The mixture of azobenzene (**1a**, 36.4 mg, 0.20 mmol), toluene (**2a**, 2 mL), $Pd(OAc)_2$ (4.6 mg, 0.02 mmol), and TBHP (15 equiv, 3 mmol) was stirred at 80 °C for 24 h and then cooled down to room temperature. The volatiles were removed under reduced pressure. The

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residue was purified by a flash column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 7:1 or 4:1) to give the diacylated product.

(*E*)-Phenyl(2-(phenyldiazenyl)phenyl)methanone 3a: red oil (46 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.9 Hz, 1H), 7.82−7.78 (m, 2H), 7.67−7.63 (m, 1H), 7.60−7.58 (m, 2H), 7.50−7.44 (m, 3H), 7.39−7.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 151.0, 149.3, 137.4, 135.9, 131.8, 130.4, 129.9, 129.8, 128.4, 127.9, 127.8, 127.3, 121.9, 119.1, 76.4, 76.1, 75.8. HRMS (ESI) Calcd For $C_{19}H_{14}N_2O$: $[M + H]^+$, 286.1106, Found: 286.1108.

(*E*)-(4-Fluorophenyl)(2-(phenyldiazenyl)phenyl)methanone 3aa: red solid (46 mg, 76%), mp 93−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.8 Hz, 1H), 7.82−7.77 (m, 2H), 7.68−7.64 (m, 1H), 7.61−7.55 (m, 2H), 7.49−7.46 (m, 2H), 7.41−7.33 (m, 3H), 7.06−7.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 165.9 (d, J_{C-F} = 253.1 Hz), 152.4, 150.7, 136.9, 135.3 (d, J_{C-F} = 3.0 Hz), 132.4 (d, J_{C-F} = 9.3 Hz), 131.9, 131.3 (d, J_{C-F} = 3.6 Hz), 129.4, 129.1, 123.3, 120.7, 115.9 (d, J_{C-F} = 21.8 Hz). IR (KBr): 3441, 3134, 2925, 2852, 1742, 1667, 1598, 1505, 1401, 1287, 1237, 1147, 1097, 932, 851, 774, 688, 603 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{13}FN_2O$: $[M + H]^+$, 305.1085, Found: 305.1088.

(*E*)-(4-Chlorophenyl)(2-(phenyldiazenyl)phenyl)methanone 3ab: red solid (56 mg, 87%), mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96−7.94 (m, 1H), 7.72−7.69 (m, 2H), 7.67−7.63 (m, 1H), 7.60−7.54 (m, 2H), 7.47−7.44 (m, 2H), 7.38−7.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 152.3, 150.7, 139.6, 137.2, 136.6, 132.0, 131.4, 131.4, 131.1, 129.4, 129.1, 123.3, 121.0. IR (KBr): 3442, 3142, 2920, 2851, 1663, 1585, 1399, 1287, 1252, 1091, 1014, 931, 846, 775, 745, 692, 549 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{13}ClN_2O$: $[M + H]^+$, 321.0789, Found: 321.0790.

(*E*)-(4-Bromophenyl)(2-(phenyldiazenyl)phenyl)methanone 3ac: red solid (60 mg, 83%), mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.5 Hz, 1H), 7.68−7.66 (m, 1H), 7.65−7.64 (m, 1H), 7.63−7.62 (m, 1H), 7.59−7.54 (m, 2H), 7.52−7.50 (m, 2H), 7.47−7.45 (m, 2H), 7.39−7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 152.3, 150.7, 137.7, 136.5, 132.1, 132.0, 131.5, 131.4, 131.3, 131.2, 129.5, 129.4, 129.4, 129.4, 129.1, 128.3, 123.3, 121.0. IR (KBr): 3433, 3135, 2923, 2851, 1668, 1584, 1397, 1286, 1256, 1067, 1011, 929, 844, 760, 692, 639, 548, 533 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{13}BrN_2O$: $[M + H]^+$, 365.0284, Found: 365.0286.

(*E*)-(2-Chlorophenyl)(2-(phenyldiazenyl)phenyl)methanone 3ad: red oil (38 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7,83 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.67−7.64 (m, 1H), 7.61−7.57 (m, 1H), 7.55−7.53 (m, 1H), 7.41−7.37 (m. 3H), 7.35−7.29 (m, 4H), 7.27−7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 152.2, 151.0, 139.9, 137.0, 132.4, 132.2, 131.8, 131.5, 130.9, 130.7, 130.6, 130.0, 128.8, 126.6, 123.2, 117.7. IR (KBr): 3441, 3134, 2920, 2851, 1742, 1671, 1470, 1435, 1401, 1300, 1240, 1150, 1059, 1038, 930, 774, 743, 687, 630, 551 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{13}ClN_2O$: $[M + H]^+$, 321.0789, Found: 321.0790.

(*E*)-(2-Bromophenyl)(2-(phenyldiazenyl)phenyl)methanone 3ae: red oil (44 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, J = 7.6 Hz, J = 1.1 Hz, 1H), 7.73−7.71 (m, 1H), 7.68−7.64 (m, 1H), 7.61−7.57 (m, 1H), 7.54−7.51 (m, 1H), 7.47 (dd, J = 7.7 Hz, J = 1.7 Hz, 1H), 7.43−7.27 (m, 6H), 7.22−7.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 152.3, 151.2, 141.8, 136.5, 133.9, 132.6, 131.7, 131.5, 130.8, 130.8, 130.4, 128.8, 127.2, 123.3, 120.4, 117.5. IR (KBr): 3435, 3135, 2919, 2851, 1741, 1671, 1587, 1432, 1401, 1299, 1240, 930, 774, 687, 629 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{13}BrN_2O$: $[M + H]^+$, 365.0284, Found: 365.0286.

(*E*)-(4-Nitrophenyl)(2-(phenyldiazenyl)phenyl)methanone 3af: red solid (30 mg, 45%), mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, J = 8.8 Hz, 2H), 8.00 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.76−7.72 (m, 1H), 7.67−7.60 (m, 2H), 7.42−7.31 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 151.7, 150.8, 150.1, 143.5, 134.7, 132.2, 132.2, 131.5, 130.1, 129.3, 129.2, 123.9, 123.0, 122.4. IR (KBr): 3442, 3134, 2922, 2852, 2360, 2341, 1743, 1661, 1603, 1592, 1522, 1401, 1344, 1291, 1244, 1014, 832, 861, 778, 710, 683, 668 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{13}N_3O_3$: $[M + H]^+$, 332.1030, Found: 332.1029.

(*E*)-(4-Methoxyphenyl)(2-(phenyldiazenyl)phenyl)methanone 3ag: red oil (46 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7,64−7.60 (m, 1H), 7.59−7.50 (m, 4H), 7.38−7.35 (m, 3H), 6.86 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 162.4, 151.2, 149.2, 136.8, 131.0, 130.3, 129.8, 129.5, 128.0, 127.6, 122.0, 118.4, 112.6, 54.5. IR (KBr): 3441, 3145, 2920, 2851, 1741, 1660, 1600, 1401, 1257, 1176, 1147, 1029, 932, 846, 775, 690, 609, 561 cm^{-1}. HRMS (ESI) Calcd For $C_{20}H_{16}N_2O_2$: $[M + H]^+$, 317.1285, Found: 317.1285.

(*E*)-(2-(Phenyldiazenyl)phenyl)(*o*-tolyl)methanone 3ah: red oil (43 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.9 Hz, 1H), 7.69 (dd, J = 7.3 Hz, J = 1.2 Hz, 1H), 7.64−7.55 (m, 2H), 7.40−7.33 (m, 5H), 7.27 (t, J = 7.3 Hz, 2H), 7.20 (d, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 152.8, 151.2, 139.5, 138.8, 138.6, 131.9, 131.8, 131.7, 131.6, 131.1, 131.1, 129.8, 129.2, 125.8, 123.3, 119.3, 21.6. IR (KBr): 3438, 3135, 2927, 2852, 1742, 1665, 1401, 1301, 1245, 1161, 928, 774, 731, 689, 635 cm^{-1}. HRMS (ESI) Calcd For $C_{20}H_{16}N_2O$: $[M + Na]^+$, 323.1155, Found: 323.1155.

(*E*)-(3,5-Dimethylphenyl)(2-(phenyldiazenyl)phenyl)methanone 3ai: red oil (41 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.8 Hz, 1H), 7.66−7.62 (m, 1H), 7.60−7.54 (m, 2H), 7.50 (dd, J = 7.7 Hz, J = 1.4 Hz, 2H), 7.38−7.34 (m, 5H), 7.12 (s, 1H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 151.2, 149.5, 137.6, 137.0, 136.5, 133.5, 130.3, 129.7, 129.7, 127.9, 127.7, 126.3, 122.0, 118.7, 20.2. IR (KBr): 3448, 3158, 2923, 2853, 1742, 1662, 1596, 1580, 1447, 1401, 1313, 1284, 1225, 1151, 925, 888, 833, 774, 704, 698, 675, 600 cm^{-1}. HRMS (ESI) Calcd For $C_{21}H_{18}N_2O$: $[M + H]^+$, 315.1492, Found: 315.1496.

(*E*)-(2-(Phenyldiazenyl)phenyl)(*m*-tolyl)methanone 3aj: red oil (53 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.0 Hz, 1H), 7.66−7.62 (m, 2H), 7.58 (d, J = 4.2 Hz, 2H), 7.53 (d, J = 7.5 Hz, 1H), 7.47 (dd, J = 4.8 Hz, J = 1.3 Hz, 2H), 7.37−7.33 (m, 3H), 7.29−7.23 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 152.5, 150.8, 138.9, 138.5, 137.6, 134.0, 131.7, 131.2, 131.1, 130.2, 129.3, 129.2, 128.6, 127.3, 123.3, 120.3, 21.6. IR (KBr): 3441, 3133, 2919, 2851, 1742, 1667, 1602, 1586, 1401, 1294, 1258, 961, 775, 724, 686, 636 cm^{-1}. HRMS (ESI) Calcd For $C_{20}H_{16}N_2O$: $[M + Na]^+$, 323.1155, Found: 323.1158.

(*E*)-(2-(Phenyldiazenyl)phenyl)(*p*-tolyl)methanone 3ak: red oil (43 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.66−7.61 (m, 1H), 7.59−7.56 (m, 2H), 7.49−7.47 (m, 2H), 7.37−7.31 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 152.5, 150.7, 144.0, 137.8, 136.3, 131.7, 131.2, 131.0, 130.0, 129.5, 129.3, 129.0, 123.3, 120.1, 22.1. IR (KBr): 3442, 3133, 2920, 2851, 2360, 1743, 1664, 1606, 1401, 1312, 1295, 1252, 1181, 1147, 930, 837, 774, 732, 688, 605 cm^{-1}. HRMS (ESI) Calcd For $C_{20}H_{16}N_2O$: $[M + Na]^+$, 323.1155, Found: 323.1159.

(*E*)-(3-Methyl-2-(*o*-tolyldiazenyl)phenyl)(phenyl)methanone 3ba: red solid (53 mg, 85%), mp 75−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.7 Hz, 2H), 7.49−7.41 (m, 2H), 7.37 (t, J = 14.7 Hz, 1H), 7.32−7.21 (m, 5H), 7.15 (d, J = 7.4 Hz, 1H), 7.08 (t, J = 15.2 Hz, 1H), 2.77 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 150.6, 150.5, 139.4, 138.5, 134.6, 132.9, 132.9, 131.7, 131.6, 130.3, 129.4, 128.6, 126.9, 126.4, 126.0, 116.0, 18.8, 17.7. IR (KBr): 3435, 3150, 2920, 2851, 1665, 1597, 1401, 1316, 1280, 1156, 774, 712, 693, 678, 651 cm^{-1}. HRMS (ESI) Calcd For $C_{21}H_{18}N_2O$: $[M + H]^+$, 315.1482, Found: 315.1496.

(*E*)-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)(phenyl)methanone 3ca: red solid (54 mg, 86%), mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.7 Hz, 1H), 7.54−7.47 (m, 1H), 7.40−7.37 (m, 3H), 7.30−7.28 (m, 1H), 7.24−7.18 (m, 2H), 7.14 (s, 1H), 2.55 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 152.7, 150.9, 141.9, 139.7, 139.1, 134.8, 132.9, 132.4, 131.9, 129.8, 129.5, 129.1, 128.6, 123.0, 121.3, 120.0, 21.9, 21.6. IR (KBr): 3434, 3134, 2923, 2853, 1742, 1655, 1603, 1578, 1447, 1401, 1315, 1289, 1254, 1155, 905, 832, 802, 751, 709, 688, 614 cm^{-1}. HRMS (ESI) Calcd For $C_{21}H_{18}N_2O$: $[M + H]^+$, 315.1492, Found: 315.1496.

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(*E*)-(2-((3,5-Dimethylphenyl)diazenyl)-4,6-dimethylphenyl)(phenyl)methanone 3da: red solid (55 mg, 81%), mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81−7.79 (m, 2H), 7.56 (s, 1H), 7.48 (d, J = 7.2 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.22 (s, 1H), 7.00 (d, J = 12.0 Hz, 3H), 2.46 (s, 3H), 2.29 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 152.6, 150.4, 140.0, 139.1, 138.7, 136.6, 135.4, 134.1, 133.1, 133.0, 129.3, 128.7, 120.9, 116.7, 21.6, 21.4, 19.2. IR (KBr): 3432, 3149, 2922, 2854, 1742, 1665, 1609, 1449, 1401, 1318, 1268, 1158, 918, 856, 713, 689, 612, 598, 565 cm^{-1}. HRMS (ESI) Calcd For $C_{23}H_{22}N_2O$: [M + H]$^+$, 343.1805, Found: 343.1808.

(*E*)-(5-Methyl-2-(*p*-tolyldiazenyl)phenyl)(phenyl)methanone 3ea: red solid (48 mg, 76%), mp 90−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.2 Hz, 1H), 7.77−7.75 (m, 2H), 7.47−7.42 (m, 2H), 7.37−7.30 (m, 5H), 7.10 (d, J = 8.2 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 150.6, 148.9, 142.1, 141.8, 139.0, 137.1, 133.0, 131.9, 129.9, 129.7, 129.6, 128.7, 123.2, 120.6, 21.8. IR (KBr): 3442, 3144, 2919, 2851, 1665, 1597, 1448, 1401, 1316, 1286, 1248, 1209, 1177, 1151, 963, 828, 752, 709, 646, 552, 531 cm^{-1}. HRMS (ESI) Calcd For $C_{21}H_{18}N_2O$: [M + H]$^+$, 315.1492, Found: 315.1494.

(*E*)-(4-Methoxy-2-((3-methoxyphenyl)diazenyl)phenyl)(phenyl)methanone 3fa: red solid (63 mg, 91%), mp 101−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (m, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.50−7.46 (m, 1H), 7.42−7.36 (m, 3H), 7.29 (d, J = 7.8 Hz, 1H), 7.22−7.15 (m. 2H), 6.97−6.94 (m, 1H), 6.79 (t, J = 2.0 Hz, 1H), 3.98 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 162.4, 160.5, 153.7, 152.2, 139.9, 132.9, 131.3, 131.1, 130.0, 129.9, 128.6, 119.3, 118.9, 118.1, 104.6, 102.1, 56.2, 55.7. IR (KBr): 3433, 3134, 3023, 2924, 2852, 1648, 1598, 1485, 1458, 1451, 1401, 1269, 1148, 1102, 1027, 785, 747, 711, 660, 622 cm^{-1}. HRMS (ESI) Calcd For $C_{21}H_{18}N_2O_3$: [M + H]$^+$, 347.1390, Found: 347.1395.

(*E*)-(5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)(phenyl)methanone 3ga: red solid (54 mg, 78%), mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 14.6 Hz, 1H), 7.36 (t, J = 15.2 Hz, 4H), 7.13 (dd, J = 11.6 Hz, J = 2.7 Hz, 1H), 7.03 (d, J = 2.7 Hz, 1H), 6.79 (d, J = 8.9 Hz, 2H), 3.91 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 162.1, 161.6, 146.7, 144.8, 138.7, 138.5, 132.9, 129.6, 128.6, 124.7, 122.2, 117.0, 114.2, 113.1, 56.1, 55.7. IR (KBr): 3444, 3161, 2964, 2934, 2837, 1665, 1599, 1580, 1499, 1480, 1440, 1413, 1318, 1290, 1224, 1179, 1143, 1107, 1026, 962, 846, 709, 558, 530 cm^{-1}. HRMS (ESI) Calcd For $C_{21}H_{18}N_2O_3$: [M + H]$^+$, 347.1390, Found: 347.1395.

(*E*)-(5-Fluoro-2-((4-fluorophenyl)diazenyl)phenyl)(phenyl)methanone 3ha: red solid (35 mg, 54%), mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99−7.95 (m, 1H), 7.78−7.76 (m, 2H), 7.50 (d, J = 7.4 Hz, 1H), 7.44−7.27 (m. 6H), 7.00 (t, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 164.8 (d, J_{C-F} = 251.5 Hz), 164.1 (d, J_{C-F} = 253.2 Hz), 148.7 (d, J_{C-F} = 2.9 Hz), 146.8 (d, J_{C-F} = 3.2 Hz), 139.4 (d, J_{C-F} = 7.1 Hz), 138.1, 133.4, 129.6, 128.8, 125.2 (d, J_{C-F} = 9.0 Hz), 122.3 (d, J_{C-F} = 9.0 Hz), 118.1 (d, J_{C-F} = 22.8 Hz), 116.2 (d, J_{C-F} = 22.8 Hz), 116.0 (d, J_{C-F} = 24.1 Hz). IR (KBr): 3431, 3128, 2923, 2852, 1658, 1598, 1402, 1279, 1229, 1134, 842, 753, 705, 557 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{12}F_2N_2O$: [M + H]$^+$, 323.0990, Found: 323.0990.

(*E*)-(5-Chloro-2-((4-chlorophenyl)diazenyl)phenyl)(phenyl)methanone 3ia: red solid (42 mg, 60%), mp 121−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.9 Hz, 1H), 7.77−7.74 (m, 2H), 7.61 (dd, J = 8.6 Hz, J = 2.1 Hz, 1H), 7.57−7.56 (d, J = 3.0 Hz, 1H), 7.53−7.52 (m, 1H), 7.41−7.34 (m, 4H), 7.31−7.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 150.5, 148.7, 138.8, 138.1, 138.0, 137.7, 133.5, 131.2, 129.6, 129.5, 129.1, 128.8, 124.4, 121.4. IR (KBr): 3441, 3134, 2922, 2851, 1665, 1588, 1484, 1469, 1448, 1398, 1311, 1295, 1274, 1242, 1176, 1149, 1085, 1007, 965, 906, 836, 802, 765, 744, 715, 694, 650, 548, 529 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{12}Cl_2N_2O$: [M + H]$^+$, 355.0400, Found: 355.0404.

(*E*)-(4-Bromo-2-((3-bromophenyl)diazenyl)phenyl)(phenyl)methanone 3ja: red solid (49 mg, 55%), mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 1.8 Hz, 1H), 7.74 (dd, J = 4.8 Hz, J = 1.4 Hz, 3H), 7.55−7.49 (m, 3H), 7.45−7.39 (m, 3H), 7.34 (t, J = 1.8 Hz, 1H), 7.23−7.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 153.0, 150.7, 138.7, 137.0, 134.7, 134.4, 133.5, 130.8, 130.6, 129.6, 128.8, 125.7, 124.8, 123.8, 123.3, 121.7. IR (KBr): 3435, 3135, 2925, 2853, 1662, 1579, 1400, 1284, 1238, 924, 87, 833, 785, 743, 707, 675, 600 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{12}Br_2N_2O$: [M + H]$^+$, 442.9389, Found: 442.9384.

(*E*)-(5-Bromo-2-((4-bromophenyl)diazenyl)phenyl)(phenyl)methanone 3ka: red solid (60 mg, 68%), mp 158−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83−7.81 (m, 1H), 7.78−7.72 (m, 4H), 7.51 (t, J = 7.3 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 150.9, 149.0, 138.9, 138.1, 134.3, 133.5, 132.6, 132.0, 129.7, 128.8, 126.6, 126.0, 124.6, 121.5. IR (KBr): 3440, 3135, 2924, 2851, 1742, 1663, 1598, 1582, 1571, 1466, 1447, 1400, 1271, 1147, 1064, 1002, 949, 889, 710, 689, 614, 547 cm^{-1}. HRMS (ESI) Calcd For $C_{19}H_{12}Br_2N_2O$: [M + H]$^+$, 442.9387, Found: 442.9389.

(*E*)-Phenyl(5-(trifluoromethoxy)-2-((4-(trifluoromethoxy)phenyl)diazenyl)phenyl)methanone 3la: red solid (45 mg, 50%), mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 7.4 Hz, 2H), 7.56−7.40 (m, 7H), 7.17 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 151.6, 151.1, 150.2, 148.3, 139.3, 138.0, 133.6, 129.7, 128.8, 124.8, 123.0, 121.7, 121.3, 121.1. IR (KBr): 3435, 3129, 2929, 2854, 1668, 1599, 1497, 1479, 1451, 1401, 1278, 1254, 1213, 1167, 921, 899, 850, 749, 688, 657, 597 cm^{-1}. HRMS (ESI) Calcd For $C_{21}H_{12}F_6N_2O_3$: [M + H]$^+$, 455.0825, Found: 455.0824.

(*E*)-(Diazene-1,2-diylbis(3-fluoro-6,1-phenylene))bis(phenylmethanone) 3m: yellow solid (58 mg, 68%), 160−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.75 (m, 2H), 7.68−7.67 (m, 2H), 7.55−7.47 (m, 2H), 7.41−7.36 (m, 5H), 7.20−7.17 (m, 1H), 7.05−7.04 (m. 2H), 6.97−6.94 (m, 1H), 6.93−6.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 194.5, 164.8 (d, J_{C-F} = 252.8 Hz), 165.3, 163.2 (d, J_{C-F} = 255.8 Hz), 162.8, 147.5 (d, J_{C-F} = 3.1 Hz), 147.4, 146.1 (d, J_{C-F} = 2.5 Hz), 140.5 (d, J_{C-F} = 7.5 Hz), 137.9 (d, J_{C-F} = 6.7 Hz), 137.8, 137.1, 133.4, 133.3, 129.6, 129.2, 128.7, 128.5, 124.8 (d, J_{C-F} = 9.2 Hz), 120.2 (d, J_{C-F} = 9.1 Hz), 118.0 (d, J_{C-F} = 23.0 Hz), 117.3 (d, J_{C-F} = 24.0 Hz), 115.9 (d, J_{C-F} = 22.9 Hz), 115.5 (d, J_{C-F} = 24.1 Hz). IR (KBr): 3434, 3135, 2925, 2855, 1742, 1664, 1595, 1580, 1499, 1478, 1450, 1401, 1317, 1281, 1236, 1204, 897, 886, 864, 845, 699, 646, 567 cm^{-1}. HRMS (ESI) Calcd For $C_{26}H_{16}F_2N_2O_2$: [M + H]$^+$, 427.1253, Found: 427.1259.

(*E*)-(Diazene-1,2-diylbis(2,1-phenylene))bis((4-fluorophenyl)methanone) 3n: red solid (55 mg, 65%), mp 188−190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72−7.68 (m, 4H), 7.52−7.42 (m, 6H), 7.21 (d, J = 8.6 Hz, 2H), 7.03 (t, J = 8.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 165.9 (d, J_{C-F} = 253.6 Hz), 150.0, 137.9, 134.8 (d, J_{C-F} = 2.9 Hz), 132.5 (d, J_{C-F} = 9.4 Hz), 131.6, 131.1, 128.7, 118.9, 115.8 (d, J_{C-F} = 21.8 Hz), 77.6, 77.3, 77.0. IR (KBr): 3432, 3144, 2924, 2853, 1741, 1662, 1594, 1503, 1402, 1299, 1247, 1232, 1222, 1152, 1143, 934, 851, 836, 773, 734, 692, 605, 587, 558 cm^{-1}. HRMS (ESI) Calcd For $C_{26}H_{16}F_2N_2O_2$: [M + H]$^+$, 427.1253, Found: 427.1255.

(*E*)-(Diazene-1,2-diylbis(2,1-phenylene))bis((4-chlorophenyl)methanone) 3o: red solid (64 mg, 70%), mp 202−205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.3 Hz, 4H), 7.53−7.43 (m, 6H), 7.32 (d, J = 8.4 Hz, 4H), 7.22 (d, J = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 150.0, 139.7, 137.4, 136.7, 131.6, 131.2, 128.9, 128.8, 119.3. IR (KBr): 3432, 3141, 2925, 2853, 1741, 1662, 1586, 1400, 1306, 1295, 1244, 1097, 1012, 931, 846, 769, 728, 679, 655, 566, 538 cm^{-1}. HRMS (ESI) Calcd For $C_{26}H_{16}Cl_2N_2O_2$: [M + H]$^+$, 459.0662, Found: 459.0662.

(*E*)-(Diazene-1,2-diylbis(3-fluoro-6,1-phenylene))bis(*o*-tolylmethanone) 3p: red solid (48 mg, 53%), mp 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 8.0 Hz, 4H), 7.14 (d, J = 7.4 Hz, 2H), 7.05 (t, J = 7.4 Hz, 2H), 6.96−6.92 (m, 2H), 6.82 (t, J = 8.4 Hz, 2H), 2.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 164.9 (d, J_{C-F} = 252.2 Hz), 163.1 (d, J_{C-F} = 254.8 Hz), 148.2, 145.6, 139.4, 138.7 (d, J_{C-F} = 6.2 Hz), 137.0, 132.2, 132.1, 131.1, 125.9, 124.8 (d, J_{C-F} = 9.1 Hz), 118.3 (d, J_{C-F} = 23.8 Hz), 116.0 (d, J_{C-F} = 22.9 Hz), 21.8. IR (KBr): 3433, 3135, 3072, 2927, 2854,

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1671, 1593, 1583, 1502, 1475, 1455, 1412, 1315, 1291, 1238, 1139, 1009, 885, 867, 843, 786, 746, 728, 648, 569, 560, 533 cm^{-1}. HRMS (ESI) Calcd For $C_{28}H_{20}F_2N_2O_2$: $[M + H]^+$, 455.1566, Found: 455.1563.

(*E*)-(2-((2-(2-Methylbenzoyl)phenyl)diazenyl)-1,3-phenylene)bis(*o*-tolylmethanone) 3q: red oil (80 mg, 75%); ^1H NMR (400 MHz, $CDCl_3$): δ 7.56−7.54 (m, 2H), 7.51−7.49 (m, 1H), 7.34−7.32 (m, 1H), 7.24−7.13 (m, 7H), 7.04 (t, J = 7.0 Hz, 5H), 6.98 (t, J = 8.2 Hz, 2H), 6.58 (d, J = 8.0 Hz, 1H), 2.34 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 197.3, 150.2, 150.1, 140.2, 139.4, 139.3, 137.6, 137.3, 136.6, 132.6, 131.7, 131.6, 131.5, 131.3, 131.2, 130.6, 129.7, 128.3, 125.6, 125.4, 117.3, 21.5, 21.4. IR (KBr): 3444, 3142, 2921, 2850, 1741, 1668, 1599, 1573, 1486, 1456, 1401, 1301, 1252, 1163, 1121, 1035, 1006, 928, 771, 731, 639, 561, 481 cm^{-1}. HRMS (ESI) Calcd For $C_{36}H_{28}N_2O_3$: $[M + H]^+$, 537.2173, Found: 537.2175.

(*E*)-(2-((2-Benzoyl-4-methylphenyl)diazenyl)-5-methyl-1,3-phenylene)bis(phenylmethanone) 3r: red solid (84 mg, 80%), mp 92−94 °C; ^1H NMR (400 MHz, CDCl3): δ 7.60−7.58 (m, 4H), 7.45−7.36 (m, 6H), 7.31−7.27 (m, 7H), 7.02 (dd, J = 4.7 Hz, J = 1.2 Hz, 1H), 6.94−6.89 (m, 2H), 2.42 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 195.7, 147.2, 146.3, 142.4, 141.8, 137.3, 137.0, 135.8, 133.1, 133.1, 131.0, 130.7, 130.1, 129.7, 128.8, 128.5, 128.3, 21.6. IR (KBr): 3432, 3135, 2924, 2854, 1673, 1656, 1595, 1579, 1449, 1400, 1323, 1261, 1210, 1178, 1141, 1035, 993, 959, 846, 762, 726, 703, 669, 650, 592, 557 cm^{-1}. HRMS (ESI) Calcd For $C_{35}H_{26}N_2O_3$: $[M + H]^+$, 523.2016, Found: 523.2013.

(*E*)-(5-Methoxy-2-((4-methoxy-2-(2-methylbenzoyl)phenyl)-diazenyl)-1,3-phenylene)bis(*o*-tolylmethanone) 3s: yellow solid (70 mg, 59%), mp 138−140 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.24−7.16 (m, 5H), 7.06−6.95 (m, 9H), 6.67−6.64 (m, 3H), 3.85 (s, 3H), 3.74 (s, 3H), 2.38 (s, 6H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 161.5, 160.6, 144.4, 143.3, 141.9, 139.7, 139.4, 138.9, 137.3, 136.7, 133.0, 131.7, 131.6, 125.5, 125.4, 119.7, 116.3, 115.7, 112.0, 56.3, 55.9, 21.7, 21.6. IR (KBr): 3434, 3146, 2923, 2853, 1742, 1670, 1591, 1573, 1457, 1401, 1330, 1291, 1252, 1225, 1149, 1035, 1012, 947, 874, 724, 652, 582 cm^{-1}. HRMS (ESI) Calcd For $C_{38}H_{32}N_2O_5$: $[M + H]^+$, 597.2384, Found: 597.2384.

(*E*)-(2-((2-Benzoyl-4-methoxyphenyl)diazenyl)-5-methoxy-1,3-phenylene)bis(phenylmethanone) 3t: yellow solid (70 mg, 63%), 101−103 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62−7.60 (m, 4H), 7.49−7.39 (m, 5H), 7.33−7.26 (m, 6H), 7.00−6.96 (m, 3H), 6.71 (dd, J = 5.9 Hz, J = 2.7 Hz, 1H), 6.59 (d, J = 2.7 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 195.0, 161.6, 160.9, 143.2, 141.9, 138.5, 137.5, 137.0, 136.5, 132.9, 132.9, 129.8, 129.5, 128.3, 128.1, 122.6, 115.8, 115.0, 112.5, 56.0, 55.7. IR (KBr): 3435, 3159, 3062, 2924, 2852, 1683, 1666, 1589, 1451, 1404, 1327, 1238, 1175, 1131, 1099, 1032, 1018, 964, 880, 850, 828, 761, 691, 626, 578 cm^{-1}. HRMS (ESI) Calcd For $C_{35}H_{26}N_2O_5$: $[M + H]^+$, 555.1914, Found: 555.1919.

(*E*)-(5-Methoxy-2-((4-methoxy-2-(4-methylbenzoyl)phenyl)-diazenyl)-1,3-phenylene)bis(*p*-tolylmethanone) 3u: red solid (86 mg, 72%), 84−86 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.1 Hz, 4H), 7.31 (d, J = 8.1 Hz, 2H), 7.10−7.03 (m, 7H), 6.90 (s, 2H), 6.71 (dd, J = 5.9 Hz, J = 2.6 Hz, 1H), 6.57 (d, J = 4.0 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 2.38 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 194.9, 161.7, 161.0, 143.9, 143.8, 143.5, 141.9, 139.3, 138.0, 134.7, 134.4, 130.3, 129.9, 129.2, 128.9, 122.6, 116.0, 114.9, 112.5, 56.2, 55.9, 22.1, 22.0. IR (KBr): 3441, 3141, 2923, 2853, 1741, 1667, 1605, 1590, 1402, 1332, 1291, 1231, 1175, 1131, 1029, 965, 840, 780, 721, 675, 805, 571 cm^{-1}. HRMS (ESI) Calcd For $C_{38}H_{32}N_2O_5$: $[M + H]^+$, 597.2384, Found: 597.2384.

■ ASSOCIATED CONTENT

Supporting Information

Typical experimental procedure, characterization for all products, and crystallographic information for **3o**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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