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Palladium-Catalyzed Direct Oxidative C–H Cross-Coupling of Azoarenes with Alcohols

Hui Tang,[+a] Cheng Qian,[+a] Dongen Lin,[a,*] Huanfeng Jiang,[a] and Wei Zeng[a,*]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China
E-mail: denlin@scut.edu.cn or zengwei@scut.edu.cn

[+] These two authors contributed equally to this work.

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Abstract: A palladium-catalyzed cascade oxidative C–H cross-coupling of azoarenes with alcohols was developed using *tert*-butyl hydroperoxide (TBHP) as oxidant. This reaction provides a convenient access to *ortho*-acylazoarenes under mild conditions in which readily available alcohols were used as the acyl sources.

Keywords: *ortho*-acylation; alcohols; azoarenes; cross-coupling; palladium

Introduction

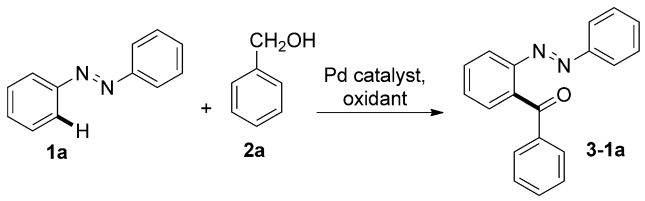
Transition metal-catalyzed direct C–H cross-coupling reactions of two organic molecules are among the most attractive and challenging hot topics in organic chemistry.[1] Recently, much attention has been particularly focused on the regioselective cross-coupling *via* C–H bond activation with the chelation assistance of a directing group.[2] In the past decade, most elegant work has demonstrated that various functional groups containing heteroatoms, such as ketone,[3] nitrile,[4] carboxylic acid,[5] alcohol,[6] triazoene,[7] pyridine,[8] ester,[9] amide,[4b,10] aldehyde,[9a,11] imine,[12] or oxazoline[13] group, etc., could be used as an anchor to form cyclometalated intermediates, and the corresponding cyclometalated species would further react with electrophiles or nucleophiles to realize versatile C–H functionalizations. However, although significant progress in C–H cross-coupling has been achieved with the assistance of various directing groups, there are only rare reported examples employing the azo group as a directing group to accelerate the C–H activation/functionalization process.[14]

Azo-substituted aryl ketones are important structural motifs of photochemical materials and biosensors. Moreover, these compounds could be easily converted into the corresponding amino or hydrazino products which are widely utilized in the field of organic synthesis.[15] The present synthetic methods involve the coupling of diazonium salts with arenes or the oxidation of the corresponding azo-containing secondary alcohols,[16] and these methodologies suffer from harsh reaction conditions and a relatively limited substrate scope. Therefore, developing a straightforward and concise synthetic strategy to access azo-substituted aryl ketones therefore is still desirable. Recently, Wang realized the Pd-catalyzed direct acylation of azoarenes using prefunctionalized aldehydes as the acyl sources.[17] Considering that stable and readily available alcohols could be converted into aldehydes by various oxidants including O_2 and TBHP, etc.,[18] and also that the direct acylation of *N*-benzyltriflamides, acetanilides and 2-arylpyridines with alcohols in the presence of Pd(II)/oxidants reaction system has been successively reported, respectively,[19] herein we describe a convenient Pd-catalyzed direct C–H oxidative cross-coupling of azoarenes with non-prefunctionalized alcohols as ideal *in situ* generated acylating agents to provide *ortho*-acylated azoarenes.

Results and Discussion

Azobenzene (**1a**) and benzoyl alcohol (**2a**) were first used as the model substrates to screen the reaction conditions for the optimization of the catalyst, oxidant, solvent, and temperature under an argon atmosphere (Table 1). We were pleased to find that when the mixture of azobezene (0.15 mmol) and benzoyl alcohol (0.15 mmol) was treated with 4.0 equiv. of

Table 1. Optimization of the Pd-catalyzed *ortho*-acylation of azobenzene with toluene.[a]



Entry	Pd catalyst	Oxidant	Solvent	Yield [%][b]
1	$PdCl_2$	TBHP	DCE	37
2	$Pd(TFA)_2$	TBHP	DCE	34
3	$PdCl_2(MeCN)_2$	TBHP	DCE	35
4	$PdCl_2(PPh_3)_2$	TBHP	DCE	trace
5	$Pd(OAc)_2$	TBHP	DCE	40
6	$Pd(PPh_3)_4$	TBHP	DCE	30
7	–	TBHP	DCE	0
8	$Pd(OAc)_2$	DDQ	DCE	trace
9	$Pd(OAc)_2$	MnO_2	DCE	trace
10	$Pd(OAc)_2$	$Na_2S_2O_8$	DCE	trace
11	$Pd(OAc)_2$	O_2	DCE	trace
12	$Pd(OAc)_2$	$PhI(OAc)_2$	DCE	trace
13	$Pd(OAc)_2$	TBHP	TCE	47
14	$Pd(OAc)_2$	TBHP	CH_3NO_2	28
15	$Pd(OAc)_2$	TBHP	EtOAc	22
16	$Pd(OAc)_2$	TBHP	$PhCF_3$	58
17	$Pd(OAc)_2$	TBHP	PhCl	68
18	$Pd(OAc)_2$	TBHP	PhCl	81[c]
19	$Pd(OAc)_2$	TBHP	PhCl	68[d]
20	$Pd(OAc)_2$	TBHP	PhCl	68[e]

[a] Unless otherwise noted, the reactions were carried out using azobenzene (**1a**) (0.15 mmol) and phenylmethanol (**2a**) (0.15 mmol) with palladium catalyst (10 mol%) in the presence of oxidant (0.60 mmol, 4.0 equiv.) in solvent (2.0 mL) at 110 °C for 30 h under an argon atmosphere in a sealed reaction tube, followed by flash chromatography on SiO_2.
[b] Isolated yield.
[c] Reaction temperature: 80 °C.
[d] Reaction temperature: 60 °C.
[e] 1.5 equiv. of **2a** were used.

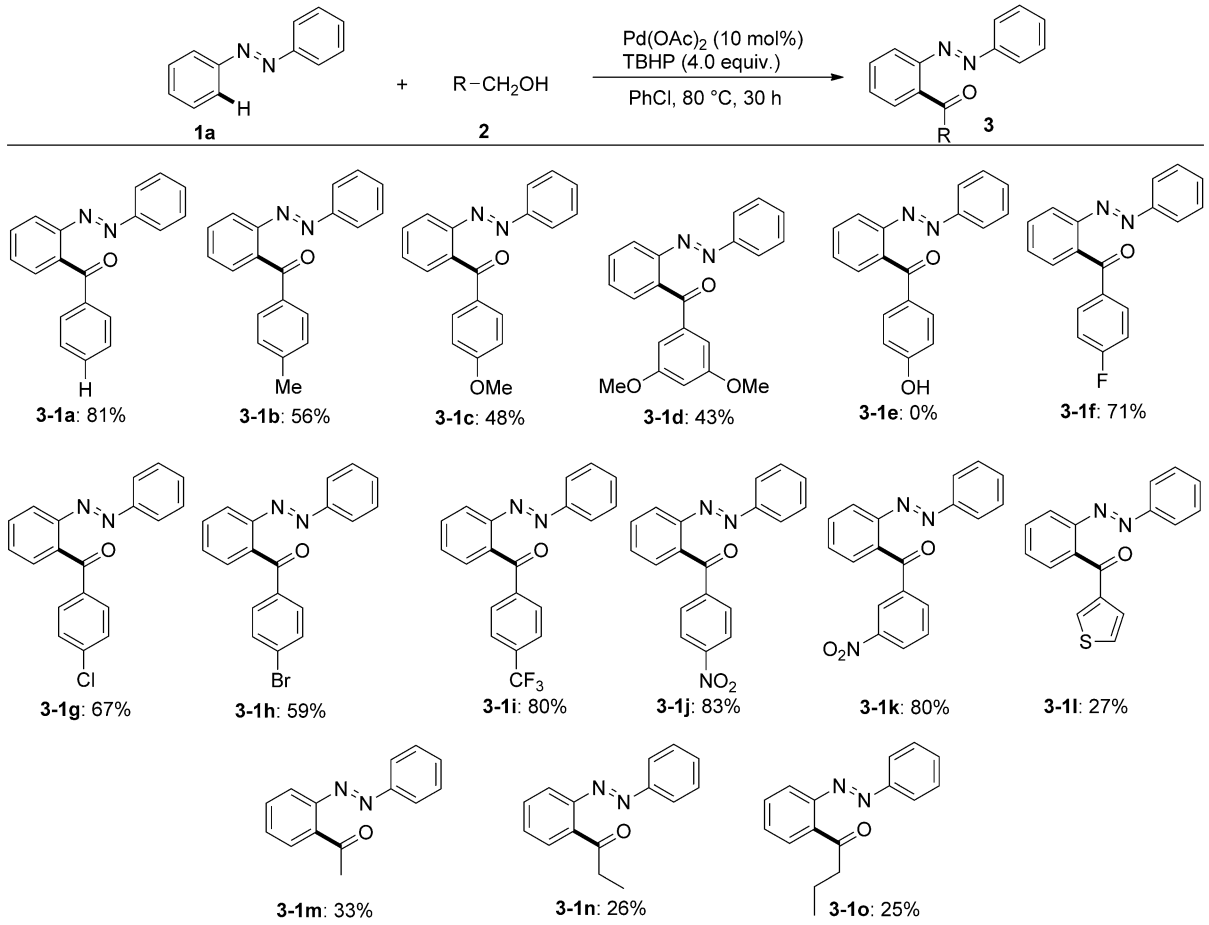
TBHP in DCE (2.0 mL) at 110 °C for 30 h in the presence of various palladium catalysts (10 mol%) including $PdCl_2$, $Pd(TFA)_2$, $Pd(PPh_3)_4$, and $Pd(OAc)_2$, etc. (entries 1–6), $Pd(OAc)_2$ provided a 40% yield of the desired product (**3-1a**) (entry 5). Notably, no desired **3-1a** was detected by TLC and ^1H NMR methods in the absence of palladium salts even after 48 h (entry 7). Encouraged by these positive results, we further investigated the effect of various oxidants on this transformation, and found that TBHP was the most suitable oxidant, other oxidants such as DDQ, MnO_2 and $Na_2S_2O_8$, etc., afforded poorer reactivities (compare entries 8–12 with entry 5). Subsequently, the effect of the solvent was also investigated (compare entry 5 with entries 13–17), and TCE, DCE and trifluorotoluene were the better solvents, with chlorobenzene being the best (entry 17). When the reaction temperature was lowered to 80 °C, the yield could be increased up to 81% (compare entries 17 with 18). Further lowering the reaction temperature or changing the ratio of **1a**/**2a** resulted in poorer yields (compare entry 18 with entries 19 and 20) (see the Supporting Information for more details).

With the optimized reaction conditions in hand, the scope of this transformation was subsequently investigated with regard to alcohols as the *in situ* generated acyl source. As shown in Table 2, the C–H cross-coupling reaction of azobenzene with various alcohols could proceed smoothly and furnish the corresponding acylated products. A wide range of arylmethanols with substituents on the benzene rings was investigated. The results demonstrated that the substitution on the benzene ring showed significant electronic effects, the substrates with a *para* or *meta* electron-withdrawing group (such as 4-Cl, 4-F, 4-Br, 4-NO_2, 3-NO_2, 4-CF_3) on the phenyl ring afforded the desired products in moderate to excellent yields (59–83%, **3-1f**–**3-1k**). On the contrary, a *para* or *meta* electron-donating group-substituted benzyl alcohol (4-Me, 4-MeO, 3-MeO) gave a low yield of the corresponding acylated product (43–56%, **3-1b**–**3-1d**), especially for the 4-hydroxybenzyl alcohol, no C–H cross-coupling reaction occurred, and azobenzene **1a** was completely recovered (**3-1e**). Moreover, we also extended the substrate scope to heteroarylmethanols and aliphatic alcohols, and obtained the desired acylated azoarenes (**3-1l**–**3-1o**).

The scope of the transformation with regard to azoarenes was then explored with benzyl alcohol as an acylating agent. The results from Table 3 showed that no deleterious electronic effect of the *para*-substituted azoarene was found, and electronic-rich and electronic-poor azoarenes gave the desired acylated products in moderate to excellent yields (**3-2a**, **3-2b**, **3-2d**–**3-2h**). Yet, the *ortho*-substituted azobenzene gave an inferior product yield to that of the *para*- or *meta*-substituted azobezene due to steric hindrance (compare **3-2c** with **3-2a** and **3-2b**). Moreover, we also investigated the electronic effect of various substituents on the regioselectivity of the *ortho*-acylation of unsymmetrical azoarenes, and found that *ortho*-acylation reactions took place mainly on the electron-rich azo aromatic rings (compare **3-2i**, **3-2k** and **3-2m** with **3-2j**, **3-2l** and **3-2n**, respectively). Finally, we tried to use 3-azopyridine as substrate, but no *ortho*-acylation was observed under our reaction conditions (**3-2o**).

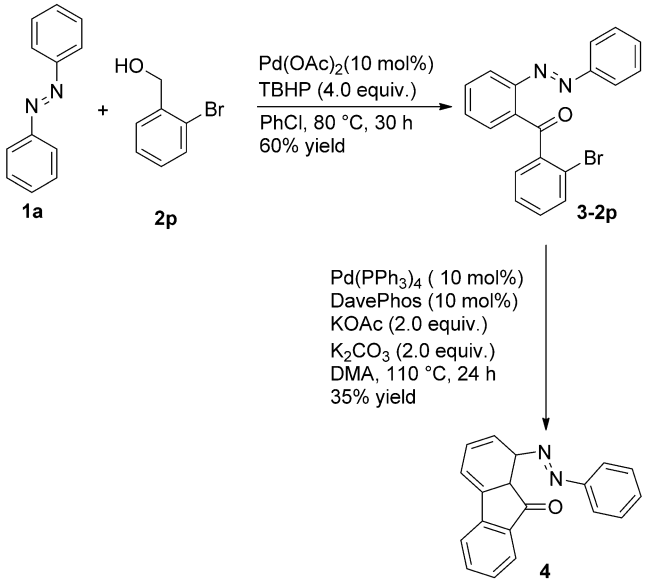
We also ran the *ortho*-regioselective C–H oxidative cross-coupling of azoarene **1a** with (2-bromophenyl)-methanol **2p** under our reaction conditions, and got the acylated intermediate **3-2p** in 60% yield (Scheme 1). Then a subsequent Pd-catalyzed intramolecular cyclocoupling reaction[20] of **3-2p** could further furnish the corresponding azofluorenone **4**, which has

Table 2. Scope of alcohols.[a,b]



[a] All the reactions were carried out using azobenzene (**1a**) (0.15 mmol) and alcohol (**2**) (1.0 equiv.) with $Pd(OAc)_2$ (10 mol%) in the presence of TBHP (4.0 equiv.) in PhCl (2.0 mL) at 80 °C for 30 h under an argon atmosphere in a sealed reaction tube, followed by flash chromatography on SiO_2.

[b] Isolated yield.

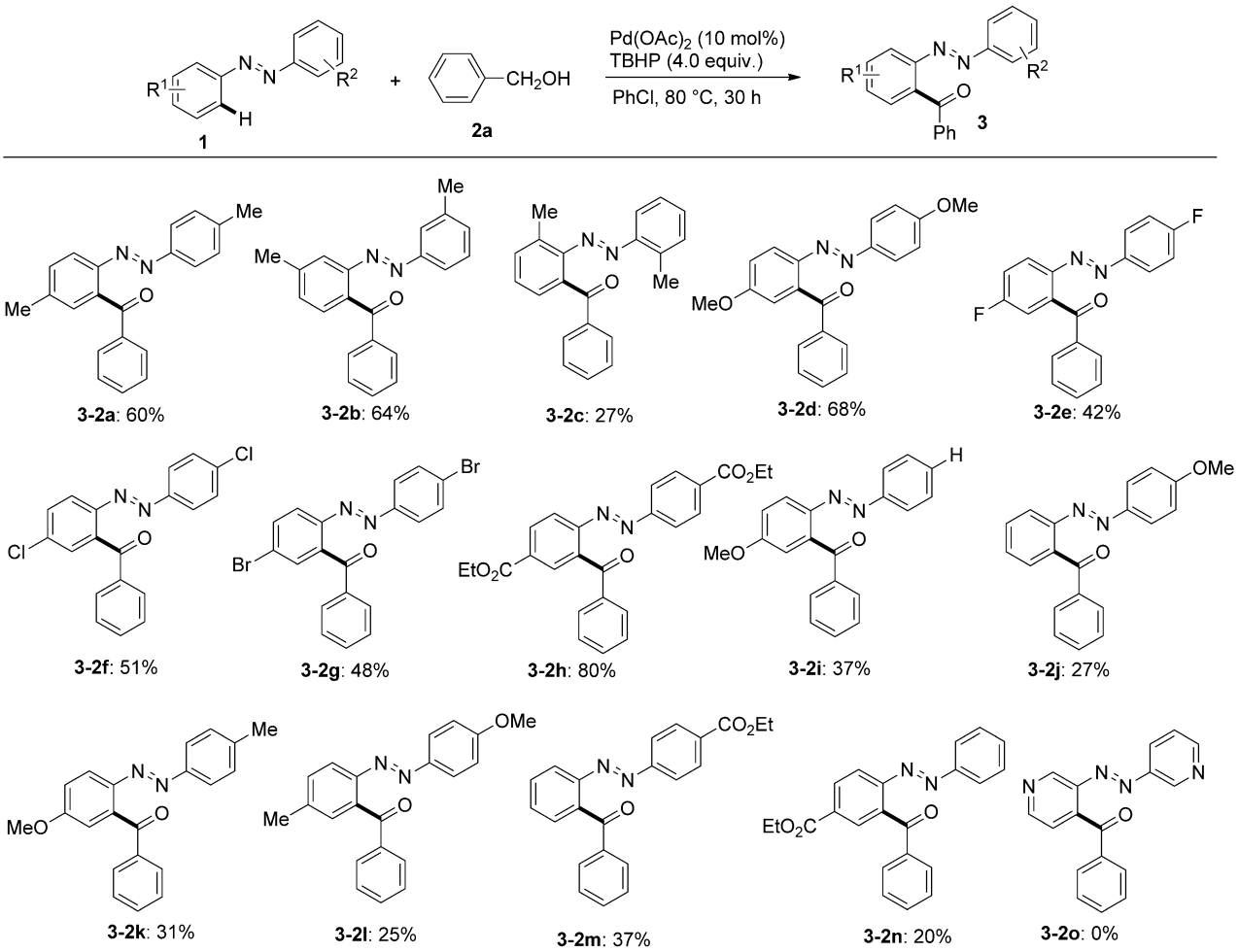


Scheme 1. Synthetic application of this transformation.

potential use as a promising industrial dye or nonlinear optical device.[15d,f]

To further investigate the possible mechanism, the mixture of phenylmethanol (1.0 mL)/$Pd(OAc)_2$ (10 mol%)/TBHP (4.0 equiv.) in the absence of azobenzene was conducted and the reaction progress monitored using GC-MS. After the reaction had been carried out at 80 °C for 12 h, we could observe the formation of benzaldehyde (58% GC yield) (Scheme 2, a). We further ran the *ortho*-acylation of azobenzene with benzaldehyde under our optimized reaction conditions, and got a 75% yield of the *ortho*-acylated azobenzene **3**-**1a** (Scheme 2, b). Moreover, we also ran the Pd-catalyzed oxidative C–H cross-coupling of azobenzene (**1a**) with phenylmethanol (**2a**) in the presence of TEMPO under the same reaction conditions, and no desired **3**-**1a** was observed (Scheme 2, c). This control experiment indicated that a radical process was possibly involved in this reaction system.

Table 3. Scope of azoarenes.[a,b]



[a] Unless otherwise noted, the reactions were carried out using azoarene (**1**) (0.15 mmol) and phenylmethanol (**2**) (1.0 equiv.) with $Pd(OAc)_2$ (10 mol%) in the presence of TBHP (4.0 equiv.) in PhCl (2.0 mL) at 80 °C for 30 h under an argon atmosphere in a sealed reaction tube, followed by flash chromatography on SiO_2.

[b] Isolated yield.

Based on the previously reported Pd-catalyzed sp^2 C–H acylation,[17,21] and in combination with the results from the above-mentioned control reactions, a possible mechanism for this transformation involves the oxidation of alcohols to aldehydes under the reaction conditions, then the corresponding aldehydes are further converted into acyl radicals which can afford *ortho*-acylation products probably *via* a Pd(II)-catalyzed C–H activation process.[22,23]

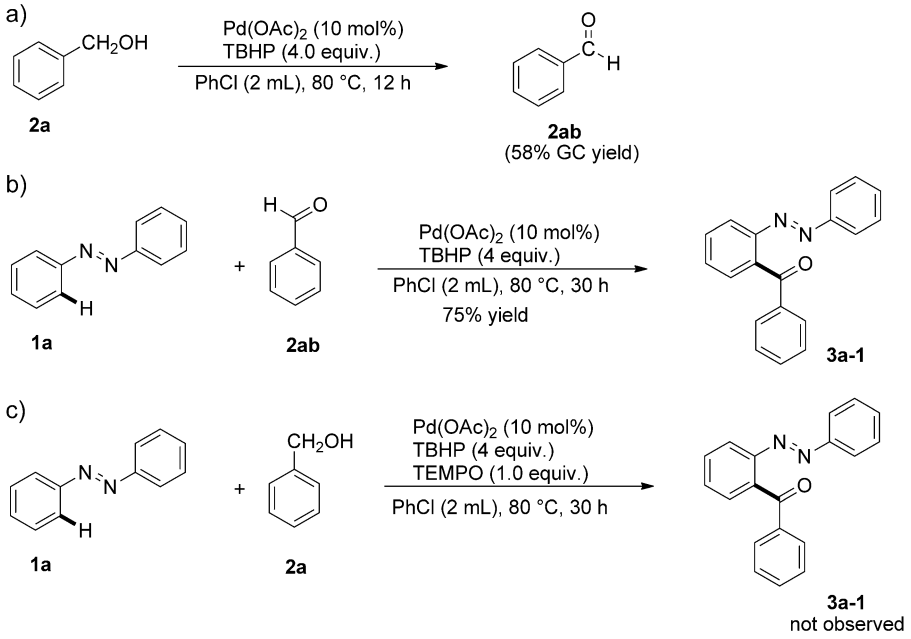
Conclusions

In summary, we have developed a Pd (II)-catalyzed oxidative C–H cross-coupling reaction of azoarenes with alcohols using TBHP as an oxidant. This protocol allows us to use simple and readily available alcohols as *in situ* generated acyl sources, and provides a convenient route for the synthesis of *ortho*-acylazoarene derivatives. Further studies of the transition metal-catalyzed C–H *ortho*-acylation of azoarenes using alkanes as acyl sources are currently underway in our lab.

Experimental Section

General Information

Unless otherwise noted, all other commercially available reagents and solvents were used without further purification. Purifications of reaction products were carried out by flash chromatography using silica gel (40–63 mm). Infrared spectra (IR) were recorded on an FT-IR spectrophotometer 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 tet-



Scheme 2. Control reactions.

ramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a standard spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. 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), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Melting points were determined on a microscopic melting point apparatus and are uncorrected. Low resolution mass spectra were taken on an LC-MS instrument. High resolution mass spectra (HR-MS) were recorded on an IF-TOF spectrometer (Micromass). All the azobenzene substrates were prepared according to the previously reported procedures.[24]

General Procedure for the *ortho*-Acylation of Azobenzenes

A sealed tube was charged with azo compound (0.15 mmol), alcohol (0.15 mmol), $Pd(OAc)_2$ (0.015 mmol), TBHP (0.60 mmol) and chlorobenzene (2.0 mL) under an argon atmosphere. The reaction vessel was placed in an oil bath. After the mixture had been stirred at 80 °C for 30 h, it was cooled to room temperature and concentrated under vacuum. The corresponding crude product was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:20, v/v) to afford the desired acylated products.

(*E*)-Phenyl[2-(phenyldiazenyl)phenyl]methanone (3-1a):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 7.9$ Hz, 1H), 7.77 (d, $J = 7.5$ Hz, 2H), 7.67–7.62 (m, 1H), 7.58 (d, $J = 4.2$ Hz, 2H), 7.50–7.42 (m, 3H), 7.39–7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.14$, 152.04, 150.38, 138.47, 136.92, 132.76, 131.35, 130.87, 130.82, 129.42, 128.90, 128.81, 128.34, 122.89, 120.06; MS (EI, 70 eV): $m/z =$ 286.11 (M^+); IR (KBr): $\nu = 3852$, 3738, 3618, 2922, 2852, 2360, 17887, 1754, 1664, 1595, 1454, 1389, 1282, 1232, 1177, 996, 840, 740, 682, 530, 475 cm^{-1}.

(*E*)-[2-(Phenyldiazenyl)phenyl](*para*-tolyl)methanone (3-1b):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.89$–7.83 (m, 1H), 7.59 (t, $J = 5.9$ Hz, 2H), 7.5–7.51 (m, 1H), 7.52 (d, $J = 1.2$ Hz, 2H), 7.41 (ddd, $J = 8.2$, 5.4, 3.0 Hz, 2H), 7.27 (qd, $J = 4.5$, 1.0 Hz, 3H), 7.10 (d, $J = 8.0$ Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.83$, 152.11, 150.27, 143.65, 137.43, 135.94, 131.29, 130.81, 130.59, 129.67, 129.05, 128.89, 128.65, 122.95, 119.69, 21.66; MS (EI, 70 eV): $m/z =$ 300.13 (M^+); IR (KBr): $\nu = 3829$, 3744, 2923, 2854, 1661, 1602, 1461, 1286, 1150, 1025, 928, 835, 769, 687, 538, 472 cm^{-1}.

(*E*)-(4-Methoxyphenyl)[2-(phenyldiazenyl)phenyl]methanone (3-1c):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.92$ (d, $J = 7.8$ Hz,1H), 7.76 (d, $J = 8.5$ Hz, 2H), 7.65–7.49 (m, 5H), 7.35 (q, $J = 4.4$ Hz, 3H), 6.86 (d, $J = 8.5$ Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 195.78$, 163.39, 152.17, 150.16, 137.78, 131.92, 131.43, 131.28, 130.80, 130.43, 128.92, 128.52, 122.94, 119.34, 113.60, 55.45; MS (EI, 70 eV): $m/z = 316.12$ (M^+); IR (KBr): $\nu = 3779$, 3712, 2943, 2824, 1761, 1702, 1501, 1234, 1202, 1017, 825, 785, 678, 558, 476 cm^{-1}.

(*E*)-(3,5-Dimethoxyphenyl)[2-(phenyldiazenyl)phenyl]methanone (3-1d):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 7.8$ Hz, 1H), 7.69–7.61 (m, 1H), 7.6–7.51 (m, 4H), 7.40–7.33 (m, 3H), 6.91 (d, $J = 2.3$ Hz, 2H), 6.57 (s, 1H), 3.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 196.74, 160.66, 152.04, 150.45, 140.39, 136.65, 131.36, 130.75, 130.73, 128.93, 128.62, 122.96, 120.52, 107.33, 105.24, 55.58; MS (EI, 70 eV): $m/z =$ 346.04 (M^+); IR (KBr): $\nu = 3729$, 3446, 2360, 2341, 2026, 1603, 1384, 1130, 1110, 992, 669, 638, 616 cm^{-1}.

(*E*)-(4-Fluorophenyl)[2-(phenyldiazenyl)phenyl]methanone (3-1f):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (d, $J = 7.9$ Hz, 1H), 7.86–7.79 (m, 2H), 7.64 (dtd, $J =$ 17.0, 7.2, 1.7 Hz, 3H), 7.50 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.43–

7.35 (m, 3H), 7.07 (t, $J=8.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.55$, 151.96, 150.28, 136.53, 134.85, 132.03, 131.94, 131.52, 130.94, 130.91, 128.98, 128.67, 122.85, 120.29, 115.60, 115.38; MS (EI, 70 eV): $m/z=304.01$ (M^+); IR (KBr): $\nu=3790$, 3492, 2921, 2850, 2360, 2341, 1786, 1738, 1710, 1480, 1450, 848, 762, 750, 577, 480 cm^{-1}.

(*E*)-(4-Chlorophenyl)[2-(phenyldiazenyl)phenyl]methanone (3-1g):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.96$ (d, $J=8.0$ Hz, 1H), 7.71 (d, $J=8.5$ Hz, 2H), 7.66 (td, $J=7.8$, 1.6 Hz, 1H), 7.57 (dt, $J=7.4$, 6.8 Hz, 2H), 7.46 (dd, $J=7.8$, 1.4 Hz, 2H), 7.36 (dd, $J=15.8$, 8.0 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.86$, 151.90, 150.32, 139.16, 136.85, 136.17, 131.58, 131.03, 130.98, 130.71, 129.00, 128.71, 128.69, 122.87, 120.56; MS (EI, 70 eV)*:* $m/z=320.07$ (M^+); IR (KBr): $\nu=3063$, 2925, 2855, 1669, 1587, 1481, 1398, 1290, 1150, 1092, 1031, 928, 844, 771, 683, 531, 475 cm^{-1}.

(*E*)-(4-Bromophenyl)[2-(phenyldiazenyl)phenyl]methanone (3-1h):[25] Orange solid; mp 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.96$ (d, $J=7.9$ Hz, 1H), 7.65 (dd, $J=16.2$, 7.9 Hz, 3H), 7.56 (dd, $J=11.3$, 7. Hz, 2H), 7.51 (d, $J=8.4$ Hz, 2H), 7.46 (d, $J=7.4$ Hz, 2H), 7.37 (p, $J=6.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=151.90$, 150.34, 137.28, 136.10, 131.67, 131.58, 131.05, 130.97, 130.82, 129.00, 128.72, 127.87, 122.87, 120.57; MS (EI, 70 eV): $m/z=365.90$ $(M+H)^+$; IR (KBr): $\nu=3061$, 2924, 2853, 2362, 1914, 1669, 1480, 1432, 1302, 1068, 928, 875, 686, 642, 587, 530, 492 cm^{-1}.

(*E*)-[2-(phenyldiazenyl)phenyl][4-(trifluoromethyl)phenyl]methanone (3-1i): Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.01$ (d, $J=7.9$ Hz, 1H), 7.89 (d, $J=8.1$ Hz, 2H), 7.77–7.70 (m, 1H), 7.65 (dd, $J=5.0$, 4.5 Hz, 4H), 7.40 (d, $J=7.1$ Hz, 3H), 7.38–7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=196.00$, 151.78, 150.46, 141.46, 135.53, 134.00, 131.69, 131.47, 131.08, 129.45, 129.00, 128.98, 125.41, 125.37, 122.79, 122.26, 120.85; HR-MS (ESI): $m/z=355.1052$, calcd. for $[M+H]^+$ $C_{20}H_{13}F_3N_2O$: 355.1053; IR (KBr): $\nu=3727$, 3623, 2924, 2853, 2360, 2341, 1672, 1325, 1310, 1260, 1129, 749, 687, 669 cm^{-1}.

(*E*)-(4-Nitrophenyl)[2-(phenyldiazenyl)phenyl]methanone (3-1j):[25] Orange solid; mp 75–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.19$ (d, $J=8.8$ Hz, 2H), 8.02 (d, $J=7.6$ Hz, 1H), 7.89 (d, $J=8.9$ Hz, 2H), 7.7–7.67 (m, 1H), 7.68–7.59 (m, 2H), 7.45–7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.21$, 151.48, 150.51, 149.82, 143.27, 134.45, 131.96, 131.74, 131.25, 129.83, 129.09, 128.98, 123.64, 122.76, 122.14; MS (EI, 70 eV): $m/z=331.02$ (M^+); IR (KBr): $\nu=3728$, 3705, 2923, 2852, 2360, 2341, 1661, 1548, 1344, 750, 684, 669, 650 cm^{-1}.

(*E*)-(3-Nitrophenyl)[2-(phenyldiazenyl)phenyl]methanone (3-1k): Orange solid; mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.57$ (s, 1H), 8.30 (d, $J=8.1$ Hz, 1H), 8.04 (dd, $J=14.8$, 7.9 Hz, 2H), 7.73 (t, $J=7.5$ Hz, 1H), 7.63 (dd, $J=19.8$, 7.5 Hz, 2H), 7.55 (t, $J=8.0$ Hz, 1H), 7.43 (d, $J=7.7$ Hz, 2H), 7.35 (dt, $J=14.7$, 6.5 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): $\delta=194.65$, 151.58, 150.51, 148.30, 140.03, 134.50, 134.47, 131.85, 131.70, 131.23, 129.56, 129.06, 128.93, 126.77, 123.73, 122.77, 121.94; HR-MS (ESI): $m/z=354.0847$, calcd. for $[M+Na]^+$ $C_{19}H_{13}N_3O_3$: 354.0849; IR (KBr): $\nu=3753$, 3700, 2978, 2908, 2878, 2378, 2321, 1654, 1532, 1312, 780, 676, 652, 610 cm^{-1}.

(*E*)-[2-(Phenyldiazenyl)phenyl](thiophen-3-yl)methanone (3-1l): Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.91$ (d, $J=7.9$ Hz, 1H), 7.73 (s, 1H), 7.68–7.52 (m, 5H), 7.49 (d, $J=5.0$ Hz, 1H), 7.37 (d, $J=6.1$ Hz, 3H), 7.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=190.55$, 152.20, 150.19, 143.50, 137.84, 134.03, 131.40, 130.80, 130.75, 128.97, 128.45, 127.61, 126.16, 122.95, 119.56; HR-MS (ESI): $m/z=293.0731$, calcd. for $[M+H]^+$ $C_{17}H_{12}N_2OS$: 293.0743; IR (KBr): $\nu=3264$, 3061, 2956, 2821, 1814, 1673, 1550, 1445, 1300, 1094, 1068, 934, 867, 636, 612, 545, 507, 472 cm^{-1}.

(*E*)-1-[2-(Phenyldiazenyl)phenyl]ethanone (3-1m):[26] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.94$ (d, $J=7.7$ Hz, 2H), 7.78 (d, $J=7.9$ Hz,1H), 7.68 (d, $J=7.5$ Hz, 1H), 7.62 (d, $J=7.3$ Hz, 1H), 7.56 (q, $J=9.4$ Hz, 5H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=202.63$, 152.35, 150.34, 138.23, 131.74, 131.56, 130.75, 129.28, 128.25, 123.27, 118.53, 32.64; MS (EI, 70 eV): $m/z=224.02$ (M^+); IR (KBr): $\nu=3469$, 3062, 2923, 2851, 2360, 2341, 1959, 1765, 1642, 1423, 1357, 772, 745, 689, 657, 548, 438 cm^{-1}.

(*E*)-1-[2-(Phenyldiazenyl)phenyl]propan-1-one (3-1n):[27] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.89$ (d, $J=8.1$ Hz, 2H), 7.79 (d, $J=7.5$ Hz, 1H), 7.60–7.48 (m, 6H), 2.91 (q, $J=7.3$ Hz, 2H), 1.20 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=206.30$, 152.34, 150.01, 138.52, 131.64, 131.02, 130.80, 129.24, 127.94, 123.21, 119.04, 38.16, 8.48; MS (EI, 70 eV): $m/z=238.11$ (M^+); IR (KBr): $\nu=3729$, 3433, 2920, 2367, 2339, 1593, 1275, 1261, 1208, 750, 686, 503 cm^{-1}.

(*E*)-1-[2-(Phenyldiazenyl)phenyl]butan-1-one (3-1o):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.92$–7.87 (m, 2H), 7.81–7.75 (m, 1H), 7.59–7.47 (m, 6H), 2.89 (t, $J=7.3$ Hz, 2H), 1.81–1.67 (m, 2H), 0.94 (t, $J=7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=205.81$, 152.37, 150.01, 138.90, 131.63, 131.03, 130.79, 129.23, 127.94, 123.22, 118.56, 46.94, 17.92, 13.86; MS (EI, 70 eV): $m/z=$ 252.04 (M^+); IR (KBr): $\nu=3742$, 3501, 3063, 2962, 2873, 2362, 1692, 1592, 1457, 1385, 1204, 1151, 1077, 992, 770, 686, 543 cm^{-1}.

(*E*)-[5-Methyl-2-(*para*-tolyldiazenyl)phenyl](phenyl)methanone (3-2a):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.85$ (d, $J=8.2$ Hz, 1H), 7.76 (d, $J=7.1$ Hz, 2H), 7.44 (dd, $J=14.9$, 7.6 Hz, 2H), 7.39–7.28 (m, 5H), 7.10 (d, $J=8.1$ Hz, 2H), 2.47 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=197.53$, 150.18, 148.49, 141.69, 141.39, 138.61, 136.69, 132.61, 131.49, 129.53, 129.34, 129.16, 128.27, 122.75, 120.20, 21.45; MS (EI,70 eV): $m/z=314.14$ (M^+); IR (KBr): $\nu=3472$, 2921, 2853, 2361, 1663, 1593, 1448, 1277,1208, 1146, 961, 826, 744, 698, 644, 544 cm^{-1}.

(*E*)-[4-Methyl-2-(*meta*-tolyldiazenyl)phenyl](phenyl)methanone (3-2b): Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.76$ (d, $J=7.6$ Hz, 2H), 7.70 (s, 1H), 7.52 (d, $J=7.7$ Hz, 1H), 7.46 (t, $J=7.3$ Hz, 1H), 7.37 (dd, $J=16.8$, 9.0 Hz, 3H), 7.26–7.14 (m, 3H), 7.10 (s, 1H), 2.51 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=197.35$, 152.28, 150.53, 141.52, 139.07, 138.74, 134.39, 132.50, 132.01, 131.52, 129.43, 129.08, 128.66, 128.24, 122.59, 120.87, 119.58, 21.49, 21.16; HR-MS (ESI): $m/z=315.1519$, calcd. for $[M+H]^+$ $C_{21}H_{18}N_2O$: 315.1492; IR (KBr): $\nu=3736$, 3502, 3055, 2822, 2853, 1721, 1716, 1562, 1521,1471, 883, 825, 749, 702, 687, 660, 516, 452 cm^{-1}.

(*E*)-[3-Methyl-2-(*ortho*-tolyldiazenyl)phenyl](phenyl)methanone (3-2c): Orange liquid, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.65$ (d, $J=7.6$ Hz, 2H), 7.45 (dt, $J=14.9$, 7.5 Hz, 2H), 7.37 (t, $J=7.3$ Hz, 1H), 7.30 (d, $J=8.1$ Hz,

1H), 7.28–7.20 (m, 4H), 7.15 (d, $J=7.5$ Hz, 1H), 7.07 (t, $J=7.6$ Hz, 1H), 2.76 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=196.58$, 150.25, 150.12, 138.94, 138.09, 137.22, 132.52, 132.44, 131.33, 131.29, 131.15, 129.93, 129.01, 128.16, 126.49, 125.96, 115.64, 18.43, 17.28; HR-MS (ESI): $m/z=315.1486$, calcd. for $[M+H]^+$ $C_{21}H_{18}N_2O$: 315.1492; IR (KBr): $\nu=3845$, 3727, 3533, 2360, 2339, 1641, 1384, 1261, 1089, 749, 669, 493 cm^{-1}.

(*E*)-{5-Methoxy-2-[(4-methoxyphenyl)diazenyl]phenyl}-(phenyl)methanone (3-2d):[25] Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.93$ (d, $J=8.9$ Hz, 1H), 7.78 (d, $J=7.5$ Hz, 2H), 7.47 (t, $J=7.3$ Hz, 1H), 7.36 (t, $J=7.8$ Hz, 4H), 7.13 (dd, $J=8.9$, 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, $CDCl_3$): $\delta=197.13$, 161.81, 161.33, 146.44, 144.56, 138.43, 138.26, 133.62, 132.68, 130.16, 129.30, 128.47, 128.30, 124.43, 122.00, 116.77, 113.99, 112.88, 55.80, 55.48; MS (EI, 70 eV): $m/z=346.13$ (M^+); IR (KBr): $\nu=3723$, 3397, 2921, 2851, 2363, 1745, 1712, 1699, 1652, 1574, 1473, 1419, 1316, 837, 749, 692, 515 cm^{-1}.

(*E*)-{5-Fluoro-2-[(4-fluorophenyl)diazenyl]phenyl}-(phenyl)methanone (3-2e): Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.99$ (dd, $J=8.8$, 5.1 Hz, 1H), 7.79 (d, $J=7.8$ Hz, 2H), 7.54 (t, $J=7.4$ Hz, 1H), 7.49–7.26 (m, 6H), 7.03 (t, $J=8.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.47$, 165.15, 163.29, 162.62, 148.42, 146.54, 139.22, 139.15, 137.85, 133.14, 129.37, 128.49, 124.96, 124.87, 122.11, 122.02, 117.98, 117.75, 116.08, 115.88, 115.85, 115.64; HR-MS (ESI): $m/z=323.0996$, calcd. for $[M+H]^+$ $C_{19}H_{12}F_2N_2O$: 323.0991; IR (KBr): $\nu=3072$, 2924, 1730, 1656, 1592, 1491, 1309, 1274, 1226, 1128, 1083, 843, 749, 701, 638, 551 cm^{-1}.

(*E*)-{5-Chloro-2-[(4-chlorophenyl)diazenyl]phenyl}-(phenyl)methanone (3-2f):[25] Orange solid; mp 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.81$ (d, $J=8.6$ Hz, 1H), 7.68 (d, $J=7.8$ Hz, 2H), 7.56–7.47 (m, 2H), 7.43 (t, $J=7.3$ Hz, 1H), 7.30 (dd, $J=17.1$, 8.4 Hz, 4H), 7.24–7.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.37$, 150.26, 148.42, 138.53, 137.88, 137.70, 137.39, 133.20, 130.98, 129.39, 129.28, 128.81, 128.52, 124.17, 121.12; MS (EI, 70 eV): $m/z=354.03$ (M^+); IR (KBr): $\nu=3062$, 2923, 1661, 1583, 1474, 1397, 1267, 1146, 1081, 853, 905, 830, 801, 702, 642, 539 cm^{-1}.

(*E*)-{5-Bromo-2-[(4-bromophenyl)diazenyl]phenyl}-(phenyl)methanone (3-2g): Orange solid; mp 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.82$ (d, $J=8.6$ Hz, 1H), 7.79–7.71 (m, 4H), 7.51 (t, $J=7.3$ Hz, 1H), 7.46 (d, $J=8.5$ Hz, 2H), 7.39 (t, $J=7.6$ Hz, 2H), 7.28 (d, $J=8.5$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.20$, 150.64, 148.81, 138.68, 137.89, 133.97, 133.20, 132.28, 131.73, 129.38, 128.51, 126.29, 125.73, 124.37, 121.21; HR-MS (ESI): $m/z=464.9203$, calcd. for $[M+Na]^+$ $C_{19}H_{12}Br_2N_2O$: 464.9209; IR (KBr): $\nu=3433$, 2360, 2340, 1660, 1275, 1261, 750, 483 cm^{-1}.

(*E*)-Ethyl 3-benzoyl-4-{[4-(ethoxycarbonyl)phenyl]diazenyl}benzoate (3-2h): Orange solid: mp 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.37$–8.26 (m, 2H), 8.00 (dd, $J=13.0$, 8.4 Hz, 3H), 7.76 (d, $J=7.4$ Hz, 2H), 7.50 (dd, $J=16.1$, 8.0 Hz, 3H), 7.40 (t, $J=7.7$ Hz, 2H), 4.41 (dq, $J=24.6$, 7.1 Hz, 4H), 1.41 (dt, $J=14.1$, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=195.95$, 165.77, 165.24, 154.33, 152.53, 137.99, 137.29, 133.19, 133.01, 132.88, 132.04, 130.43, 130.29, 129.46, 128.53, 122.85, 119.75, 61.68, 61.35, 14.28; HR-MS (ESI): $m/z=431.1601$, calcd. for $[M+H]^+$ $C_{25}H_{22}N_2O_5$: 431.1602; IR (KBr): $n=2923$, 2852, 1720, 1668, 1589, 1450, 1402, 1364, 1244, 1147, 1096, 1016, 856, 766, 687, 635 cm^{-1}.

(*E*)-[5-Methoxy-2-(phenyldiazenyl)phenyl](phenyl)-methanone (3-2i): Orange solid; mp 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.97$ (d, $J=8.9$ Hz, 1H), 7.79 (d, $J=7.8$ Hz, 2H), 7.48 (t, $J=7.3$ Hz, 1H), 7.42–7.33 (m, 4H), 7.29 (d, $J=6.3$ Hz, 3H), 7.14 (d, $J=8.9$ Hz, 1H), 7.05 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=196.91$, 161.86, 152.06, 144.39, 138.88, 138.32, 132.78, 130.68, 129.34, 128.82, 128.34, 122.58, 122.16, 116.74, 112.93, 55.84; HR-MS (ESI): $m/z=317.1285$, calcd. for $[M+H]^+$ $C_{20}H_{16}N_2O_2$: 317.1285; IR (KBr): $\nu=3059$, 2923, 2849, 1663, 592, 1474, 1292,1240,1098, 1031,960, 891, 849, 815, 770, 691, 628, 553, 520 cm^{-1}.

(*E*)-{2-[(4-methoxyphenyl)diazenyl]phenyl}(phenyl)-methanone (3-2j): Orange solid; mp 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.91$ (d, $J=8.0$ Hz, 1H), 7.76 (d, $J=7.5$ Hz, 2H), 7.63 (t, $J=7.1$ Hz, 1H), 7.59–7.52 (m, 2H), 7.45 (dd, $J=14.1$, 8.1 Hz, 3H), 7.35 (t, $J=7.6$ Hz, 2H), 6.81 (d, $J=8.9$ Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=197.36$, 162.35, 150.57, 146.48, 138.60, 136.45, 132.61, 130.77, 130.21, 129.36, 128.75, 128.27, 124.86, 120.02, 114.05, 55.52; HR-MS (ESI): $m/z=317.1292$, calcd. for $[M+H]^+$ $C_{20}H_{16}N_2O_2$: 317.1285; IR (KBr): $\nu=3735$, 3433, 3062, 2921, 2849, 2360, 2339, 1734, 1663, 1597, 1581, 1314, 1285, 1252, 1141, 764, 623, 548, 515 cm^{-1}.

(*E*)-[5-methoxy-2-(*para*-tolyldiazenyl)phenyl](phenyl)-methanone (3-2k): Orange solid; mp 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.95$ (d, $J=8.9$ Hz, 1H), 7.78 (d, $J=7.3$ Hz, 2H), 7.46 (t, $J=7.4$ Hz, 1H), 7.36 (t, $J=7.6$ Hz, 2H), 7.28 (d, $J=8.2$ Hz, 2H), 7.15–7.02 (m, 4H), 3.90 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=197.01$, 161.63, 150.19, 144.47, 141.26, 138.63, 138.40, 132.72, 129.50, 129.32, 128.31, 122.57, 122.07, 116.74, 112.92, 55.82, 21.41; HR-MS (ESI): $m/z=331.1456$, calcd. for $[M+H]^+$ $C_{21}H_{18}N_2O_2$: 331.1441; IR (KBr): $\nu=2921$, 2851, 2361, 2339, 1665, 1594, 1449, 1416, 1314, 1284, 1234, 1177, 1149, 1101, 1030, 962, 828, 749, 700, 553, 507 cm^{-1}.

(*E*)-{2-[(4-Methoxyphenyl)diazenyl]-5-methylphenyl}-(phenyl)methanone (3-2l): Orange solid; mp 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.83$ (d, $J=8.2$ Hz,1H), 7.78–7.74 (m, 2H), 7.51–7.31 (m, 7H), 6.80 (d, $J=9.0$ Hz, 2H), 3.80 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=197.58$, 162.10, 148.59, 146.47, 140.93, 138.67, 136.43, 132.54, 131.45, 129.32, 129.12, 128.24, 124.66, 120.16, 114.00, 55.49, 21.40; HR-MS (ESI): $m/z=331.1450$, calcd. for $[M+H]^+$ $C_{21}H_{18}N_2O_2$: 331.1441; IR (KBr): $\nu=2919$, 2849, 2361, 2338, 1659, 1596, 1499, 1443, 1384, 1249, 1209, 1175, 1140, 1101, 836, 694, 501 cm^{-1}.

(*E*)-Ethyl 4-[(2-benzoylphenyl)diazenyl]benzoate (3-2m): Orange solid; mp 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.00$ (d, $J=8.5$ Hz, 2H), 7.96 (d, $J=8.2$ Hz, 1H), 7.81–7.73 (m, 2H), 7.71–7.60 (m, 3H), 7.53–7.42 (m, 3H), 7.38 (t, $J=7.6$ Hz, 2H), 4.37 (q, $J=7.1$ Hz, 2H), 1.39 (t, $J=7.1$ Hz,3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=196.96$, 165.90, 154.40, 150.21, 138.42, 137.36, 132.91, 132.44, 131.58, 130.92, 130.36, 129.39, 128.97, 128.41, 122.60,119.89, 61.27, 14.29; HR-MS (ESI): $m/z=359.1395$, calcd. for $[M+H]^+$ $C_{22}H_{18}N_2O_3$: 359.1390; IR (KBr): $\nu=2920$, 2850, 1868, 1792, 1772, 1748, 1714, 1447, 1401, 1364, 1271, 860, 752, 697, 631, 544 cm^{-1}.

(*E*)-Ethyl 3-benzoyl-4-(phenyldiazenyl)benzoate (3-2n): Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.34$ (d, $J = 8.4$ Hz, 1H), 8.29 (s, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 7.6$ Hz, 2H), 7.52 (dd, $J = 14.0$, 7.2 Hz, 3H), 7.47–7.32 (m, 5H), 4.45 (q, $J = 7.1$ Hz, 2H), 1.45 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.14$, 165.37, 152.78, 152.06, 138.04, 136.86, 133.03, 132.27, 132.01, 131.96, 130.16, 129.48, 129.00, 128.45, 123.16, 119.92, 61.58, 14.30; HR-MS (ESI): $m/z = 359.1410$, calcd. for $[M+H]^+$ $C_{22}H_{18}N_2O_3$: 359.1390; IR (KBr): $\nu = 2931$, 2876, 1968, 1893, 1768, 1732, 1711, 1523, 1412, 1401, 1365, 1257, 980, 860, 688, 577, 523, 497 cm^{-1}.

(*E*)-(2-Bromophenyl)[2-(phenyldiazenyl)phenyl]methanone (3-2p): Orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.57$ (s, 1H), 8.30 (d, $J = 8.1$ Hz, 1H), 8.04 (dd, $J = 14.8$, 7.9 Hz, 2H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.69–7.59 (m, 2H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 7.7$ Hz, 2H), 7.35 (dt, $J = 14.7$, 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.65$, 151.58, 150.51, 148.30, 140.03, 134.50, 134.47, 131.85, 131.70, 131.23, 129.56, 129.06, 128.93, 126.77, 123.73, 122.77, 121.94; HR-MS (ESI): $m/z = 365.0297$, calcd. for $[M+H]^+$ $C_{19}H_{13}BrN_2O$: 365.0284; IR (KBr): $\nu = 3021$, 2918, 2868, 1978, 1673, 1504, 1478, 1313, 1043, 845, 634, 577, 534, 497 cm^{-1}.

Synthesis of (*E*)-1-(Phenyldiazenyl)-9*H*-fluoren-9-one (4)

Anhydrous KOAc (19.6 mg, 0.20 mmol), DavePhos (4 mg, 0.01 mmol) and K_2CO_3 (27.6 mg, 0.20 mmol) were successively added to a solution of $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol) in DMA (1.5 mL) and the resulting suspension was stirred at room temperature for 15 min, then a solution of the corresponding acylated intermediate **3-2p** (36.4 mg, 0.10 mmol) in DMA (0.5 mL) was introduced. The system was heated at 110 °C for 24 h. Then, the solvent was removed under vacuum, and the corresponding residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **4** as an orange liquid; yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.06$ (d, $J = 7.2$ Hz, 2H), 7.70 (d, $J = 7.3$ Hz, 1H), 7.64–7.49 (m, 7H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.34 (t, $J = 7.3$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.31$, 153.01, 150.56, 145.54, 143.78, 135.18, 134.55, 134.38, 131.90, 129.51, 129.22, 128.21, 124.30, 123.62, 121.56, 120.36, 116.91; HR-MS (ESI): $m/z = 285.1037$, calcd. for $[M+H]^+$ $C_{19}H_{12}N_2O$: 285.1022; IR (KBr): $\nu = 3861$, 3742, 3649, 3620, 2361, 1741, 1707, 1646, 1515, 1378, 1250, 1143, 759, 678, 520 cm^{-1}.

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